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Monoexponential Microsecond Decay of Blue Photoluminescence in Aged Porous Silicon Prepared with Ar$^+$ 488 nm *

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Blue photoluminescence is observed in aged porous silicon samples anodized under Ar$^+$ 488 nm laser illumination. No samples have been undergone any heating treatment process. Both nanosecond and microsecond decay of blue photoluminescence have been measured. Samples show a good monoexponential microsecond decay with lifetimes of about 5.3 μs. Photoluminescence excitation spectra of blue and red Photoluminescence indicate there is a large Stokes shift (about 800–900 meV) in the excitation spectra of red photoluminescence while no this marked Stokes shift in that of blue photoluminescence. The possible origin of the photoluminescence is discussed based on the experimental results.

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In the study on photoluminescence (PL) of porous silicon (PS), it has been found that there mainly exist two PL bands, red band and green-blue band.[1] Experimental results have indicated that the spectral decay of the red band can be generally described by a stretched exponential function in microsecond or even longer time region and the blue band shows a mono- or multi-exponential decay with lifetime in nanoseconds or shorter.[1] Almost all of these results about the blue band were obtained from the PS samples which had undergone a high temperature heating treatment process. However, Mizuno *et al.*[2] have reported the oxide-free blue PL from photochemically etched PS and found its lifetime is in the region from several hundred nanoseconds to microsecond scale, which is much longer than that of the blue emission PS obtained by heating treatment. So, to clarify the decay profile of the blue PL, more study is needed.

Another way to get blue PL from PS without the heating process is the storage of as-prepared samples in atmosphere.[3] As we know, there are few reports on the dynamics of this kind blue emission although the dynamics is very helpful for us to understand the mechanism of the blue PL. In this paper, we achieve the two-peak PL spectra of both red and blue emission from aged PS prepared under argon ion 488 nm laser illumination, and firstly report the monoexponential microsecond decay of blue PL.

PS samples were prepared from n-type Si wafers [100], with a resistivity of 3–8.5 Ω·cm. The anodization was carried out in HF-ethanol solution (40 wt.% HF:ethanol = 6:4, in volume) at a constant current density of 2 mA/cm^2 for one hour. During anodization the wafer was illuminated by Ar$^+$ 488 nm laser. Different power density of the laser have been used to acquire different samples. After the anodization, the wafers were rinsed in ethanol, then dried by blowing and finally stored in an atmospheric environment as long as 21 monthes at room temperature. Samples used in this paper are summarized in Table 1.

Table 1. Samples used in this paper.

Name	(a)	(b)	(c)	(d)	(e)
Illumination	Ar$^+$ laser, 488 nm				
Power Density (mW/cm^2)	2	5	7	10	~150

The PL spectra were excited by a 325 nm He–Cd laser line. All spectra were corrected for the wavelength response of the measurement system. The nanosecond PL decay was excited by a 355 nm Nd:YAG mode-locking laser with the pulse width of about 400 ps. The microsecond PL decay was excited by a 325 nm He–Cd laser with the pulse width of about 10 ns.

Figure 1 gives the typical PL spectra of aged samples (a), (d), and (e). The PL spectra of aged samples (a)–(d) can be well fitted with a deconvolution of two Gaussian bands, red and blue band, while sample (e) shows only one blue band. The red band centers at 1.87 eV (~663 nm) with the full width at half maximum (FWHM) of about 0.49 eV while the blue band centers at 2.51 eV (about 494 nm) with the FWHM of about 0.91 eV. It is found with the increasing power density of the illuminating laser during the fabrication process, from sample (a) to (e), blue PL increases while red PL decreases and vanishes at last.

To understand the recombination process of the PL, especially the blue PL, nanosecond and microsecond decay of the PL are measured. Figure 2 shows a typical PL nanosecond decay of sample e detected at the peak position of its static PL spectra. The PL intensity is somewhat weak, and the decay approximately accords with the monoexponential law with a lifetime value of 1.39 ns. Measurements are repeated many times and the final results of the lifetime lists in Table 2. It can be seen that the lifetime have a weak tendency to increase from sample (a) to (e) although the value of sample (c) is somewhat less. This maybe means that the recombination in this time region is influenced by other recombination process, e.g. the red PL. However, more study is needed to confirm this.

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Table 2. Lifetime of the blue PL decay in nanoseconds.

Sample	(a)	(b)	(c)	(d)	(e)
lifetime (ns)	0.90±0.12	0.96±0.25	0.80±0.14	1.36±0.42	1.43±0.44

These lifetime values of the nanosecond decay are consistent with those reported in early references.[4,5]

The case of blue PL microsecond decay is shown in Fig. 3. All samples show a good monoexponential decay over 3 orders and the lifetime are 5.24, 5.38, 5.15, and 5.36 μs for sample (b), (c), (d), and (e), respectively. Unlike the nanosecond decay, the blue PL microsecond decay of different samples exhibits an approximately equal lifetime value. As we know, there is no similar experimental reports before. To study the origin of the PL and the relation between the red and blue PL as shown in Fig. 1, we have measured the photoluminescence excitation (PLE) spectra of above both PL. Figure 4 gives.the PLE spectra of the red PL (monitored at 1.8 eV). The inset shows the case after normalization. Significant increases of the PLE signal in the samples occur around 2.6–2.7 eV, and there exists a large Stokes shift (about 800–900 meV) between the energy of the PLE and PL. The excited energy below 2.6 eV gives little contribution to the red PL.

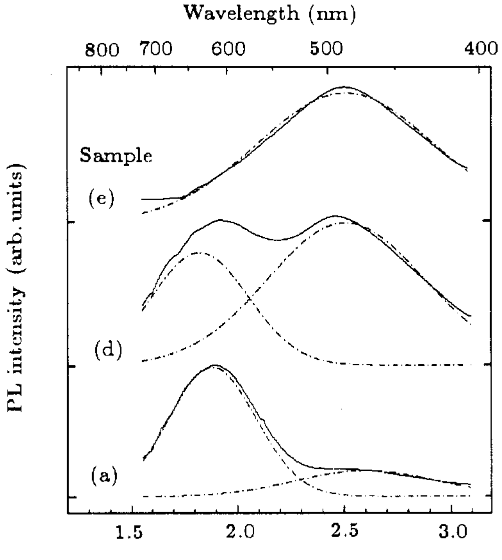

Fig. 1. PL spectra of aged PS samples (a), (d) and (e) anodized under the illumination of laser with power density of 2 mW/cm^2, 10 mW/cm^2, and about 150 mW/cm^2, respectively.

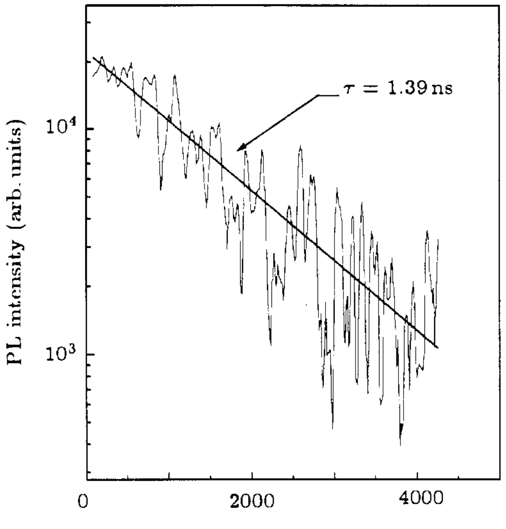

Fig. 2. A typical blue PL nanosecond decay of sample (e) (curved line) and the exponential fits (straight line) with τ = 1.39 ns.

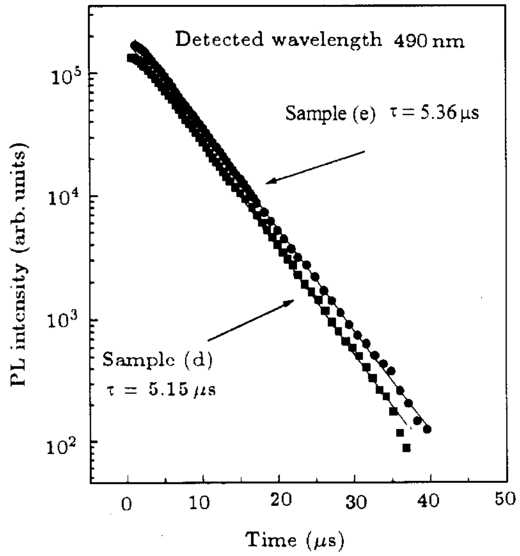

Fig. 3. Observed blue PL microsecond decay of samples (d) ■ and (e) •, and the exponential fits (solid line).

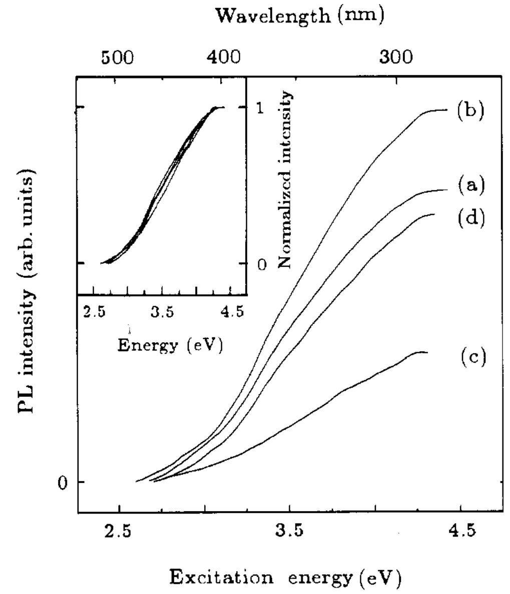

Fig. 4. PL excitation spectra of the red PL at 1.8 eV with samples (a)–(d). The inset shows the case after normalization.

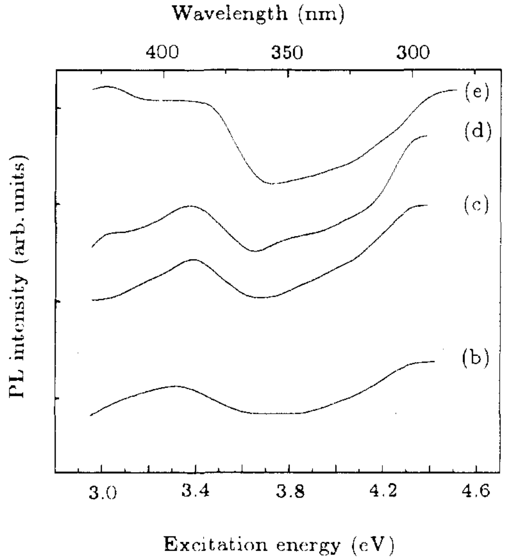

Fig. 5. PL excitation spectra of the blue PL at 2.5 eV with samples (b)–(e).

This implies there maybe exists a band gap of about 2.6 eV in these PS samples.

Figure 5 shows the PLE spectra of the blue PL (monitored at 2.5 eV). There is much difference between the PLE spectra of the blue and red PL. One of the most important difference is that there is no marked Stokes shift in the PLE spectra of blue PL. As for the PLE peak around 3.3–3.4 eV, it has been debated by several groups, although its origin is still unclear.[6] However, this peak is not the main thing in this paper, and we will not discuss this peak more.

We notice there are two main models to explain the origin of the red and blue band in PS nowadays. In one model,[1] the red PL is attributed to the quantum confinement effect of the nanometer silicon crystallite in PS and the blue PL is believed coming from the oxide surface of the nanometer *c*-Si. But in another model,[7] almost everything is opposite. Blue PL is due to the radiative recombination in the nanocrystalline core and the red PL originates from the radiative recombination of excitons in the surface localized states. Although the experimental results in this paper do not give the definite judgment to clarify which model is right, the large Stokes shift shown in the PLE spectra of red PL do not directly support the simple quantum confinement model of red PL.

In our experiments, we find that the illuminating laser used during the sample preparation markedly influences the luminescent properties of the PS. To our knowledge, there may exist two main effect of the illuminating laser in our experiment. Firstly, according to the infrared measurements, upon the increasing laser power intensity used during sample preparation, relevant aged samples have a better oxide layer with less disorder, amorphous, strain and enhanced connectivity of silicate network.[8] These results indicate that a better qualitative oxide layer is helpful to the stronger blue PL, which can be understood by considering that the blue PL comes from the nanometer *c*-Si core while the oxide layer enhances the quantum confinement effect. Secondly, considering the theory of Lehmann and Gosele on PS formation,[9] the illumination of Ar^+ 488 nm (about 2.54 eV) laser during PS preparation on n-type silicon will lead to form the nanocrystalline silicon with the band gap of the energy of the incident laser. Mimura *et al.* have studied the PL properties of PS anodized with various light illuminations, and confirmed the influences of the energy of the illuminating light on the band gap of the PS.[10] We find this value of the band gap is consistent with the energy of the observed blue PL.

Other evidences, which support that the blue PL comes from the radiative recombination in the nanometer *c*-Si core, come from the microsecond lifetime of the blue PL. Delerue *et al.* have calculated the radiative lifetime using the linear combination of atomic orbital technique.[11] They found the blue band energies are compatible with the crystallite sizes (1.5–3.5 nm), and the lifetime values of this kind of crystallite are found to be 1–10 μs near 2.5 eV PL energy.[11,12] On the other hand, Mizuno *et al.* reported firstly the blue PL from non-oxygen PS, where blue PL could not comes from the oxide layer. The lifetime of the PL nearby 2.5 eV is in about 1 μs range.

Owing to all above reasons, we believe that the monoexponential decay in microsecond scale of blue PL comes from the nanocrystalline silicon in PS samples. As to the weak nanosecond decay of blue PL shown in Fig. 2, it may be related to the radiative recombination in oxide surface after excitation[4] although we can not conclude this point in this paper.

In summary, we have found the blue PL in age PS samples anodized under argon ion 488 nm laser illumination and firstly observed the monoexponential microsecond decay of blue PL. PLE measurements indicate that unlike the excitation spectra of the red PL, there is no marked Stokes shift in that of the blue PL. Based on the experimental results in this paper, it is likely that the blue PL observed in the aged PS samples originates from the nanocrystalline silicon covered with an oxide layer.

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