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Transient photoluminescence decay in porous silicon and siloxene

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The photoluminescence decay after laser pulse excitation is studied in porous silicon and siloxene as a function of sample temperature, detection wavelength, laser intensity, and pulse length. The time dependence in all samples is characterized by a nonexponential decay directly after the laser excitation and a single exponential decay for long times after the laser pulse. The exponential decay is *identical* for the porous silicon samples and annealed siloxene and depends only on detection wavelength and sample temperature. As prepared siloxene exhibits the same decay characteristics. However, the nonexponential decay is more pronounced and the single exponential decay is a factor of 2–5 faster compared with annealed siloxene. The decay of the photoluminescence is another indication of the identical origin of the strong visible luminescence in porous Si and in annealed siloxene.

1. Introduction

At present there is a vivid discussion about the origin of the strong visible photoluminescence (PL) in porous silicon (por-Si). In essence, two controversial explanations have been suggested and experiments are needed to clearly distinguish between them. The quantum confinement model [1,2], which explains the increase in the Si band gap by strong quantization effects in small Si particles, is supported by the particular etching conditions [3] and recent PL investigations [4]. The other group of models accounts for the strong PL by recombination processes in silicon-based polymers (polysilane, siloxene, etc.) [5–8] or hydrogen saturated Si surfaces [9]. The evidence for these models arises mainly from the identical characteristics of the PL from por-Si and chemically synthesized polymers.

A detailed investigation of the recombination process is important in order to understand the origin of the strong visible PL. In this paper we present results on the recombination behavior in por-Si and siloxene after pulsed laser excitation.

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2. Experimental

In the present study, three differently prepared por-Si samples and two siloxene powder samples with different PL spectra are studied. The room temperature (RT) PL spectra of all samples are shown in Fig. 1. The por-Si samples with PL maxima at 670 nm (p-por Si) or 700 nm (n-por Si) were anodically etched with different parameters to generate a different porosity (p-por Si: Si:B 5–7 Ω cm, ethanoic HF (1:1, ethanol:50 w/o HF), 100 mA/cm^2, 30 min etch time, rinsed in water and blown dry in nitrogen gas; n-por Si: Si:P 10 Ω cm, ethanoic HF (1:1, ethanol:25 w/o HF), 25 mA/cm^2, 20 min etch time, rinsed in water and blown dry in nitrogen gas). A stain-etched por-Si sample (Si:B 0.6 Ω cm, 50 w/o HF:70 w/o HNO_3:H_2O = 4:1:3, etch time 4 min) exhibits a PL maximum at 680 nm. Siloxene was prepared from $CaSi_2$ powder according to the recipe given by Wöhler [10]. The as-prepared sample gives a PL maximum at 530 nm, and after annealing in air

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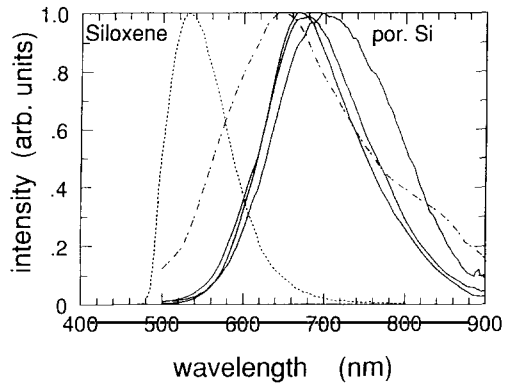

Fig. 1. Normalized room-temperature PL spectra of the samples used in this investigation. Porous silicon samples (full lines): two anodically etched samples with different parameters (λ_{max} = 670 and 700 nm), one stain etched sample (λ_{max} = 680 nm). Siloxene samples (broken lines) as prepared (λ_{max} = 530 nm) and annealed (λ_{max} = 650 nm). Excitation wavelength: 457 nm.

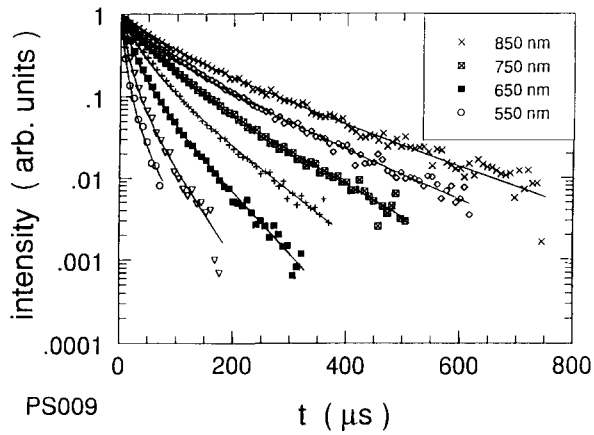

Fig. 2. Room-temperature PL decay of a porous Si sample (λ_{max} = 670 nm) after pulsed laser excitation. Decay curves are given for different detection wavelengths. Excitation wavelength: 457 nm.

(T = 400° C, 10 min), the PL maximum changes to 650 nm.

The total PL intensity of the anodically etched por-Si and the as prepared siloxene powder are comparable. The PL intensity for the annealed siloxene sample and the stain-etched sample is a factor of 5 smaller at room temperature compared to the anodically etched samples and as-prepared siloxene.

The argon ion laser beam was modulated by an acousto-optical modulator (time resolution 20 ns), and the PL decay was detected by a GaAs photomultiplier and a transient recorder. The laser wavelength was varied from λ = 476 to 352 nm without any effect on the decay characteristics. The laser power had to be selected very carefully due to the strong optical degradation of the luminescent layers.

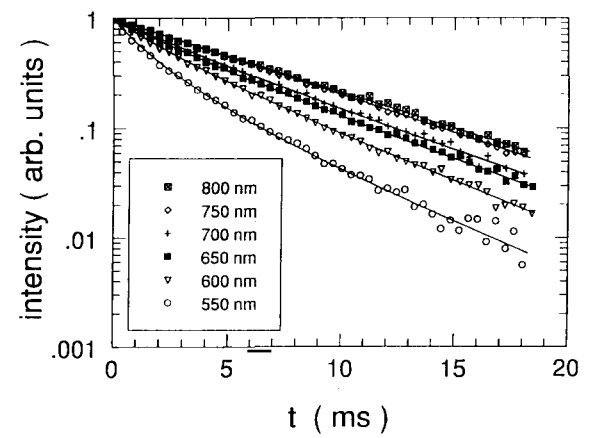

Fig. 3. PL decay at T = 4.2 K of a porous Si sample (λ_{max} = 700 nm) after pulsed laser excitation. Decay curves are given for different detection wavelengths. Excitation wavelength: 457 nm.

3. General features of the PL decay

The PL decay of a porous Si sample at room temperature is detected, as shown in Fig. 2, at different wavelengths. The decay is nonexponential and is a function of the detection wavelength. The decay is faster for detection towards shorter wavelengths. A qualitatively similar behavior is found for lower sample temperatures (Fig. 3), although the decay times are much slower (ms regime at 4.2 K instead of μs regime at room temperature). In addition, a single exponential decay, especially for long detection wavelengths, is clearly observable at lower sample temperatures.

Table 1
Fitting parameters X and τ_0 for the decay curves presented in Figs. 2 and 3

T (K)	λ (nm)	550	600	650	700	750	800	850
295	X	3.6	1.9	1.3	1	0.8	0.7	0.6
	τ_0 (μs)	39	42	58	81	110	144	175
4.2	X	0.9	0.4	0.2	0.2	0.02	0.06	–
	τ_0 (ms)	5.0	5.3	5.9	6.2	6.4	6.9	–

Several models have been suggested to account for the PL decay, in por-Si [3,11,13–16]. We propose a simple band-to-band recombination process to describe the PL decay in which the carrier recombination is predominantly radiative due to the high external quantum efficiency of all our samples. The recombination rate is proportional to the concentration of free electrons and holes [17], and the time dependence for the PL after pulsed laser excitation is given by:

$$I(t) \sim \frac{e^{t/\tau_0}}{[(X+1)e^{t/\tau_0} - X]^2} \quad (1)$$

with τ_0 characterizing the single exponential decay for long decay times and X describing the increase in carrier concentration due to laser excitation, X is given in multiples of the carrier concentration without laser excitation. A least-squares fit to our data yields τ_0 and X. The straight lines in Figs. 2 and 3 are the result of the fit process. Table 1 lists τ_0 and X obtained from the decay curves presented in Figs. 2 and 3.

Surprisingly, all other porous Si samples and the annealed siloxene sample exhibit the same τ_0 for the same detection wavelength and sample temperature. The spread in the data is only $\sim 10\%$, which corresponds also to the error bar of our fitting process. All samples, however, show different X values (which account for the fast nonexponential decay), in particular the X values for the annealed siloxene samples can be in the range of 2–5. As prepared siloxene shows the same decay characteristics however with a much more pronounced nonexponential decay (X values in the range of 4–10) and with a single exponential lifetime τ_0 which is a factor 2–5 smaller compared to the

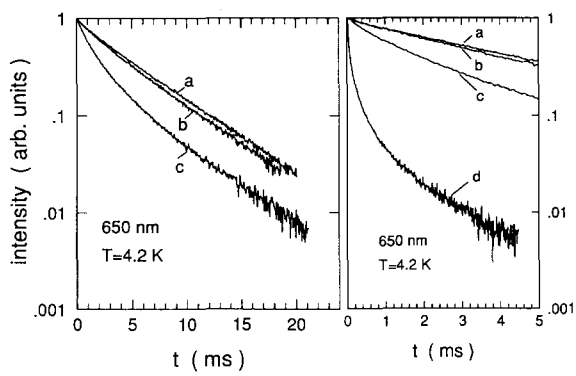

Fig. 4. Comparison of the decay curves for samples n-por Si (a), p-por Si (b), annealed siloxene (c) and as prepared siloxene (d) at the detection wavelength 650 nm. Samples were cooled in liquid helium.

por-Si samples and the annealed siloxene. A comparison of the different decay curves of por-Si and siloxene is presented in Fig. 4. The por-Si samples (n-por-Si (a), p-por-Si (b)) and annealed siloxene (c) exhibit all the same exponential decay time τ_0. The as-prepared siloxene (d) shows basically the same decay features with a single exponential decay which is similar, but by a factor of 3.5 faster than the other samples.

Our model for the recombination process was checked by the two following experiments. The pulse width was varied as is shown in Fig. 5 from 15 to 200 μs and in agreement with our model, no change in X and τ_0 was found. However, an increase in laser power by a factor of 100 gives rise to a change in X, as can be seen in Fig. 4 by the more pronounced nonexponential behavior of the decay curve.

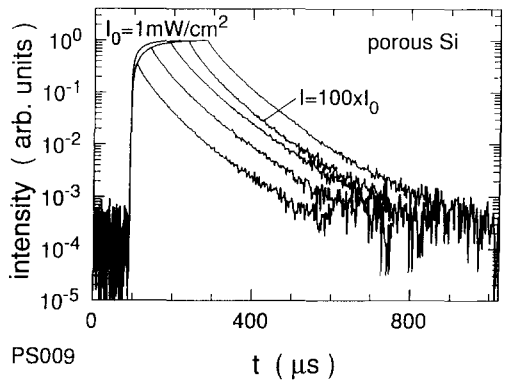

Fig. 5. Rise and decay of the PL intensity (at 690 nm) of a por-Si sample at room temperature. The exciting laser pulse lengths were 15, 50, 100, 150 and 200 μs. Excitation density (at 352 nm): 1 mW/cm^2 (except the measurement with 150 μs pulse length (100 mW/cm^2)).

4. Discussion of experimental results

The time decay of porous Si and siloxene samples shows an excitation dependent nonexponential decay and a single exponential decay for low excitation conditions. The lifetime τ_0 for the single exponential decay is identical for all por-Si and annealed siloxene samples and depends only on sample temperature and detection wavelength. This single lifetime clearly demonstrates that the recombination processes in both materials are identical.

Our experiments suggest a spatial variation of the band gap in both materials. Laser excitation creates carriers, which relax to the different band edges. Recombination from there is then described by Eq. (1). Within this expanded model, the wavelength dependence of the decay time τ_0 and the term X characterizing the excess carrier density have to be considered. The strong temperature dependence of τ_0 presumably originates in the participation of phonons in the indirect optical transition.

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