Absence of Carrier Hopping in Porous Silicon

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It is often presumed that the stretched exponential decay of photoluminescence in porous silicon is a consequence of a variable range hopping of photoexcited carriers between the localized states of the three dimensional silicon sponge structure. We show unambiguously, however, that carrier hopping in porous silicon is absent in the microsecond time range, from ambient temperature up to 450 K. We demonstrate this by comparing resonantly and nonresonantly excited photoluminescence decays. The invariance of the decay shape is interpreted in the light of different carrier recombination models. [S0031-9007(98)05780-9]

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The discovery [1] in 1990 that porous silicon can be highly luminescent even at room temperature has originated extensive efforts to understand and to improve its luminescence properties. A common point of all luminescence models is that carrier localization must play an important role for high photoluminescence (PL) quantum efficiency (QE). Some experimental evidence and simple arguments underline this fact. Transport properties and PL efficiency are strongly correlated: Highly luminescent porous silicon, at room temperature, has low values of dark conductivity and photoconductivity [2], becoming insulatinglike for the most luminescent samples. Theoretical estimates [3] and experimental results [4,5] shows that porous silicon, like crystalline silicon [6], keeps an indirect gap character with long radiative lifetimes. In the bulk case, the photoexcited carriers diffuse into the semiconductor volume and find a nonradiative (NR) center. The introduction of localized states diminishes this NR recombination channel and drastically increases the QE. This is common for hydrogenated amorphous silicon [7] (a-Si:H) or semiconductor alloys [8] where localization of the carriers due to the fluctuating potential induces high QE.

In porous silicon, the origin of the localized states remains a central controversial subject. The broad PL emission line is inhomogeneous and the associated broad density of states is taken to be due to a quantum confinement distribution (the size distribution of the Si nanocrystallites) or to surface states or various silicon compounds associated with the internal surface of the porous silicon. However, starting from these localized states, the details of the carrier recombination have been discussed less, as they were assumed to be roughly similar in most luminescence models.

Time-resolved measurements have provided clear evidence of anomalous relaxation behavior of the luminescence. The decay line shape is strongly nonexponential [9] and is described well by a stretched exponential function [10]. This type of relaxation was compared with that in a-Si:H and chalcogenide glasses, being associated with the same typical recombination mechanism [11]: In the first few nanoseconds after the excitation, most of the photocreated electron-hole pairs thermalize and are trapped in the localized states. The trapped electrons and holes hop among localized states and finally radiatively recombine. The central point of all of these recombination models is the trap-controlled hopping mechanism, and most effort was devoted to simulate numerically the diffusion of carriers in the complex disordered system of porous silicon.

The aim of our paper is to determine the weight of the carrier hopping in the global recombination mechanism of the photoexcited carriers. We use the method of resonant excitation [5] associated with time-resolved PL analysis [12]. We compare the PL decay acquired at the same detection wavelength, but excited at different excitation wavelengths: one close to the detection wavelength (resonantlike excitation) and a second at high energy compared to detection (nonresonant).

The excitation sources were as follows: for the steady-state measurements, a Hg lamp (363 nm) and for the time-resolved PL measurements, a N_2 laser ($\lambda = 337$ nm, with 3 ns pulse width, 20 Hz repetition rate), or the second harmonic ($\lambda = 532$ nm) of a Nd^{3+}:YAG laser (10 ns, 10 Hz). The last was also used to pump a dye laser (spectral range 600–700 nm). The time resolution of the analysis chain was about 5 ns. As PL decays are nonexponential, we measure the PL signal over four decades of time, from the nanosecond time scale to several hundreds of microseconds. The absorption coefficient, in porous silicon, for orange-red light has low values; thus, in order to have enough signal to follow the PL decay for at least three decades of intensity, we needed very thick, highly luminescent porous layers. We studied high porosity (80%) samples, freshly formed (on p-type Si 4–6 Ω cm, 15% HF, 10 mA/cm^2), 10–40 μm in thickness. To avoid cracking of the porous silicon layer (which often occurs at such porosities and thicknesses), we studied the porous layer without drying, keeping it in pentane during the experiment [13].

Figure 1 shows the different PL spectra obtained for the same sample excited at several wavelengths. These spectra show that, on decreasing the energy of the excitation

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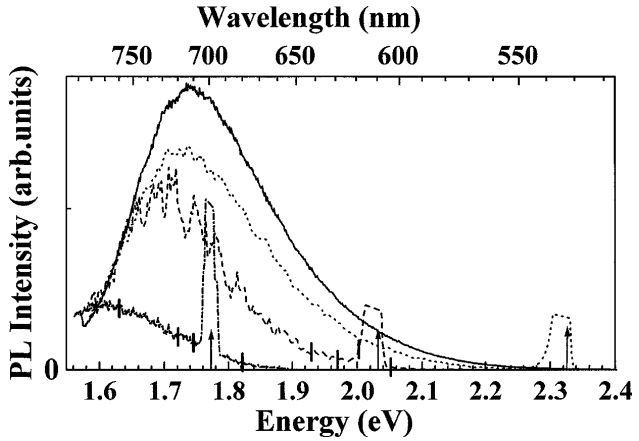

FIG. 1. Luminescence spectra of an 80% porous silicon layer excited at different energies (indicated by arrows on the figure). The upper spectrum, excited at 3.385 eV, is a steady-state measurement. The rest of the spectra are obtained integrating the PL decay. The spectra measured at room temperature were normalized by the excitation intensities and the absorption coefficient in order to have the same order of magnitude for the deposited excitation energy per unit volume. The different detection energies, where the PL decay were compared, are indicated by vertical bars on the PL spectra.

photons, one selects only a part of the luminescent sites: those with the luminescence energy lower than or close to the excitation line. As can be seen in Fig. 2, the PL decay shape remains practically unchanged (for $t \geq$ 100 ns), whatever the excitation wavelength. For a more quantitative analysis, Fig. 3 compares the parameters τ and β resulting from a fit of each decay with a modified stretched exponential function:

$I_{\mathrm{PL}}(t) = I_0 t^{\beta-1} \exp[-(t/\tau)^{\beta}]$ (see comments in Ref. [14]). In the limit of the fitting error, we find the same shape factor β, independent of excitation wavelength. The effective lifetime τ is only slightly different, the decay being roughly 20% slower for resonant excitation. Note that this variation of 20% is not significant compared to the strong exponential variation of the lifetime with the detection energy.

In order to check the universality of these observations, we made the same measurements on samples with different porosities and internal surface coverages: a 8 μm thick, one-year-old layer of 70% porosity and an anodically and thermally oxidized porous silicon waveguide made up of 2 layers, 3 μm of 65% and 5 μm of 70% porosity (preparation details in Ref. [15]). As this last sample was stable and highly luminescent, it was also possible to verify (inset of Fig. 3) any temperature effect on these measurements (from ambient up to 450 K). In all cases, the same results were obtained: The PL decay shape is independent of the excitation wavelength.

Before discussing the meaning of these results, note that the only assumptions that we adopt are the existence of localized states (whatever their origin) and a carrier recombination mechanism as described in Refs. [11], with a radiative recombination rate (W_{R}) at room temperature

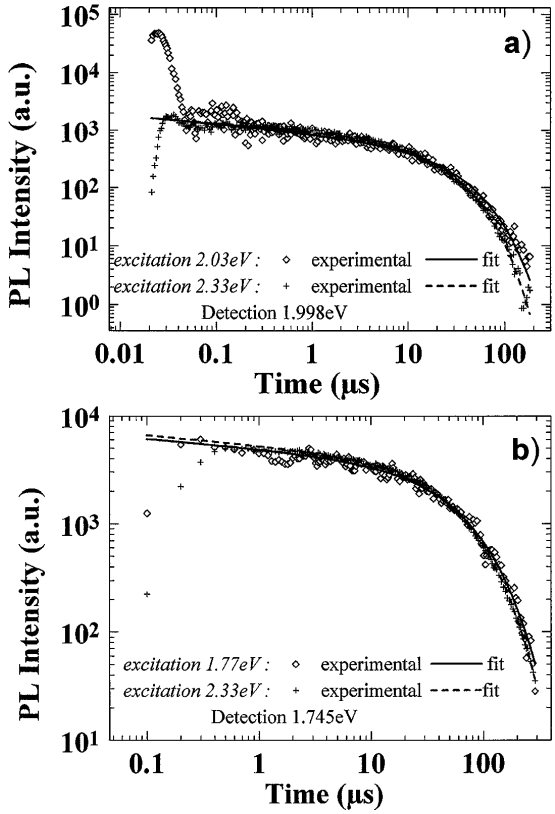

FIG. 2. Comparison of PL decay for two detection energies, (a) 1.998 eV and (b) 1.745 eV. The nonresonant excitation (+) was in both cases at 2.33 eV and the resonantlike excitation ($\diamond$) was (a) 2.03 eV and (b) 1.77 eV. For each decay, we also display the corresponding stretched exponential fit (continuous line for the resonantlike excitation and dashed line for the nonresonant case). A log-log representation is required to span the four-decade decay. The time resolution of the analysis chain was 5 ns in (a) and 200 ns in (b).

that is lower than the NR recombination rate (W_{NR}) [16]. We used low excitation intensities, less than 10% of the PL saturation threshold [17,18]; thus, as the photoluminescence is in the linear regime, we considered only geminate recombination.

The slope of the PL decay at one detection wavelength is determined *at any time* by the proportion of carriers entering the sites emitting at this wavelength, by the carriers departing to others sites, and by the probability of local recombination, radiatively or not. If the flow in one of these "circulation" channels is reduced or suppressed, the PL decay shape will also change. In our experiments, we modified the first channel, that of arriving carriers, by reducing it under resonant excitation. This can be expressed easily using the master equation

$$\frac{dN_i(t)}{dt} = -N_i(t)\left(W_{\mathrm{R}} + W_{\mathrm{NR}} + \sum_j P_{ij}\right) + \sum_j N_j(t) P_{ji}\,, \tag{1}$$

where N_i is the number of sites emitting at energy E_i that contain an electron-hole pair, and P_{ij} and P_{ji} are the rates

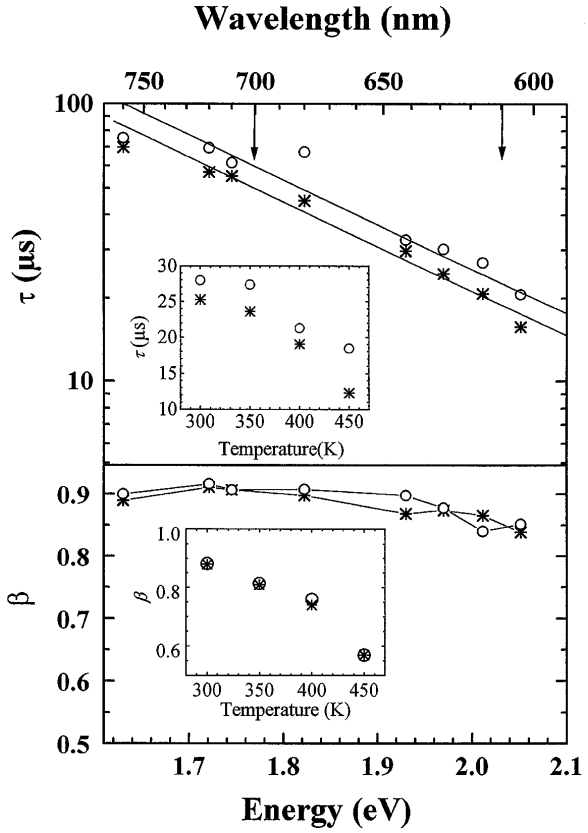

FIG. 3. Comparison of stretched exponential fitting parameters τ (upper panel of the figure) and β (lower panel) for nonresonant ($*$) and resonantlike excitation ($\circ$). In abscissa, common for the two parts of the figure, is the detection energy (or the PL wavelength). The laser excitation energies are indicated by arrows. The solid lines represent the exponential dependence of the lifetime on the detection energy. Insets: Comparison of τ (upper panel) and β (lower panel) for nonresonant [$E_{ex} = 2.33$ eV ($*$)] and resonantlike excitation [$E_{ex} = 2.03$ eV ($\circ$)] for different temperatures. The detection energy is 1.97 eV.

of carrier flow to and from sites emitting at the energy E_j. Solving Eq. (1) also yields the time dependence of the luminescence at energy E_i: $I_{PL}(t, E_i) \propto W_R N_i(t)$. Equation (1) is valid in the particular case of equivalent environments for each class of emitting sites N_i. Differences in the environment give essentially different NR recombination rates (W_{NR}^k) or carrier flow rates (P_{ij}^m or P_{ji}^n), and can be taken into account by writing similar equations for each subclass: $[dN_i^{km}(t)]/dt = -N_i^{km}(t)(W_R + W_{NR}^k + \sum_j P_{ij}^m) + \sum_{j,n} N_j^n(t) D(P_{ji}^n) P_{ji}^n$ and $N_i(t) = \sum_{k,m} D(W_{NR}^k) D(P_{ij}^m) N_i^{km}(t)$, with $D(W_{NR}^k)$, $D(P_{ij}^m)$, and $D(P_{ji}^n)$ as the corresponding distributions of W_{NR} and carrier flow rate, respectively. W_{NR}, P_{ij}, and P_{ji} are basically dependent on the structural characteristics of the sample (e.g., distance to the NR trap or between sites, intersite energy barrier) and temperature, but not on the excitation wavelength [19]. Thus, for our experiment, the distributions $D(W_{NR}^k)$, $D(P_{ij}^m)$, and $D(P_{ji}^n)$ are constant, the behavior of one subclass being sufficient to characterize the whole class. We, therefore, restrict the analysis to the effect of the excitation wavelength on the solution of Eq. (1).

The two terms (loss, with negative sign, and the feeding, with positive sign) on the right-hand side of the Eq. (1) determine the slope of the PL decay (e.g., the reduction of one or the other term slows down or accelerates the PL decay). The essential contribution to the feeding term comes from sites with higher energy than the detection ($E_j > E_i = E_{det}$) and the hopping of carriers out of the emitting site is essentially toward lower energy sites ($E_{det} > E_j$). Without expanding the expressions for P_{ij} and P_{ji} (see, e.g., Refs. [11]), the reason for this can be easily understood: The flow of carrier hopping has a predominant direction, from sites of higher energy to lower ones. The opposite direction, achievable only by thermal activation, is less efficient [20].

Selective excitation affects the spectral distribution of occupied luminescent sites, particularly for the sites with higher energy than the resonant excitation ($E_j > E_{resonant}$): At low temperature, these sites are no longer excited N_j ($t = 0+$, $E_j > E_{resonant}$) $= 0$. With increasing temperature, coupling with photons becomes possible, but, anyway, the number of excited sites remains much lower than in the nonresonant case. In these conditions, the feeding term in Eq. (1) is diminished compared to the nonresonant case, since the loss term remains almost unchanged. The consequences on the decay shape are clear: For the resonant excitation, one expects an acceleration of the PL decay. This acceleration will be more significant as the feeding term becomes comparable to the loss term.

In the light of the recombination models from Refs. [11], the magnitude of the expected decrease of the lifetime can be roughly estimated. The hopping of carriers to lower energy levels is given as the reason for the strong exponential decrease of the PL lifetime with detection energy (see Fig. 3): For the lower energy sites, the feeding term is important while it becomes negligible for those of higher energy. Applying the same arguments to our experiment, the resonantly excited lower energy sites become equivalent to the highest ones in the case of nonresonant excitation. The lifetime for the resonantly excited sites should be the same as for the highest energy sites (e.g., 2.2 eV), so we should have a decrease of the PL lifetime by about 5 times for the 1.77 eV and 2 times for the 2.03 eV excitation.

The experimental results, however, show almost the same decay, with a slight opposite tendency, i.e., slowing down (see Figs. 2 and 3). It is, therefore, simple to conclude that, independently of the excitation wavelength, the feeding term contributes negligibly to the PL decay shape: Thus, after the first 100 ns following the excitation pulse, the fraction of hopping carriers is insignificant in PL dynamics. As we obtained the same results up to 450 K, it follows that, even at high temperature, the luminescence is not related to carrier hopping. In these conditions, $P_{ji}, P_{ij} \ll W_{NR}$ and Eq. (1) is rewritten

as $[dN_i^k(t)]/dt = -N_i^k(t)\,(W_R + W_{NR}^k)$. This means that the luminescent centers in porous silicon must be considered as independent and the recombination mechanism as a local competition between radiative or NR recombination of the photoexcited electron-hole pair.

This is not the only result that challenges the hopping hypothesis. The presence of a feeding term, in general, is confirmed by the presence of a rise time in the response of the system to a pulsed excitation [21]. Time-resolved measurements [22] have been performed, up to the picosecond range, without any PL rise time being detected. Likewise, in a recent paper [12], we reported that, for temperatures above 300 K, the strong QE decrease is associated with a progressive evolution of the PL decay shape from a stretched exponential to a t^{-1} decay (the shape factor β decreases from 0.7 to less than 0.3). This fact casts doubt on the existence of carrier hopping in porous silicon, since the carrier recombination models based on this hypothesis [11] predict either an increase of β with temperature or a decrease of β, but with no change in the PL intensity.

The hypothesis of local recombination of carriers has already been suggested and has been shown to be sufficient to explain other observations such as saturation of the luminescence by the Auger effect [17] and optically induced polarization anisotropy [18] in porous silicon. In our previous paper [12], we also used a model based on isolated luminescent centers to explain the dependence of luminescence decay shape upon various parameters. The new experimental results presented here allow, for the first time, to conclude unambiguously that the absence of the carrier hopping between luminescent centers in porous silicon is not only sufficient but also necessary.

In summary, time-resolved measurements associated with the selective excitation method show no dependence of the PL decay shape on the excitation wavelength. This is a strong proof that, in porous silicon, the electron-hole pairs which contribute to the luminescence are strongly localized, the proportion of hoping carriers being unimportant in the PL dynamics in the microsecond time range.

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