Dynamic Quenching of Porous Silicon Excited States

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Received April 25, 1996. Revised Manuscript Received July 19, 1996[⊗]

Porous silicon samples have been prepared from p-type single-crystal silicon ⟨100⟩ by a galvanostatic and an open-circuit etch in 50% HF. The materials display bright red-orange room-temperature photoluminescence (PL) in air and toluene solution. Infrared measurements show that the porous silicon surface is partially oxidized. Exposure to anthracene (An) or 10-methylphenothiazine (MPTZ) results in dynamic quenching of the material's excited state(s). Nanosecond time-resolved PL decays are complex and wavelength dependent, with average lifetimes in neat toluene of 0.3−16 μs. Quenching by An and MPTZ is more efficient and rapid at short observation wavelengths. The steady-state and time-resolved quenching data are well fit to the Stern−Volmer model. The PL decays are well described by a skewed distribution of recombination rates.

Canham recently reported the preparation of silicon materials that display efficient, visible, room-temperature photoluminescence (PL).[1] Silicon has long been the backbone of the electronics industry, but its indirect bandgap and weak PL properties have precluded applications in many optical devices. Canham's discovery may one day change this, and an explosion of studies have been initiated to develop silicon-based electroluminescent devices from this material commonly referred to as porous silicon, po-Si.[2] More fundamentally, researchers have probed the origin of the PL and its interesting physical and optical properties.[2] An important goal is to develop a more complete understanding of the radiative and nonradiative decay pathways of po-Si's excited states. Toward this goal a number of researchers have used well-defined molecular species, such as organic compounds,[3,8] amines,[4] metal salts,[5] and hydroxide ions,[6] to probe the optical properties of po-Si.

The PL intensity from a semiconductor can be influenced by modulations in the surface electric field, the surface recombination velocity, or both. Even with well-defined single-crystal materials, it is experimentally difficult to quantify the underlying optoelectronic processes which drive PL intensity changes.[8] The situation is even more complex for po-Si where the distribution of emissive states remains uncertain.[2] The mechanism for quenching po-Si by molecular species cited above is therefore largely unknown. We recently reported that exposure of 10-methylphenothiazine (MPTZ) or anthracene (An) to porous silicon in neat toluene quenches both the PL intensity and the average excited-state lifetime indicative of dynamic quenching.[8] Further, the initial PL properties could be restored with toluene solvent. To our knowledge this represents the first demonstration of a reversible dynamic quenching mechanism for porous silicon excited states. The observation is important as it suggests that the surface recombination velocity at this technologically important interface can be reversibly tuned on a molecular level. Here we report more detailed studies of this dynamic quenching process.

Experimental Section

Materials. Toluene (Fisher Scientific), 50% HF (Fisher Scientific), and zone refined anthracene (Aldrich, 99+%) were used as received. 10-Methylphenothiazine (Pfaltz & Bauer) was recrystallized three times from toluene. Water was deionized with a Barnstead Nanopure system. Single crystal silicon wafers (⟨100⟩ 0.5 orientation, p-type, boron doped, ρ = 1 Ω cm) were obtained from Virginia Semiconductors, Inc.

Sample Preparation. The Si wafers were cut into ~3 cm^2 sections using a diamond scribe, placed in an HF bath for ~5 min and rinsed with deionized water (18 MΩ, Barnstead Nanopure System). The wafer was then etched galvanostatically at a current density of 13.4 mA/cm^2 for 40 min in a 50 wt % HF solution in a custom-built Teflon two-chambered cell,[9] washed with deionized water, and allowed to air dry for several minutes. The sample was then placed in the HF bath at open circuit for an additional 10−20 min, taken out, rinsed with deionized water, and dried. This procedure was repeated until intense red-orange PL was observed with UV light excitation. The samples were then stored in a desiccator until use. Prior to optical experiments, the samples were etched at open circuit in a 50% HF bath for 5−10 min. The samples were then dried and glued to a glass rod with Ducco cement, fitted in a thermometer adapter, and clamped into a 14/20 ground glass joint inside a custom-built glass cell. The cell has a Teflon stopcock at the bottom and a glass inlet at the top, which allows solution to be changed without altering the po-Si geometry.

Optical Measurements. *Steady-State PL.* Corrected PL spectra were obtained with a Spex Fluorolog, Model 112A. The

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

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

(2) (a) Benshalet, D. C., et al., Eds. *Optical Properties of Low Dimensional Silicon Structures;* Kluwer Academic Publishers: Holland, 1993. (b) Brus, L. *J. Phys. Chem.* **1994**, *98*, 3575.

(3) (a) Lauerhaas, J. M.; Credo, G. M.; Heinrich, J. L.; Sailor, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1911. (b) Lauerhaas, J. M.; Sailor, M. J. *Science* **1993**, *261*, 1567. (c) Fisher, D. L.; Harper, J.; Sailor, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 7846.

(4) Coffer, J. L.; Lilley, S. C.; Martin, R. A.; Files-Sesler, L. A. *J. Appl. Phys.* **1993**, *74*, 2094.

(5) Andsager, D.; Hilliard, J.; Hetrick, J. M.; AbuHassan, L. H.; Plisch, M.; Nayfeh, M. H. *J. Appl. Phys.* **1993**, *74*, 4783.

(6) Chun, J.; Bocarsly, A. B.; Cottrell, T. R.; Benziger, J. B.; Yee, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3024.

(7) Ellis, A. B. In *Chemistry and Structure at Interfaces: New Laser and Optical Techniques;* Hall, R. B., Ellis, A. B., Eds.; VCH: Deerfield Beach, FL, 1986; Chapter 6.

(8) Ko, M. C.; Meyer, G. J. *Chem. Mater*. **1995**, *7*, 12.

(9) (a) Friedersdorf, L. E.; Searson, P. C.; Prokes, S. M.; Glembocki, O. J.; Maccaulay, J. M. *Appl. Phys. Lett.* **1992**, *60*, 2285. (b) Searson, P. C.; Macaulay, J. M.; Ross, F. M. *J. Appl. Phys.* **1992**, *72*, 253.

S0897-4756(96)00247-5 CCC: $12.00

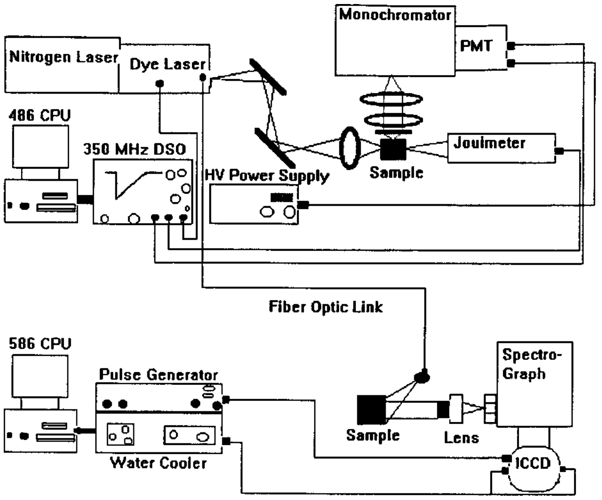

Figure 1. Schematic diagram of the apparatus employed to obtain kinetic and gated PL spectra of po-Si materials. A detailed description is given in the Experimental Section.

PL was obtained in a front-face mode with a Hamamatsu R668 PMT optically coupled to a Spex dual-grating monochromator. The PL spectra were corrected with a calibration curve generated with 2.0 mm slits by using a NBS calibrated 250 W lamp (Optronics Laboratories, Inc. Model 220M), controlled by a precision current source at 6.50 W (Optronics Laboratories, Inc. Model 65). For excitation spectra, a beam splitter redirects a portion of the excitation light into a rhodamine B quantum counter to monitor the wavelength-dependent irradiance of the Xe lamp. The excitation spectra is recorded as the ratio between the PL intensity and the excitation irradiance.

Time Resolved PL. Time-resolved PL studies were performed with the apparatus shown in Figure 1. A Laser Photonics LN 100/107 nitrogen-pumped dye laser with Coumarin 460 (exciton) was used for excitation. Typical excitation irradiance was 40−60 μJ/pulse monitored with a Molectron J3-09 joulemeter at a repetition rate of ~1 Hz. The PL was collected with two *f*/2 lenses to a McPherson Model 272 *f*/2 scanning monochromator. A long-pass 495 filter was placed between the sample and the monochromator to remove scattered light. A Hamamatsu R928 photomultiplier tube (PMT) mounted in an EMI-shielded housing was optically coupled to the monochromator. The PMT base was wired for fast response and biased at −900 V with a Thorn EMI Model 3000R power supply. The signal from the PMT was terminated into 50 Ω of a LeCroy 9450 350 MHz digital storage oscilloscope optically triggered with a photodiode (Motorola MRD 500) mounted in the dye laser. The instrument response function was measured to be 14 ns with colloidal SiO_2 (LUDOX) as a light scatterer. The extrema and average of 100−200 decays were collected and subsequently transferred to a 486 microprocessor via a GPIB bus. For data fitting, the time base was adjusted such that the initial PL response occurs at time zero and data analysis was initiated at 30 ns. The data were analyzed by a Marquardt algorithm and/or a Nelder−Mead modified simplex routine with code written in ASYST (Keithly).

Alternatively, a fiber optic link (FOL) brought the excitation to the sample positioned in front of an Instruments SA HR-320 spectrograph coupled to a Princeton Instruments intensified charge-coupled device (ICCD). The PL was collected with a 50 mm camera lens. The ICCD was controlled with a Princeton Instruments Controller and a PG-200 pulse generator. Data were sent from the Controller to a 486 or 586 microprocessor via a direct memory access (DMA) cable. The ICCD was calibrated with a Hg(Ar) lamp (Oriel).

Infrared. IR spectra were taken on a Perkin-Elmer 1600 Series FTIR (±4 cm^{-1}) instrument in a transmission mode. The sample compartment was purged with dry N_2 gas during all experiments.

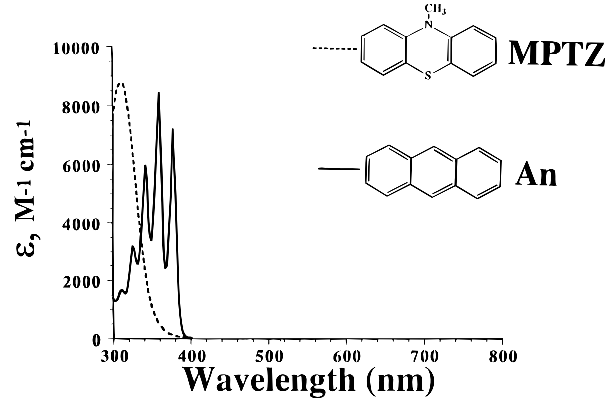

Figure 2. Absorbance spectrum of anthracene (—) and 10-methylphenothiazine (- - -) in toluene. The instrument resolution is ±2 nm.

UV−Vis. UV−vis absorbance measurements were made on a Hewlett-Packard 8451A diode array, with ±2 nm and ±0.005 au resolution.

Results

The absorbance spectra of anthracene (An) and 10-methylphenothiazine (MPTZ) in toluene is given in Figure 2. At wavelengths longer than 400 nm there is negligible absorbance, which indicates that the organic compounds do not absorb light at the excitation or observation wavelengths.

Porous silicon samples were prepared by a galvanostatic etch in 50% HF for 40 min at a current density of 13.4 mA/cm^2. A significant change from our previous studies is that an open-circuit etch in 50 wt % HF was performed immediately before optical measurements. The open circuit etch is known to increase the PL intensity and porosity of the po-Si.[9] FTIR spectra of po-Si before and after the steady-state quenching studies with An and MPTZ described below are typical of partially oxidized porous silicon and the absorbances can be assigned based on previously reported studies.[10] Spectral features near 1100 cm^{-1} are assigned to Si−O−Si.[10a] There are three very distinct peaks centered at 2137, 2110, and 2088 cm^{-1} and a peak at 907 cm^{-1} which have been ascribed to SiH_x vibrations.[10b] IR measurements before and after PL quenching experiments showed a slight increase in intensity of the signal near 1100 cm^{-1} with no significant changes in the (SiH_x) modes near 2100 cm^{-1}.

Upon illumination of po-Si in toluene with ~1−2 mW/cm^2 of 460 nm light, a gradual decrease in PL intensity is observed over the first 20−30 min. After this time a stable PL intensity is observed with only minor changes in intensity after hours of illumination. Steady-state measurements were generally performed after this illumination/conditioning period. The corrected PL and excitation spectrum of a representative sample in neat toluene is shown in Figure 3. The corrected PL maximum is typically 710 ± 30 nm and the full width at half maximum is 2500 ± 200 cm^{-1} with 460 nm excitation. When the excitation wavelength is decreased, the PL maximum shifts toward higher energy. For example, the PL maximum shifts from 695 to 760 nm when the

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(10) (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. in *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981; pp 175. (b) Brodsky, M. H.; Cardona, M.; Cuomo, J. J. *Phys. Rev. B* **1977**, *16*, 3556.

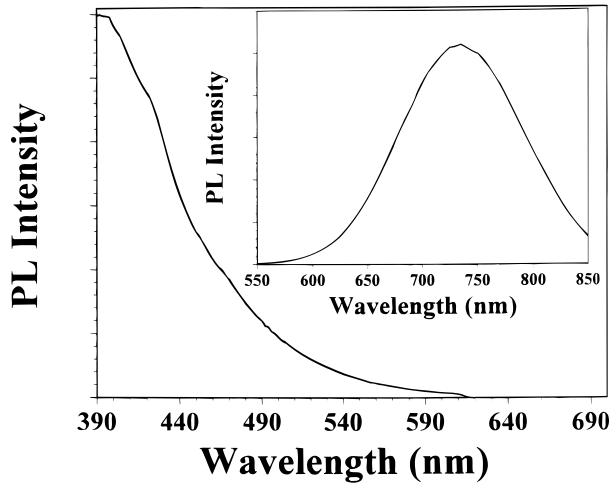

Figure 3. Corrected room-temperature PL (inset) and excitation spectra of po-Si in neat toluene. The excitation spectra was recorded at λ_{mon} = 735 nm and the PL spectra was recorded at λ_{ex} = 460 nm. The incident irradiance at 460 nm was 1.79 mW/cm^2 and all wavelengths are ±3 nm.

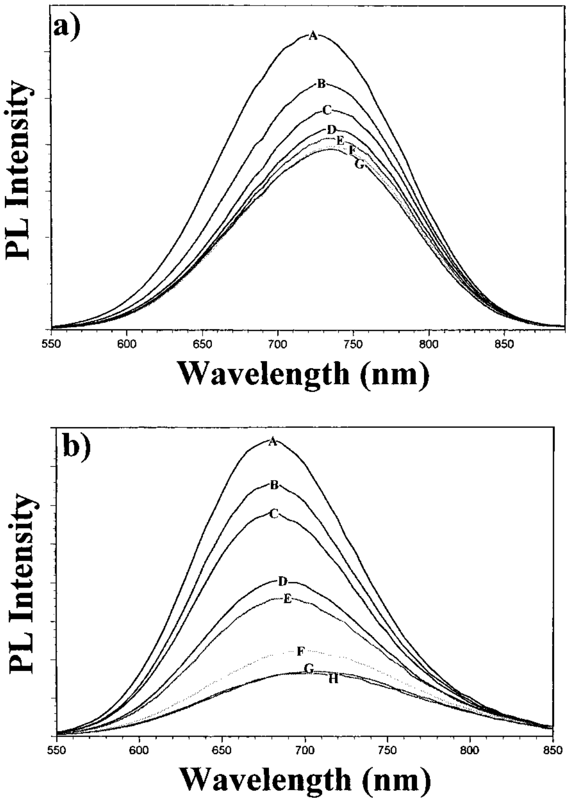

Figure 4. (a) PL spectra of a po-Si sample as a function of anthracene (An) concentration in toluene. The millimolar concentrations are (A) = 0.00; (B) = 0.60, (C) = 1.05, (D) = 1.40, (E) 1.68, (F) = 1.91; and (G) = 2.10. (b) PL spectra of a po-Si sample as a function of 10-methylphenothiazine (MPTZ) concentration in toluene. The millimolar concentrations are (A) = 0.00, (B) 0.06, (C) 0.13, (D) 0.20, (E) 0.26, (F) 0.54, (G) 0.78, and (H) 0.99. The excitation wavelength was 460 ± 3 nm.

excitation wavelength is moved from 420 to 500 nm. The incident irradiance at 420, 460, and 500 nm was 1.68, 1.79, and 1.47 mW/cm^2, respectively.

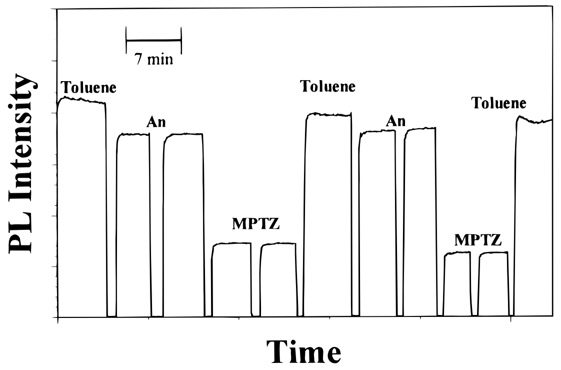

Figure 5. PL intensity of a po-Si sample with alternate exposures to neat toluene (initial intensity) and to 4 mM An or 4 mM MPTZ recorded in a time-base mode. The extent of quenching was ~15% for An and ~66% for MPTZ. The sample was excited with 460 ± 3 nm and monitored at 730 ± 3 nm.

PL quenching as a function of quencher concentration with 460 nm excitation is shown in Figure 4. Addition of An or MPTZ results in a reversible decrease in the PL intensity and red-shift in the PL spectra. Excitation at shorter wavelengths leads to a more dramatic red-shift with added quencher than does excitation with longer wavelengths of light. In our previous studies, with 475 nm light excitation the spectral shift with added quencher could not be resolved, for example.[8] The data shown in Figure 4 were collected with 460 nm excitation, and the spectral shift is clearly seen. With 400 nm excitation, addition of quencher results in a more pronounced red shift. All the steady-state and time-resolved data reported here were obtained with 460 nm excitation so that internal comparisons could be made and to avoid the possibility of direct excitation of the quenchers.

To explore the reproducibility and reversibility of the quenching processes, experiments were performed where the PL intensity from an individual po-Si sample was monitored in neat toluene and toluene–quencher solutions in a time-base mode. Shown in Figure 5 are typical results from a po-Si sample monitored at 730 nm. The sample is initially in neat toluene and is then exposed to 4 mM An which results in a 15% decrease in PL intensity. The solution is then changed to 4 mM An a second time to demonstrate the reproducibility of the quenching. The sample is then exposed to 4 mM MPTZ and a more dramatic ~66% decrease in PL intensity is reproducibly observed. Neat toluene restores the PL intensity to within 95% of the initial value. Studies with a large number of samples have shown that continued cycling between neat toluene and toluene–quencher solutions results in an increased degree of reversibility.

Time-resolved PL decays from porous silicon in neat toluene are complex and dependent on the monitoring wavelength. With 50 ± 10 μJ/pulse excitation at 460 nm the decays were nonexponential at all monitoring wavelengths and quencher concentrations studied. Normalized and unnormalized PL decays were analyzed by the Kohlrausch–Williams–Watts function (KWW)[11] which has been used extensively for po-Si materials, (eq 1).[12] Here α is the initial PL intensity, β is related to the width of an underlying Levy distribution of rates,

$$\mathrm{PLI}(t) = \alpha \exp(-t/\tau)^{\beta} \qquad 0 < \beta < 1 \qquad (1)$$

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[11] (a) Kohlrausch, R. *Annalen* **1847**, *5*, 430. (b) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.

Table 1. KWW Analysis of Time-Resolved PL[a]

	toluene			anthracene			methylphenothiazine		
$\lambda_{\text{mon}}{}^{b}$	τ	β	$\langle\tau\rangle$	τ	β	$\langle\tau\rangle$	τ	β	$\langle\tau\rangle$
600	1.16	0.44	3.03	0.320	0.54	0.560	0.0035	0.36	0.016
620	2.98	0.55	5.13	0.438	0.56	0.723	0.0020	0.30	0.018
640	4.10	0.56	6.73	0.611	0.58	0.969	0.0020	0.28	0.025
660	3.77	0.52	7.13	0.651	0.54	1.12	0.0100	0.30	0.092
680	3.92	0.50	7.73	0.767	0.53	1.61	0.0100	0.29	0.100
700	3.01	0.45	7.46	0.768	0.48	1.66	0.0588	0.37	0.238
720	2.46	0.43	6.78	0.734	0.45	1.82	0.128	0.42	0.373
740	3.42	0.49	7.10	0.593	0.40	1.97	0.0823	0.38	0.317
760	0.890	0.36	4.07	0.289	0.35	1.45	0.0360	0.32	0.253
780	0.116	0.27	1.63	0.132	0.31	1.06	0.0170	0.30	0.156
800	0.006	0.21	0.440	0.016	0.24	0.410	0.0460	0.35	0.233

[a] Kohlrausch–Williams–Watts (KWW) analysis of the time resolved photoluminescence (PL) decays in neat toluene, 4 mM anthracene, and 4 mM methylphenothiazine. The KWW function is given in equation 1. Lifetimes τ and mean lifetimes $\langle\tau\rangle$, calculated with eq 2, are given in microseconds. The samples were excited with 50 ± 10 μJ/pulse of 460 nm light. [b] Uncorrected wavelength PL was monitored at ±3 nm.

and τ is the lifetime at the maximum amplitude of the distribution. An average lifetime, $\langle\tau\rangle$, was calculated with eq 2, where Γ represents the gamma function.[13]

$$\langle\tau\rangle = \left(\frac{\tau}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right) \tag{2}$$

Low β values indicate a highly skewed distribution of rates, and thus the average lifetimes can be up to an order of magnitude greater than τ. The best-fit parameters τ and β were determined and the corresponding average lifetime calculated (Table 1). Goodness of fits as judged by residuals and sum-of-squared errors (SSE) were excellent at all wavelengths and quencher concentrations. Since the accuracy of the fit parameters highly depends on the degree of correlation, contour plots were constructed from the relative error over a wide range of τ and β for each individual PL decay. The error surfaces constructed from decays in neat toluene, 4 mM MPTZ, and 4 mM An from 600 to 750 nm observation wavelengths reveal a well-defined global minima for all data. With MPTZ the error surface becomes somewhat elongated, but even in the worst case scenarios, uncertainties of ±0.04 in β and ±10% for $\langle\tau\rangle$ are recovered. However, from 760 to 800 nm observation wavelengths the uncertainty in β rises to ±0.06 and ±70% in $\langle\tau\rangle$ which is due, in part, to the decreased PL intensity and sensitivity of the photomultiplier tube.

Mean lifetimes calculated from eq 2 were somewhat sample dependent, and values of 7 ± 4 μs at 700 nm were typically calculated for multiple representative po-Si samples in neat toluene. In all cases, the addition of An or MPTZ results in a shortened, concentration-dependent mean lifetime. Figure 6 shows the time-resolved quenching at 600 and 700 nm observation wavelengths. KWW parameters obtained from fits to the PL decays observed every 20 nm from 600 to 800 nm are summarized in Table 1. From these data it is seen that the fractional quenching is significantly larger at higher energy observation wavelengths. At the conclusion of the time resolved quenching studies, the cell was drained of the quencher solution and washed three times with neat toluene, and neat toluene was restored. The mean lifetime can be restored to the initial within experimental error.

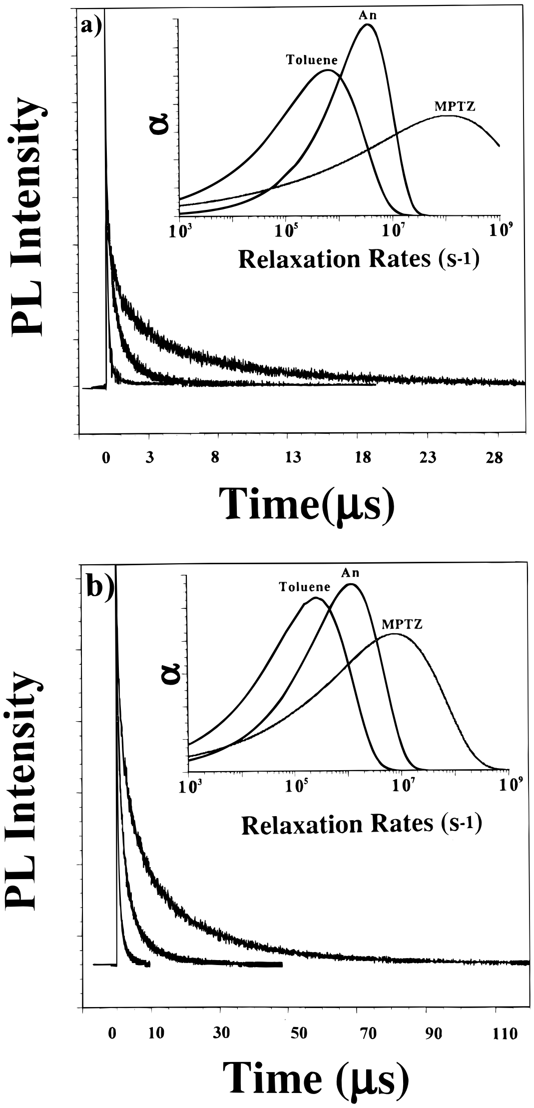

Figure 6. PL decays for po-Si in neat toluene (upper trace), 4 mM An (middle trace), and 4 mM MPTZ (bottom trace). The data were recorded at (a) 600 nm and (b) 700 nm observation wavelengths. The insets represent inverse Laplace transformations of the KWW fits of the data. See text for additional details.

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(12) (a) Xie, Y. H.; Wilson, W. L.; Ross, F. M.; Mucha, J. A.; Fitzgerald, E. A.; Macaulay, J. M.; Harris, T. D. *J. Appl. Phys.* **1992**, *71*, 2403. (b) Finkbeiner, S.; Weber, J.; Rosenbauer, M.; Stutzman, M. *J. Lumin.* **1993**, *57*, 231. (c) Pavesi, L.; Ceschini, M.; Rossi, F. *J. Lumin.* **1993**, *57*, 89. (d) Pavesi, L.; Ceschini, M. *Phys. Rev. B* **1993**, *48*, 17625.

(13) Linsey, C. P.; Patterson, G. D. *J. Chem. Phys.* **1980**, *73*, 3348.

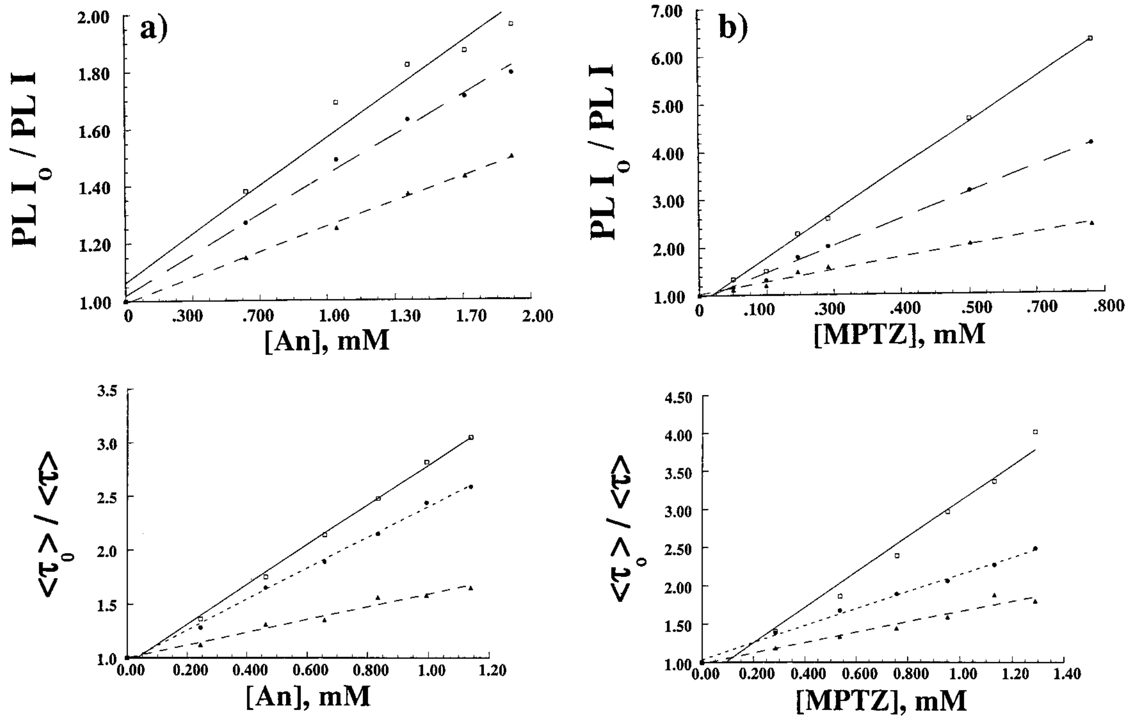

Figure 7. Stern−Volmer plots for the quenching of po-Si by (a) An and (b) MPTZ. The observation wavelengths were 650 nm (squares), 700 nm (circles), and 750 nm (triangles), and the slopes are summarized in Table 1. For steady-state measurements the samples were excited with 1.8 mW/cm^2 of 460 nm light, and the transient data were recorded with 50 ± 5 μJ/pulse of 460 nm light.

Table 2. Stern−Volmer Constants, K_{SV} (M^{-1})[a]

	anthracene				methylphenothiazine			
	650 nm	700 nm	750 nm	integrated	650 nm	700 nm	750 nm	integrated
PLI$_0$/PLI	500	420	260	320	7000	4200	1900	4200
$\langle\tau_0\rangle/\langle\tau\rangle$	1900	1400	590		2300	1100	700	
$10^{-8}k_q$ (M^{-1} s^{-1})[b]	2.7	1.2	1.0		9.0	2.6	3.0	

[a] Stern−Volmer constants calculated by linear regression of the data shown in Figure 7. [b] The bimolecular quenching rate constant calculated with eq 4 for a representative po-Si sample.

Collectively, the steady-state and time-resolved PL are well fit to the Stern−Volmer model, (eq 3).[14]

$$\frac{\mathrm{PLI_0}}{\mathrm{PLI}} = 1 + K_{SV}[\mathrm{Q}]$$

$$\frac{\langle\tau_0\rangle}{\langle\tau\rangle} = 1 + K_{SV}[\mathrm{Q}] \qquad (3)$$

PLI$_0$, PLI, $\langle\tau_0\rangle$, and $\langle\tau\rangle$ represent the PL intensity and mean lifetimes in the absence and presence of the quencher Q (An or MPTZ), respectively. K_{SV} is the Stern−Volmer constant. The K_{SV} values calculated from lifetime quenching measurements were converted to apparent bimolecular quenching rates, k_Q, using eq 4.

$$k_Q = K_{SV}/\langle\tau_0\rangle \qquad (4)$$

Stern−Volmer analysis was performed with 460 nm excitation at 650, 700, and 750 nm observation wavelengths, (Figure 7). At these wavelengths the quenching consistently follows the Stern−Volmer model by PL intensity and lifetime quenching. Under steady-state conditions the integrated PL intensity also follows the Stern−Volmer model (Table 2). K_{SV} values from steady-state data were within a factor of 2−4 of those measured by lifetime quenching. K_{SV} values were consistently larger at short observation wavelengths for either quencher (Table 2). At a given wavelength, K_{SV} values for MPTZ were usually larger than for An. k_Q measured at 650 nm was typically 2−3 times greater than that measured at 700 or 750 nm observation wavelengths. Although large sample-to-sample deviation precludes direct comparisons, k_Q values were typically (0.8−90) × 10^8 M^{-1} s^{-1}.

Shown in Figure 8 are the integrated PL spectra recorded at different delay times after excitation with a 460 nm laser pulse. The spectra are shown from 570 to 820 nm which represents the maximum window achievable with this grating/spectrograph. The spectra were integrated for 150 ns and the delays given in the caption (t = 30 ns, 500 ns, 5 μs, and 10 μs) correspond to the time delay between laser excitation and initiation of integration. The wavelength-dependent quenching processes are clearly observed in these spectra. Consistent with the kinetic data, the presence of 4 mM quenchers quenches the PL intensity, shifts the PL spectra toward the red, and sharpens the PL spectra as a function of time.

Discussion

The porous silicon samples prepared here display optical properties typical of partially oxidized po-Si.[2,4−6,15] The quenching of the material's excited states

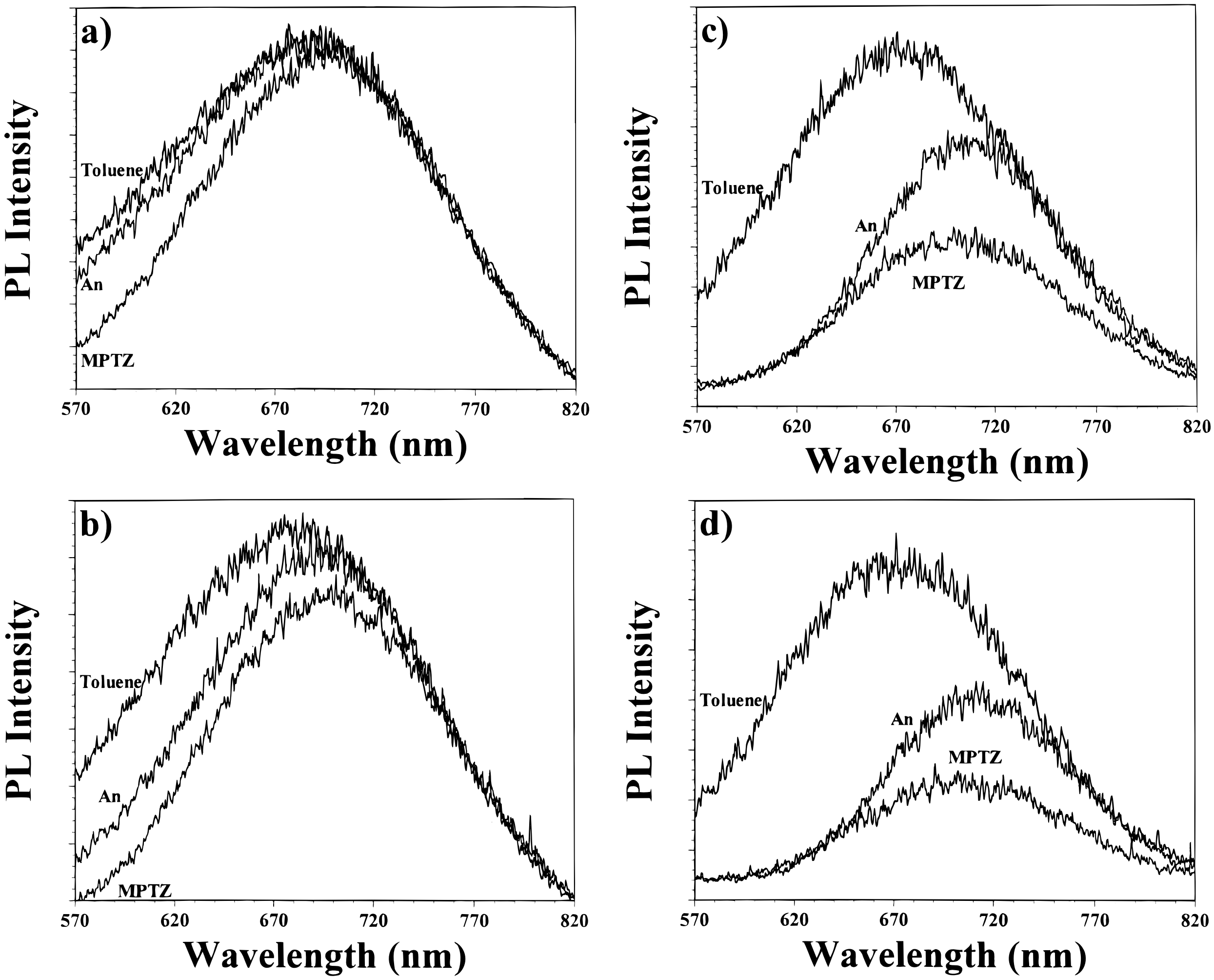

Figure 8. Integrated PL spectra recorded at delay times, *t*, after excitation with a 460 nm laser pulse: (a) $t = 30$ ns; (b) $t = 500$ ns; (c) $t = 5$ μs; and (d) $t = 10$ μs. The spectra were integrated for 150 ns with an intensified CCD camera as described in the Experimental Section. The spectra were recorded in neat toluene (Toluene), 4 mM anthracene (Ar), and 4 mM methylphenothiazine (mPTZ).

is dependent on the wavelength at which the PL is monitored: Photons emitted toward the blue are more efficiently quenched by anthracene and 10-methylphenothiazine than those toward the red. This observation has been previously reported for the steady-state quenching of po-Si by metal ions and organic compounds.[3c,5] An important conclusion that can be drawn from these studies is that the bimolecular quenching rate constant is larger at short observation wavelengths. The excited states in po-Si which emit light at higher energy are more rapidly and efficiently quenched by An and MPTZ than the excited states which emit at lower energy. This can be seen in the gated PL spectra of Figure 8 and indicate that po-Si materials would be useful as ratiometric chemical sensors.

A goal of these studies was to explore the possibility that some underlying static quenching processes might also be present. Static and dynamic quenching processes are both well documented in the semiconductor literature.[16] Static quenching generally occurs when there is a ground-state interaction between the semiconductor and the quencher. Dynamic quenching occurs in the absence of such interactions. In many assemblies both static and dynamic quenching processes occur. For purely dynamic quenching, plots of τ_0/τ and $\mathrm{PLI}_0/\mathrm{PLI}$ are linear and coincident. For the system at hand, the plots are linear and the slopes are generally within a factor of 2−4; however, they are not coincident. It is unclear whether this is due to some static processes or an artifact from modeling the complex time-resolved PL data. Therefore, the Stern−Volmer analysis alone does not provide conclusive evidence of a purely dynamic quenching mechanism.

A second diagnostic for dynamic quenching is that the initial PL amplitude following pulsed excitation is independent of quencher concentration.[17] In the time-resolved PL studies of po-Si it is experimentally difficult to remove scattered light which results in significant uncertainty in the time zero PL amplitude. To circumvent this difficulty, we employed an ICCD camera gated 30 ns after the laser pulse. At this delay time the scattered light was eliminated and the early time PL amplitude was cleanly observed. The near coincidence of spectra observed in toluene and 4 mM An reveal a purely dynamic quenching process for anthracene. For MPTZ, the quenching at longer wavelengths, ≥700 nm,

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(14) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.

(15) Sagnes, I.; Haliaoui, Vincent, G.; Badoz, P. A. *Appl. Phys. Lett.* **1993**, *62*, 1155.

(16) Kamat, P. V. *Prog. Inorg. Chem.* **1996**, *44*, 273.

(17) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543.

is also dynamic in origin. However, at shorter wavelengths there is some evidence for an underlying static component to the quenching by MPTZ.

A final goal of these studies was to evaluate the physical significance of the Kohlrausch–Williams–Watts (KWW) function used to model the PL decays. This function was first empirically proposed by Kohlrausch, popularized by Williams and Watts, and has since been shown to model a wide range of time-dependent phenomena.[11,18] Although the KWW function models the po-Si data reported here and elsewhere,[12] it is unclear what, if any, physical meaning the fit parameters have. Qualitatively the fit parameters do reflect the observed kinetics. Mean lifetimes obtained as a function of quencher concentration are well fit to the Stern–Volmer model with well defined minima over a large wavelength range.

Since the KWW function does analytically describe the data, it is worthwhile to consider the distribution of relaxation rates which underlie them. This can be accomplished by direct inverse Laplace transform of the time-resolved PL data or the function which describes them.[19] The inverse Laplace transform of the KWW model has only analytical solutions at discrete β values but has been evaluated more generally by series expansion and a saddle-point calculation.[20] We have used the saddle-point calculation[20b] to generate the relaxation rate distributions depicted in Figure 6 for po-Si decays in the presence and absence of quenchers at 600 and 700 nm observation wavelengths.

The distribution of rates recovered have significant amplitude over 3 decades of rate space. We previously suggested that the distributions retain their general shape in toluene and shift in rate space with added quencher.[8] This appears to be approximately the case for quenching by An. In contrast, the recovered distributions in the presence of MPTZ broaden significantly with respect to toluene. Since there exists some evidence of adduct formation between po-Si and MPTZ, i.e., static quenching, the adduct(s) will likely have unique radiative and nonradiative decay pathways which could account for the broadened distributions recovered for this quencher. While this distribution analysis appears reasonable, we emphasize that inverse Laplace transformations are inherently ill-conditioned.[19] There exist a large class of skewed distributions which will describe these data equally well. A larger data base is required before the physical significance of these distributions can be accurately assessed.

Conclusions

The results demonstrate that the surface recombination velocity of po-Si can be controlled with molecular quenchers, in agreement with our previous conclusion.[8] Excited states which emit light at high energy are quenched more rapidly and efficiently than those which emit at lower energy. The concentration and wavelength dependence of the quenching indicates that po-Si may be useful as lifetime and ratiometric chemical sensors. The complex kinetic data are well described by a skewed distribution of rates. It is difficult to ascertain whether the PL quenching is driven, in part, by modulations in the surface electric field.[7] However, we note that if the po-Si emission is from quantum-sized Si particles, large PL intensity changes are not expected to be driven solely by modulations in the surface electric field due to the small particle size.[21] More studies are clearly required before the electronic and optical properties of these fascinating excited states can be fully rationalized.

Acknowledgment. This work was supported by the Army Research Laboratory.

Supporting Information Available: The supplementary data include representative error surfaces for fits of the time-resolved PL data to the Kohlrausch–Williams–Watts model.

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(18) (a) Palmer, R. K.; Stein, D.; Abrahams, E. S.; Anderson, P. W. *Phys. Rev. Lett.* **1984**, *53*, 958. (b) Scher, H.; Schlesinger, M. F.; Bendler, J. T. *Phys. Today* **1991**, *588*, 26 and references therein.

(19) Ware, W. R. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers, Inc.: New York, 1991; Chapter 13.

(20) (a) Linsey, C. P.; Patterson, G. D. *J. Chem. Phys.* **1980**, *73*, 3348. (b) Majumdar, C. K. *Solid State Commun.* **1971**, *9*, 1087.

(21) Albery, W. J.; Bartlett, P. N. *J. Electrochem. Soc.* **1992**, *96*, 5983.