

Trends in the Interaction of the Strong Acids HCl, HBr, and HI with a Photoluminescing Porous Silicon Surface

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The influence of the strong acids HCl, HBr, and HI on the nitrogen laser-excited photoluminescence (PL) from a porous silicon (PS) surface is established. In contrast to the stabilizing effect of hydrochloric acid on a PS surface photoluminescing in doubly deionized water, HI almost completely quenches the photoluminescence. The effect of an HBr solution is intermediate. These observations focus attention on (1) the importance of ambient oxygen in the region of a photoluminescing sample and (2) the likelihood that the PS photoluminescence results exclusively from a surface bound triplet exciton with little contribution from low-lying singlet states.

Introduction

The discovery of room-temperature visible luminescence¹ from high surface area porous silicon (PS) structures formed in wafer scale, through electrochemical etching, has attracted considerable interest primarily because of its potential use in the development of silicon-based optoelectronics, displays, and sensors. While the luminescence is thought to occur near the silicon surface,^{2,3} the source of the luminescence is controversial as the efficiency and wavelength range of the emitted light can be affected by the physical and electronic structure of the surface, the nature of the etching solution,^{4,5} and the nature of the environment in which the etched sample is placed. Here, we outline experiments in which we examine the effect of HCl, HBr, and HI as they interact with a silicon surface photoluminescing in solution. The observed effect of these strong acids on the PS photoluminescence follows a trend that can be correlated with simple redox processes at the surface. The experiments suggest that the luminescence originates from a surface bound fluorophor and point to the importance of ambient and absorbed (solution) oxygen in the photoluminescence process.

The most widely considered hypothesis to explain the luminescence from PS suggests that it results from the radiative recombination of quantum-confined electrons and holes in columnar structures or undulating wires.^{6–8} It has also been suggested that surface localized states, involving irregularly shaped small crystallites that are not perfectly passivated, produce elementary excitations that are first trapped prior to recombination.^{9,10} Yet a third explanation contends that the luminescence results from the presence of surface confined molecular emitters. These include polysilane¹¹ and siloxene ($\text{Si}_6\text{O}_3\text{H}_6$) and its derivatives.^{12–14} Stutzmann and co-workers^{12–14} have used the optical detection of magnetic resonance (ODMR) to establish that the PS “red” emission results from a triplet exciton. On the basis of the similarity of the ODMR, optical excitation (PLE), and photoluminescence spectra of PS and annealed siloxene, Stutzmann et al.^{12–14} suggested this molecule as the origin of the PS photoluminescence. We have recently suggested a more general origin for the observed features that

we ascribe to the fluorophors associated with the silanone-based silicon oxyhydrides.^{15,16} These conclusions concur with Steckl et al.,¹⁷ who have obtained evidence for the silicon oxyhydrides in stain-etched porous silicon thin films, correlating their observations with crystallinity and photoluminescence. Yan et al.¹⁸ also suggest that SiOH can be found on the PS surface.

In general, PL spectra have been observed for PS samples formed in HF etching solutions and dried in air. These *ex situ* samples provide spectral information but indicate little about the evolution of the PS luminescence. It is of interest to observe the PL as it evolves, *in situ*, during the etching process and following, while the sample is still wet by the etching solution or by an appropriate rinse. We have carried out an extensive series of *in situ* experiments^{5,15} in both aqueous and nonaqueous media which coupled with quantum chemical calculations¹⁶ suggest that the source of the PS photoluminescence may well be a silicon oxyhydride-like fluorophor strongly bound to the PS surface. Here we report experiments that not only suggest the importance of a surface bound emitter (silicon oxyhydride fluorophor) but also demonstrate the important role that oxygen, both ambient and as it is present in the etching solution, must play in the luminescence process. In sharp contrast to the strong stabilizing influence of hydrochloric acid⁶ on the PS photoluminescence, hydroiodic acid almost completely quenches the *in situ* luminescence from PS. We observe an apparent trend in the nature of the interactions of HCl, HBr, and HI with the photoluminescent PS surface as the behavior of HBr appears intermediate to that of HCl and HI. Here, we consider this behavior within a redox framework.

Experimental Section

Boron-doped p-type silicon from MEMC (Dallas, TX) with a resistivity of 2 Ω cm was used here. Electrical contact was made to the back of the silicon by first sputtering aluminum followed by the attachment of a metal wire using conductive paint. The PL experiments have used several light sources including a mercury lamp, a nitrogen laser at 337.1 nm, and a KrF excimer at 248 nm.¹⁵ The experiments reported here used primarily (pulsed) nitrogen laser excitation. The PL was dispersed through a McPherson monochromator and detected with a Hamamatsu 446 phototube. The output of the phototube

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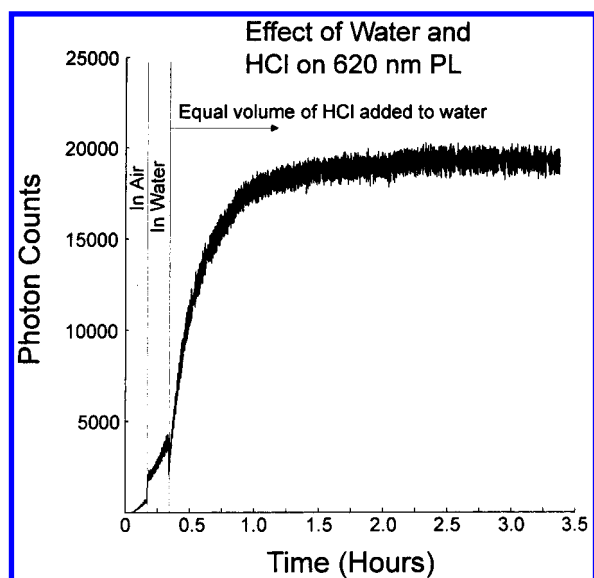


Figure 1. Effect of an HCl solution on the stabilization of PS photoluminescence (PL) for a sample previously dried in air and placed in doubly deionized water. The wavelength monitored was 620 nm, and the data were taken using nitrogen laser excitation. Here the PL rises slowly in air and water and then increases precipitously in HCl solution.

was sent to an SR400 (Stanford Research Series) photon counter. The nature of each solution is indicated in the figure captions.

Results

A. Effect of HCl on PS Photoluminescence. We depict in Figure 1 the effect of water and HCl on the orange-red PL from a PS sample previously dried in air. The porous silicon sample was first etched in a methanol/20% HF (6 mol/L HF in MeOH-(aq)) solution for 10 min, washed with methanol, dried in air, and then placed first in a solution of doubly deionized water and then ~ 6 M HCl. The intensity of the PL increases upon removal from the HF, slowly increases and sometimes plateaus in air, depending on the total time scale for the experiment. The PL then increases again when the sample is placed in water.^{15b} However, after adding HCl, the orange-red PL intensity increases significantly and remains constant over the period in which the sample is present in the HCl solution.^{15b} Within the time frame of these described processes, the wavelength-dependent spectral profile of the PL emission spectrum is virtually unaltered from the time it is removed from the HF etching solution through the period in which the sample is placed in HCl. Thus, the introduction of HCl has a profound enhancing and stabilizing effect on the PS photoluminescence.

B. Effect of HBr on PS Photoluminescence. In Figure 2, we depict the effect of water and HBr on the orange-red PL from a porous silicon sample dried in air and placed in doubly deionized water. As with HCl, the porous silicon sample was etched in a methanol/20% HF solution for 10 min, washed with methanol, dried in air, and then placed first in a solution of doubly deionized water and then ~ 4.5 M HBr. For the sample producing the luminescence depicted in Figure 2, the intensity of emission was weak after removal from the HF. The PL then increases as the sample is placed in doubly deionized water for approximately 15 min. After adding HBr, the orange-red PL intensity gradually increases to a maximum emission intensity over approximately a 75 min time frame, subsequently slowly decreasing over the next 60 min. In a series of repeat runs on a given sample the peak intensity achieved in the HBr solution typically ranges between 10 and 30% of the stable intensity

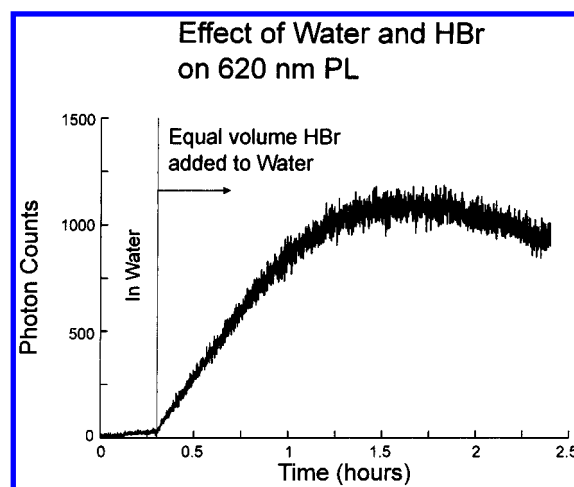


Figure 2. Effect of an HBr solution on the PS photoluminescence for a sample previously dried in air and placed in doubly deionized water. The wavelength monitored was 620 nm, and the data were taken using nitrogen laser excitation. Here the PL rises somewhat more slowly in water than the observed rise in Figure 1.

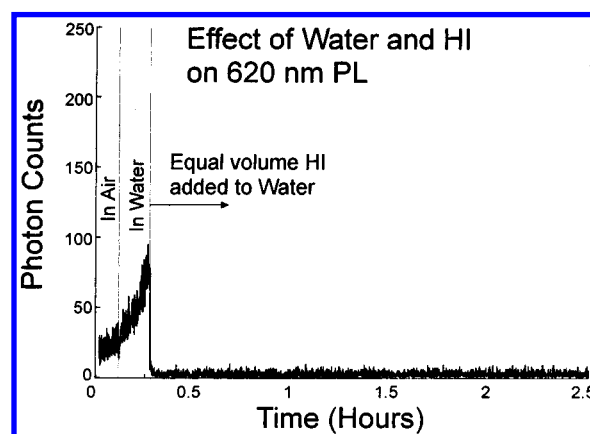


Figure 3. Effect of HI on the photoluminescence from a PS sample placed in doubly deionized water. The data from 0.0 to 0.25 min correspond to an increasing luminescence intensity for the sample placed in doubly deionized water. The scale is considerably expanded relative to Figures 1 and 2. Upon introduction of HI, the photoluminescence is immediately quenched.

achieved in the HCl solution. For the most effectively stabilized samples, the intensity in the HBr solution is close to 20% of that in the HCl solution. Again, the spectral profile of the PL emission is virtually unaltered from the time it is removed from the HF etching solution through the period in which the sample resides in the HBr solution. Thus, the strongly acidic HBr solution initially provides stabilization for the source of luminescence, but after a modest period, the luminescence begins to diminish, indicating the quenching, conversion, or dissolution of the emitters.

C. Effect of HI on PS Photoluminescence. Figure 3 depicts the effect of water and HI on the orange-red PL from a porous silicon sample that has been dried in air and placed in deionized water. It shows an increased photoluminescence relative to the sample of Figure 2. This porous silicon sample was also etched in a methanol/20% HF solution for 10 min, washed with methanol, dried in air, and then placed in a solution of doubly deionized water and then ~ 2.75 M HI. The sample is initially photoluminescent in air, and as Figure 3 demonstrates, the PL increases continuously for 15 min as the sample is subsequently placed in doubly deionized water. Note that the intensity scale is magnified relative to Figures 1 and 2 where the behavior in air and water is similar. Now, in sharp contrast to HCl and HBr, the addition of HI to the solution almost completely

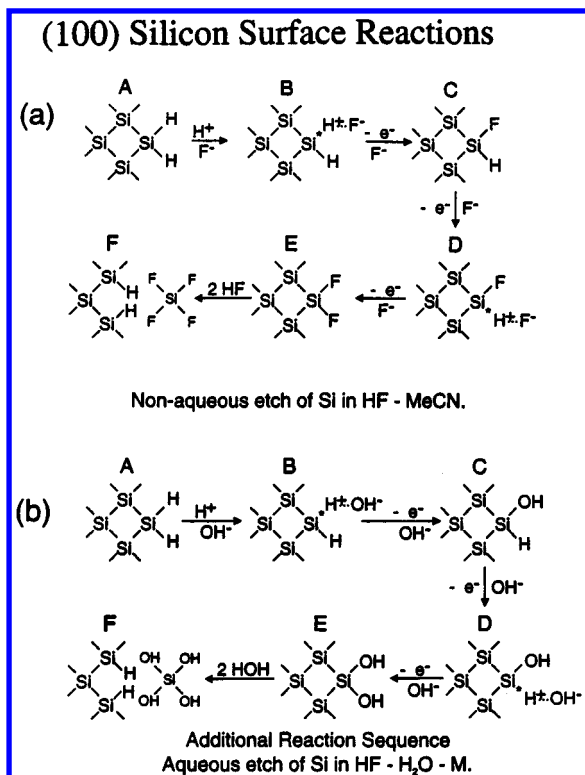


Figure 4. Reaction mechanisms for dissolution and silicon fluoride and silicon hydroxide (oxyhydroxide) bond formation in nonaqueous and aqueous HF etch solutions.

extinguishes the orange-red PL. Thus, the addition of HI has a profound quenching effect on the PS photoluminescence. Following the sudden quenching of the photoluminescence, the cuvette gradually takes on the red-purple color characteristic of iodine.

Discussion

A. Nature of the Photoluminescent Porous Silicon Surface. Several researchers^{19–21} have considered the reactions that describe the dissolution of silicon in an HF-containing electrolyte. While some adjustments of these mechanisms may be necessary to explain the nature of the PL emission from PS,^{15c,e,16} we suggest that the formation of a silanol (Si–OH) bond and thus the creation of a surface bound silicon oxyhydroxide is essential to the observed luminescent process. The formation of a silicon oxyhydroxide emitter^{15,16} would appear to be consistent with the comparative and competitive mechanisms that have been suggested for silicon dissolution in aqueous and nonaqueous media.^{19–21} We outline the suggested mechanisms, which have been discussed elsewhere,^{15,19–21} in Figure 4.

The precise nature of those sites that lead to PL in PS is the subject of continued discussion. Quantum chemical modeling¹⁶ and the results of recent experiments^{15,22} appear to demonstrate that the fluorophors are the silanone-based silicon oxyhydroxides of the form O=Si–OR where R = H, SiH₃. Changes in bonding associated with electronic transitions involving the oxyhydroxide ground electronic and low-lying triplet states and the substantial shift to larger “Si=O” internuclear distance of these excited electronic states relative to the ground states correlate with the observed character of the observed PL spectra.^{15,20} This assignment does much to explain the significant red shift of the PL spectrum (600–800 nm) from the known absorption peak wavelength of the (PLE) excitation spectrum (~350 nm).²³

B. Stabilization of Photoluminescence through Introduction of HCl. With some extrapolation, the mechanisms outlined

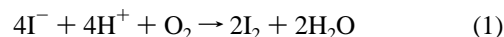
TABLE 1: Select Standard Reduction Potentials^a

electrode reaction	<i>E</i> ^o (V)	electrode reaction	<i>E</i> ^o (V)
F ₂ + 2e [−] → 2F [−]	2.87	I ₂ (s) + 2e [−] → 2I [−]	0.5345
Cl ₂ + 2e [−] → 2Cl [−]	1.36	I ₃ [−] + 2e [−] → 3I [−]	0.5355
Br ₂ + 2e [−] → 2Br [−]	1.087		

^a From ref 26, p 1159.

in Figure 4 can be used as a basis to explain the stabilization of a strong photoluminescence due to the formation of silicon oxyhydroxide bonds (Figure 4b). While HF is a weak acid with an ionization constant $K_{\text{HF}} \sim 7 \times 10^{-4}$,²⁴ HCl, a strong acid, is almost completely ionized in water producing (H⁺) and (Cl[−]) ions. After the silicon oxyhydroxides are formed (C, E) in an aqueous medium, rinsed, dried, and placed in deionized water, the PL emission rate increases somewhat in the absence of HF which, if present, can interact with the decorated silicon surface to remove a portion of the PL sources. When 12 M HCl is introduced in equal volume to this solution, the (H⁺) concentration increases dramatically. This increase in (H⁺) concentration of course influences and decreases the (OH[−]) concentration in solution. The equilibrium between silicon hydroxide surface bonds and the solution is therefore modified to stabilize the silicon hydroxide bond. The (Cl[−]) ion also can have a stabilizing effect as the stability of the SiCl bond is notably weaker²⁵ than that of the Si–F or Si–OH bonds on the oxidized PS surface. The (Cl[−]) ion will likely not remove or compete with hydroxide bond formation and, for this reason, also serves to maintain and stabilize the silicon oxyhydroxide surface entities.

C. The Redox Chemistry of HX Solutions: The Influence of Ambient Oxygen. The sharp contrast between the effect on the photoluminescence from a PS surface due to the presence of HCl and that due to HI might well be understood in terms of the redox chemistry of these two solutions. It is well-known that two important sources of error in iodometric titrations result from the air oxidation of an acid iodine solution and the loss of iodine by volatilization. Iodide in an acid medium is slowly oxidized by oxygen, viz.²⁶



While this reaction is slow in a neutral medium, its rate increases dramatically with increasing hydrogen ion concentration and is greatly accelerated by an external light source or certain substances (primarily metals) that exert a catalytic effect as they are easily air-oxidized.²⁶ The onset of reaction 1 certainly is consistent with the appearance of the red-purple color of iodine throughout the inner surfaces of the solution-containing cuvette used in these experiments. The presence of a large excess of iodide which reacts with iodine to form triiodide ions, viz.



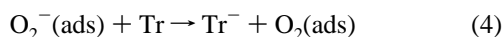
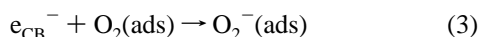
counters the volatilization of iodine from its solution. Here, it is important to note that the formed I₂ and I₃[−] should both be extremely effective quenchers for a triplet exciton fluorophor on the PS surface. They are less effective singlet quenchers.

A review of the standard reduction potentials²⁶ for the halogens outlined in Table 1 suggests that I[−] and I₃[−] are more easily oxidized than Br[−], Cl[−], and F[−]. In the presence of O₂ the fluoride and chloride ions (X[−], X = Cl, F) will remain in their reduced form, but some conversion of the bromide ions to Br₂ is anticipated. This conversion generates an effective quencher for a triplet exciton fluorophor. We suggest that the slow dropoff in the PL intensity with time in the HBr solution

is due to the creation of a sufficient Br₂ concentration in the presence of oxygen.

It is worth noting that the importance of an ambient oxygen atmosphere to the PL process has also been established by Henglein and co-workers.^{27,28} Henglein et al.^{27,28} have recently studied luminescent colloidal solutions of silicon particles prepared from oxide-coated crystalline silicon formed in the combustion of silane. These authors find that the orange-red PL must be activated by the aqueous HF etching of these silicon particles if they are suspended in a 1:1 cyclohexane–propanol-2 solution in the presence of air. The required presence of oxygen (under argon there is no luminescence) in these solution-phase studies indicates that the oxide layer created in the combustion of silane does not promote luminescence. Rather, as Henglein et al. note, the development of the orange-red PL in nonpolar cyclohexane indicates that this original oxide layer must first be removed by HF. Quartz, silica, and silicate surfaces are all characterized by surface silanol functionalities.²⁹ This would also suggest that these dangling silanol groups are present on those particles formed from the combustion of silane in air. It would appear that silanol groups alone bonded to a quartz surface will not produce the observed luminescence. Upon treatment with HF, silicon particles, with a nonpolar surface, form in a cyclohexane phase where an equilibrium is established between their surface oxidation and reduction by O₂ and HF, respectively. Near pristine silicon colloidal particles are formed whose oxidation, *to a much lower level than the original oxide-coated particles*, produces luminescence. When formed, the silanol functionality, with a zero point of charge pH of 2.0, will be positively charged in an HCl or HBr solution at a pH below 2 (>SiOH₂⁺). However, it would not be surprising to find that the Cl[−] or Br[−] ions interact with this surface group to facilitate the presence of a dangling silanol constituency.

The importance of O₂ to the solution-phase silicon-based luminescence observed by Henglein and co-workers^{27,28} also focuses attention on the role that the absorption of O₂ onto a silicon surface (in air) and its subsequent conversion to O₂[−] might play in the PL mechanism.^{15d} In a further example, these observations should be contrasted with the elegant work of Bahnmann et al.³⁰ in their study of the absorption spectra and fluorescence from illuminated ZnO colloids in the quantum size domain. Two fluorescence maxima were found to vary^{30,31} with particle size in tandem with each other to a final bandgap excitation and emission at 365 nm ($\lambda_{\text{onset}} = 310\text{--}365$ nm with increasing particle size) accompanied by a visible luminescence of 520 nm (~460–520 nm following the bandgap absorption). These authors explained the visible luminescence invoking the importance of O₂ strongly chemisorbed on the zinc oxide surface in the form of O₂[−]. They suggested that O₂ and more specifically O₂[−] acted as a relay to shuttle electrons from the conduction band to lower-lying electron traps via



forming radical ions. The subsequent visible fluorescence at 520 nm was thought to result from the tunneling of these trapped electrons to preexisting trapped holes. These authors also observed a pronounced pH dependence for various quenching reagents. The work of Bahnmann et al.³⁰ again demonstrates the important role that O₂ and O₂[−] can play in a system whose behavior appears to parallel that observed in the present study. However, there is an important distinction. Whereas the shift in the absorption of the ZnO colloids which varies from 310 to

365 nm with increasing size is correlated with a shift of the visible fluorescence from 460 to 520 nm,^{30,31} this parallel behavior is not apparent in the PS system which displays a very similar time-dependent orange-red spectral distribution as a function of a wide range (193–400 nm) of excitation wavelengths,^{15e} developing also on a very short time scale (<10 s).^{15a,e}

The trends that we observe also point to two additional conclusions. The extremely rapid quenching of the porous silicon PL by HI suggests that a surface bound fluorophor is involved in the luminescence process. The virtual absence of a decay process and the almost complete loss of the PL signal in the HI solution suggests that the PL is due overwhelmingly to a triplet-state emitter.

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