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Proton Gated Emission from Porous Silicon

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It was originally suggested that the room-temperature visible luminescence which has been recently observed from porous silicon (PS) surfaces arises from quantum structures, which form as the porous layer is created.[1] Some researchers, however, have argued that luminescence arises from surface-confined chemical species like silicon hydrides,[2] siloxanes, or siloxenes.[3,4] Although a major effort has been directed at characterizing the photophysics of this process, with the exception of a report by Sailor on the sensitivity of the excited-state lifetime to the presence of various organic solvents, little work has been directed at the photochemical nature of the luminescent reactions.[5,6] The work by Sailor et al. has been largely phenomenological in nature; the underlying chemistry associated with the observed quenching has not been determined. In addition, this work did not consider the effect of solvent exposure on the excited-state lifetime of the luminescent species; thus, whether the observed quenching effects involve a static or dynamic process was not ascertained. Herein, we report on a very specific, reversible chemical interaction between porous silicon and gas- or solution-phase bases, which demonstrates that emission is associated with the presence of a relatively acidic ($pK_a \sim 3$) ground-state surface proton. Although the current report only considers the quenching response of p-type PS,[7] a similar response is also obtained if n-type PS is employed.

Exposure of the PS surface to a variety of inorganic and organic bases produces reversible quenching of the luminescence that can be restored by exposing the PS substrate to water, mineral acids, or organic acids. The vapors of trifluoroacetic acid bring back the luminescence intensity quickly, but PS must be immersed in other acids such as HCOOH, H_2SO_4, HCl, oxalic acid, and citric acid in order to restore the luminescence. This type of reactivity is in direct contrast to that observed upon exposure of PS to aqueous hydroxide which produces irreversible quenching of the luminescence due to the known chemical reaction:[8]

$$\mathrm{Si(s)} + 4\mathrm{OH^-(aq)} \rightarrow \mathrm{SiO_4^{4-}(aq)} + 2\mathrm{H_2(g)}\uparrow \qquad (1)$$

Table I indicates a generally consistent relationship between the pK_a of the acid or base employed and its ability to quench PS luminescence. The ability to quench PS emission appears to be independent of the chemical nature of the base employed, correlating only with the pH of the quenching solution.

Table I. Effect of Acids and Bases on Visible PL Emission

acid/base	pK_a[a]	result
HCl (concd)	−6.1	no quenching/restores PL
H_2SO_4 (concd)	−3	no quenching/restores PL
HNO_3 (concd)	−1.44	no quenching/restores PL
CF_3COOH (g)	0.0	no quenching/restores PL
L-histidine (aq)	0.25	no quenching/restores PL
citric acid (aq)	0.50	no quenching/restores PL
oxalic acid (aq)	1.25	no quenching/restores PL
HF (48%)	3.18	no quenching/restores PL
HCOOH (aq)	3.74	no quenching/restores PL
aniline (non-aq)	4.60	no quenching
CH_3COOH (glacial)	4.74	no quenching/restores PL
boric acid (aq)	(5.1)[b] 9.23	no quenching/restores PL
pyridine (neat)	5.23	no quenching
H_2S (g)	7.02	no quenching
$NaHCO_3$ (aq)	(8.3)[b] 6.5	quenches/restored w/TFA[c]
KCN (aq)	9.1	quenches/restored w/TFA
NH_3 (g)	9.24	quenches/restored w/TFA
$(CH_3)_2CH_2NH_2$ (non-aq)	10.63	quenches/restored w/TFA
$(CH_3CH_2)_2NH$ (non-aq)	10.93	quenches/restored w/TFA
$((CH_3)_2CH_2)_2NH$ (non-aq)	11.13	quenches/restored w/TFA
Na_2CO_3 (aq)	(11.6)[b] 6.35, 10.33	quenches/restored w/TFA
SO_2 (g)		quenches/restored in air

[a] pK_as are for aqueous and nonaqueous solutions. [b] pH of an aqueous solution. [c] TFA = trifluoroacetic acid.

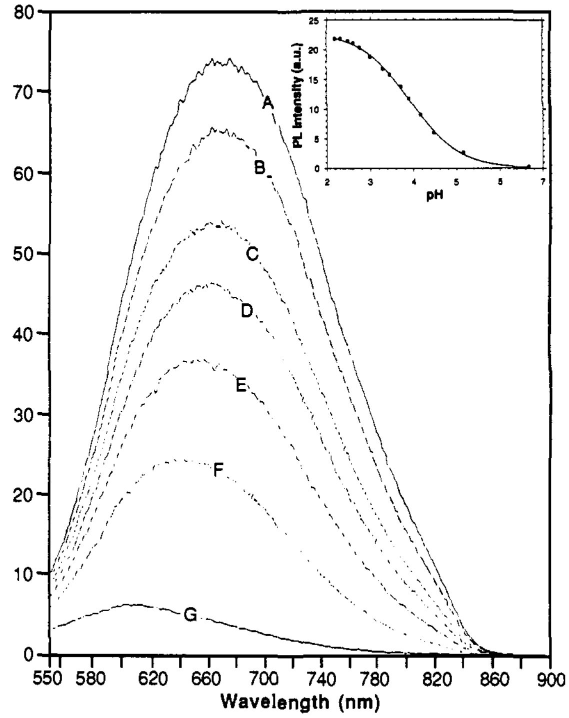

Figure 1. Room-temperature emission spectra of p-type PS as a function of added 0.03 M bicarbonate. pH = (A) 2.99, (B) 3.45, (C) 3.90, (D) 4.15, (E) 4.46, (F) 5.15, (G) 6.67. Excitation wavelength = 400 nm. (inset) PL monitored at 800 nm vs pH. Solid curves are calculated fits based on eq 2.

The reversibility of the acid/base chemistry is demonstrated by back titration of the PS in 0.01 M HCl with 0.03 M $NaHCO_3$ (Figure 1). Emission spectra exhibit an apparent blue shift from 680 nm at pH = 3 to 610 nm at pH = 6.7. The inset to Figure 1 shows the change in emission intensity as a function of pH, and the shape and slope of the curve are indicative of a monoprotic process having a $pK_a = 3.0 \pm 0.9$. Approximately 10^{16} protons/cm^2 are liberated at the equivalence point.[9]

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(7) p-PS was formed on boron-doped p-type Si ⟨100⟩ (9–11 Ω cm) by galvanostatic (25–30 mA/cm^2) etching in a 1:1 mixture of HF:EtOH (v/v). Samples were characterized by FTIR and PL spectroscopy. Freshly prepared PS samples and samples which were aged in air for several months yielded different IR and photoluminescent emission spectra but produced similar acid–base chemistry.

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It has previously been demonstrated that PS excited-state dynamics can be described by a "stretched" exponential function.[10] For the surfaces under consideration, τ, the effective lifetime, is 50 ± 10 μs when monitored at 750 nm and remains essentially unchanged, independent of the solution pH.[11] Likewise, a sample that has been deuterated by soaking a deprotonated surface in concentrated aqueous DCl shows no change in the lifetime when compared to PS in HCl. Prior FTIR work[12] has shown that porous silicon is easily deuterated, even by D_2O. That work demonstrated shifts in SiO–H, Si–H, and Si–OH vibrations with D replacement. The invariance of the observed lifetime with pH along with the lack of an H/D isotope effect strongly argues for a ground-state (i.e., static) quenching phenomena. Thus, the pK_a obtained is assigned to a ground-state surface confined acid.

The calculated surface pK_a describes a sufficiently acidic environment to rule out a surface silicon hydride, a silanol-like species, or siloxene as the source.[4,13] On the basis of the chemistry of silica, a proton associated with a bridged oxygen is expected to manifest a pK_a in the observed range.[14] This may be represented by Si–O(H$^+$)–Si.

These data also rule out an isolated group of surface-confined molecules as the luminescent species. The lack of an H/D isotope effect on radiative recombination indicates that the rate-limiting nonradiative pathway is unchanged by deuteration. The characteristics of photoluminesce from a molecular luminophore are expected to change with alterations in the proton concentration if the luminescent moiety contains the acid functionality. Therefore, a solid-state luminophore must be invoked. Two possible models are the elimination of the proton, (1) inducing a physical restructuring of the silicon particles or (2) a change in the surface energetics. In the latter case, a surface trap which shifts in energy depending on protonation may be the source of the observed behavior.

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(9) Previous work suggests that surface areas of 500–600 m^2/cm^3 typically exist on PS, and estimated surface areas for porous silicon used in these experiments were calculated from the geometric area (~30 mm^2) and the porous silicon thickness (~10 μm). (a) Canham, L. T.; Blackmore, G. W. In *Light Emission from Silicon*; Iyer, S. S., Collins, R. T., Canham, L. T., Eds.; Materials Research Society Proceedings 256; Materials Research Society: Boston, MA, 1992; pp 63–67. (b) Herino, R.; Bomchil, G.; Barla, K.; Bertrand, C.; Ginoux, J. L. *J. Electrochem. Soc.* **1987**, *134*, 1994–2000.

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(11) Lifetimes were measured for 750-nm emission and 400-nm excitation. A low-energy emission wavelength was monitored because of the strong dependence of the low-energy PL on pH. Variation in τ with emission wavelength (τ = 45μs at 750 nm to 15μs at 650 nm) is indicative of sample inhomogeneity.

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