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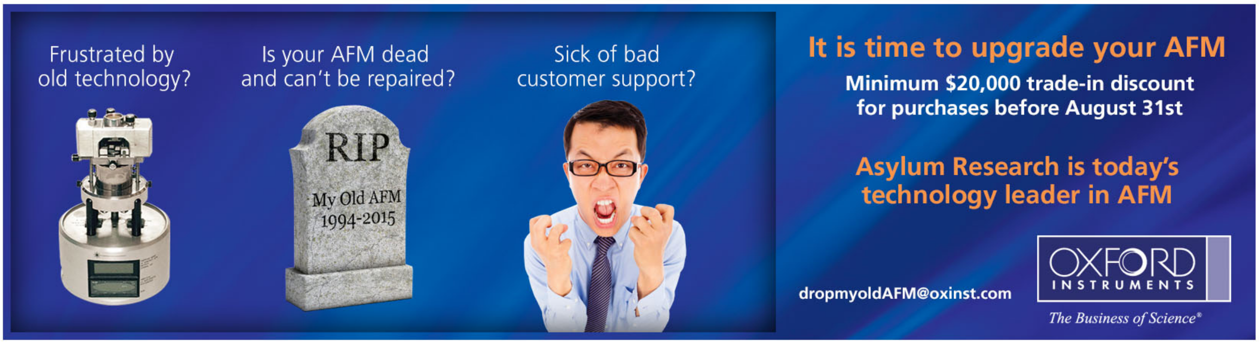

Time resolved photoluminescence of porous silicon: Evidence for tunneling limited recombination in a band of localized states

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Time resolved photoluminescence of porous silicon at room temperature was measured for several emission energies under 2 ns nitrogen laser excitation. For each emission energy studied there is a broad distribution of lifetimes extending over a few decades. The mean value of the distribution varies with the emission energy, from 3 (2.77 eV) to 50 μs (1.96 eV). The results can be explained by assuming a tunneling limited recombination mechanism between bands of localized states. We associate this behavior with a superficial disordered Si:O:H compound rather than with quantum confinement effects.

Strong visible luminescence from porous silicon at room temperature has been recently reported. This luminescence has been alternatively interpreted as due to confinement of carriers in silicon quantum wires or dots[1-4] or to the existence of Si:O:H compounds derived from siloxene on the sample surface.[5] The knowledge of the photoluminescence (PL) lifetimes as a function of the emitted photon energy can help in determining the luminescence mechanism. A wide range of decay lifetimes (mainly for the integrated PL) has been reported by several authors: Miyoshi *et al.*[6] measured values between 5 and more than 200 ns, Gardelis *et al.*[7] obtained values of 10 ns. Ookubo *et al.*[8] found 0.1–10 μs, Xie *et al.*[9] found 1–50 μs, and Bsiesy *et al.*[10] reported 5–100 μs. In this letter we report a detailed study of the room-temperature PL lifetime for emitted photon energies between 1.96 and 2.77 eV. We calculated the lifetime distribution for each photon energy. The results are modeled as due to tunneling limited recombination between bands of localized states.

Samples were prepared by the anodization of *p*-type (111) silicon (0.4 Ω cm) under a current density of 50 mA/cm^2 in HF solution (HF:H$_2$O$=$1:3) for 20 min. The aluminum ohmic contacts were made near the edge of the samples. During anodization a magnetic stirrer was used to keep the solution well mixed and to assist in removing the bubbles which accumulate in the wafer surface. The measurements took place approximately three weeks after the samples were prepared. When excited by the unfocused 2.71 eV line of a cw Ar$^+$ laser these samples presented PL at room temperature. This PL was strong enough to be visible with the naked eye, even for the smallest possible incident power with our system ($\sim$10 mW). This luminescence has a featureless wide peak (FWHM 0.65 eV) centered at 1.95 eV.

PL decay was measured at room temperature using a pulsed N$_2$ laser as an excitation source (3.68 eV, 2 ns FWHM, 120 μJ, 20 Hz repetition rate). The PL emission energy was selected by interferometric filters (1.0 nm bandwidth) and detected by a cooled ITT FW-130 (S-20) photomultiplier (10 ns pulse on 50 Ω) and a computer controlled Stanford SR400 photon counter trigged by a silicon diode exposed to part of the laser beam. The photon counter operated with both variable time window width (10 ns–1 ms) and delay (up to 10 ms). The signal accumulated after 1000 laser pulses was normalized to the window width. In order to ensure that the measured decay did not come from the possible PL of the lenses and filters (virtually everything emits luminescence under N$_2$ laser excitation), a polished silicon sample was measured. This control experiment yielded no more than one photomultiplier count in the 1 ms window width, which was the noise level of the system.

Figure 1(a) shows the PL decay for several of the photon energies studied in a logarithmic scale. There is clearly a nonexponential decay that indicates a distribution of lifetimes. A general method to calculate this distribution of lifetimes was developed by Tsang and Street.[11] Their approach assumes monomolecular recombination, an exci-

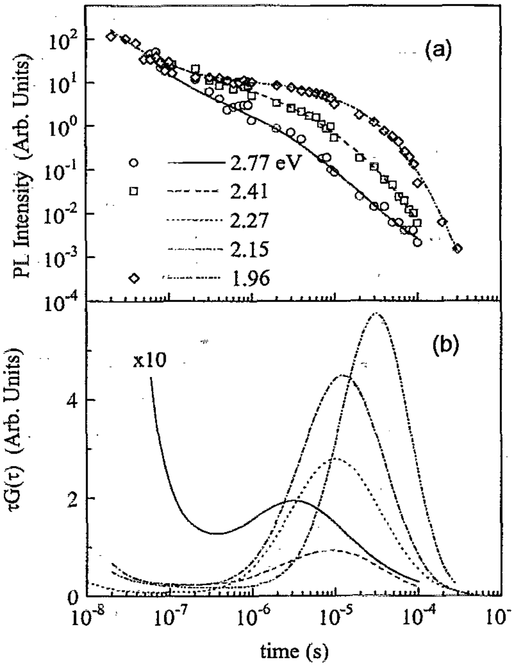

FIG. 1. (a) Time dependent photoluminescence of porous silicon in response to a 2 ns pulse for 2.77, 2.41, and 1.96 eV at room temperature. The curves for 2.27 and 2.15 eV are not represented for clarity. The lines are fits obtained from the lifetime distributions $G(\tau)$. (b) The lifetime distributions obtained from the data.

tation pulse shorter than the typical lifetimes, and a decay that is not saturated. Under such conditions, the relative probability distribution $G(\tau)$ that an electron-hole pair of radiative time τ is generated for a particular excitation condition can be written as $G(\tau) = \text{const } I d(\ln I)/d(\ln \tau)$, where $I(\tau)$ is the PL intensity at the time τ. To proceed with the calculations we construct a fourth-order polynomial in $\ln I$ versus $\ln \tau$ to solve for $G(\tau)$. $I(\tau)$ is then obtained back from the calculated $G(\tau)$. The polynomial parameters are iteratively adjusted until a good fit to the experimental data is obtained. The lines in Fig. 1(a) are fits to the experimental data obtained by this process. Figure 1(b) shows $\tau G(\tau)$ obtained using this approach. The function $\tau G(\tau)$ is chosen because of the logarithmic time scale,[11] since $G(\tau) d\tau \equiv \tau G(\tau) d(\ln \tau)$.

As shown in Fig. 1, our results indicate that the detailed lifetime distributions encompass the results of previous works.[6–10] Note that for all photon energies E_{ph} there is an increased $\tau G(\tau)$ for very short times (below 10 ns), indicating that at these time scales the PL process does not depend on E_{ph}. For $E_{\text{ph}} = 2.77$ eV, the highest energy studied (which yielded the weakest PL intensity), $\tau G(\tau)$ displays a small peak centered at 3 μs. As E_{ph} becomes smaller, this distribution narrows and shifts towards longer times up to 50 μs when $E_{\text{ph}} = 1.96$ eV, the lowest energy studied. Note that the average lifetimes for each E_{ph} are rather long and the lifetime distribution is very wide, extending over 2–3 decades of time. Also, as a consequence of the faster decay of the higher energy photons, the total spectrum shifts to lower energies as time advances, i.e., a red shift is observed.[6] This behavior is typical of tunneling limited radiative recombination of spatially separated electron-hole pairs.[11,12]

In order to explain the high energy of the PL spectra of porous silicon, some authors have suggested the existence of quantum confinement effects in small crystallites embedded in the structure.[1-4] However, an alternative interpretation based in compounds derived from siloxene has been recently proposed.[5] Indeed, Si-H and Si-O-Si infrared vibration modes have been observed in porous silicon.[8] Hydrogenated amorphous silicon (with a pseudogap of 1.7 eV) prevents a 0.3 eV wide PL peak centered in 1.3 eV at low temperatures.[12] It has been shown that the addition of oxygen to *a*-Si:H can broaden the PL peak and shift it towards higher energies, besides increasing the PL intensity at room temperature.[13] Actually both the broad lifetime distribution of porous silicon and the red shift of the PL as time evolves resemble qualitatively those observed in *a*-Si:H.[11] Our results suggest that the PL in porous silicon is probably related to a broad distribution of states associated with a disordered Si:O:H phase rather than due to quantum confinement effects. The main reasons for this are: First, exciting with 3.68 eV photons, the PL at room temperature extends up to at least 2.77 eV. This was the highest emission energy studied, and is higher than the gap values calculated even for the smallest conceivable quantum wires.[3,4] It is compatible, however, with emission from Si:O:H compounds.[5] Second, the wide distribution of lifetimes τ averaging at values $\bar{\tau}$ ranging from 3 to 50 μs, the shift of this $\bar{\tau}$ towards longer times and the narrowing of the distribution for lower photon energies are typical of radiative transitions between broad bands of localized states.

The proposed luminescence process is similar to that commonly accepted for amorphous silicon: After being generated deep in the bands, the carriers thermalize to the band edges via phonons in times of order of 1 ps.[14] After that a much slower thermalization process takes place in which carriers can hop inelastically between localized states or recombine radiatively. This hopping process can be repeated many times for a given carrier, and in each localized state there is a probability of recombining radiatively or continuing the inelastic hopping process towards states of lower energy. Carriers near the band edge have a higher probability of thermalization rather than radiative recombination because there are many nearby states of slightly lower energy. However, as the carrier moves to states of lower energy the number of available sites decreases and eventually the radiative transitions prevail. The lifetime distribution is determined by the convolution of the carrier density distribution and the density of states multiplied by the transition matrix. The density of states decreases exponentially with the energy, while the carrier density distribution widens less rapidly. Assuming a constant transition matrix, this convolution evolves towards lower energies and becomes narrower as time advances, accounting both for the red shift in the PL and the narrowing of $G(\tau)$.

The procedure to obtain the lifetime distributions assumed monomolecular recombination. Unfortunately, it is not possible to estimate the carrier separation from the generation rate since the effective area of porous silicon is not known precisely and is certainly very large.[15] However, a good test for this assumption is obtained by comparing the recombination length R_c and the thermalization distance L_D. In the radiative tunneling process the electron-hole distance at recombination R_c is related to the lifetime τ by $\tau = \tau_0 \exp(2R_c/R_0)$ where R_0 is the localization length.[16] Assuming[12] $R_0 \sim 1$ nm and $\tau_0 \sim 10^{-8}$ s, and using $\tau \cong 50$ μs (at the maximum PL emission under cw excitation), we find $R_c \cong 4.2$ nm.

The diffusion length during thermalization L_D is given by $L_D = (2\pi\hbar D \Delta E/E_0^2)^{1/2}$ where D is the diffusion coefficient, ΔE is the excess energy above the band edge, and E_0 is a typical phonon energy.[17] Assuming[12] $D \sim 0.5$ cm^2 s^{-1} for free carriers at room temperature and using a phonon energy of ~ 140 meV (the Si-O-S stretching mode in porous silicon[5,8]), an excess energy of ~ 1.7 eV (the difference between the excitation and the peak of the PL in cw conditions), we find $L_D \cong 4.8$ nm. This value is very close to the R_c calculated above, although the calculations involve rough approximations. This agreement indicates that recombination is geminate under the excitation conditions studied, which confirms the initial hypothesis of monomolecular recombination.

In conclusion, we have measured broad distributions of radiative recombination lifetimes extending for 2–3 decades and averaging from 3 to approximately 50 μs for different luminescence energies in porous silicon. The existence of such distributions and their narrowing accompanied by a red shift of luminescence with increased time are modeled assuming a distribution of localized states in a disordered Si:O:H compound. This model is also compatible with the measured cw luminescence peak position and width. The estimated average recombination distance agrees with the thermalization length, indicating geminate recombination.

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