

General Brönsted Acid Behavior of Porous Silicon: A Mechanistic Evaluation of Proton-Gated Quenching of Photoemission from Oxide-Coated Porous Silicon

Michael T. Kelly, Jonathan K. M. Chun, and Andrew B. Bocarsly*

Department of Chemistry, Frick Laboratory, Princeton University, Princeton, New Jersey 08544-1009

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Photoinduced visible light emission from porous silicon can be reversibly quenched by a wide variety of chemical species. The growth of a thin layer of oxide on the porous silicon surface disrupts the quenching ability of most species, narrowing down the number of quenchers to include primarily those which act as Brönsted bases. Electron paramagnetic resonance spectroscopy, infrared spectroscopy, photoluminescence data, and surface chemistry suggest a quenching mechanism which involves the extraction of a nonspecifically attached proton in the oxide layer upon exposure to base. This proton is loosely affiliated with a surface defect of the P_b type. This defect serves as a hole trap in the absence of a proton providing a nonradiative relaxation pathway. However, when a proton is present in the oxide layer, Coulombic interactions force the hole trap into a state which falls below the bandgap, allowing for efficient radiative recombination of electron–hole pairs. The electron paramagnetic resonance spectroscopy data also demonstrate that there are at least two distinct mechanisms of luminescence quenching of porous silicon.

Introduction

Efficient visible light emission from porous silicon¹ (PS) has attracted the interest of researchers from diverse fields of study. Large numbers of spectroscopic techniques and theoretical arguments have been applied to determining the mechanism of photoluminescence (PL), but the mechanism of light emission from porous silicon has been elusive. Researchers have begun to explore the applications of this material primarily in the areas of optoelectronics and sensors.

In earlier reports² we demonstrated that thermally oxidized PS undergoes a reversible quenching of the photoluminescence when exposed to a Brönsted base. The formation of a surface oxide on PS is important to note because a wide variety of species quench the PL of freshly etched “clean” porous silicon surfaces, most of which do not have any quenching effect on oxidized porous silicon. Significant discussion of a number of different quenching mechanisms for the clean PS surface involving charge transfer and energy transfer is available in the open literature.^{3–11} In the present work, a mechanistic framework for the observed quenching of oxide-coated PS is advanced here on the basis of surface chemistry, luminescence spectroscopy, infrared spectroscopy, and electron paramagnetic resonance spectroscopy (EPR) studies. The EPR spectroscopy presented here demonstrates the first example of an in situ, reversible, physical change in porous silicon that can be directly linked with photoluminescence quenching.

It is well established that freshly etched PS is spongelike, in that a large portion of the original crystal has been removed, leaving behind an interconnected network of silicon “wires” having nanometer dimensions.^{1,12,13} Infrared analysis indicates that the silicon atoms at the surface of the wires are terminated primarily by hydrides.¹⁴ On long term exposure to the atmosphere, the silicon hydride oxidizes, resulting in a layer of SiO_xH_y sheathing the wirelike structures and possibly creating isolated particles of crystalline Si if a wire oxidizes completely through as shown in Figure 1. Here we refer to the surface as the top of the SiO_xH_y sheath. Subsurface chemical structures

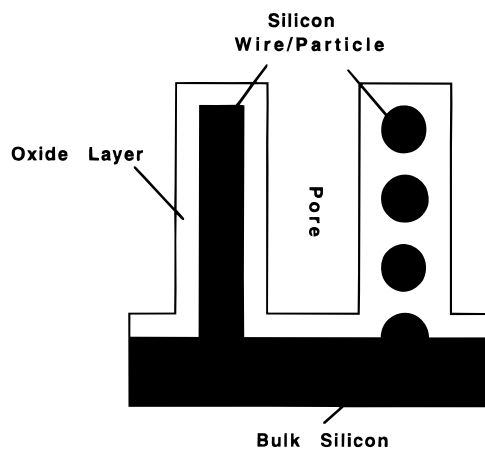


Figure 1. Idealized porous silicon. Horizontally, figure is nanometer scale. Vertically, it is micron scale. The left-hand side shows a silicon wire encapsulated by oxide. The right-hand side shows a structure that has oxidized completely through, leaving only silicon particles intact.

are within the oxide sheath. The $\text{SiO}_x\text{H}_y/\text{Si}$ interface forms the “bottom” of the oxide layer.

We have previously suggested that, in the quenched state, relaxation of the photoexcitation occurred via a nonradiative pathway created by the formation of midbandgap surface states via a ground state reaction between the quencher and the oxide interface.^{15,16} Photon emission is observed when an unspecified surface state in the oxide interface is present below the valence band edge. Quenching occurs when the energy of this surface state is chemically raised above the valence band edge, thereby providing an electron–hole recombination route. Restoration of the PL by treatment with acid reverts the surface energetics back to their original state.

Two physical models which might be responsible for the alteration of the surface states have been hypothesized. On freshly etched porous silicon, Coffey has proposed that quenching occurs via a Lewis acid–base interaction in which the base “docks” with some electrophilic surface site through a lone pair of electrons on the base.⁴ This model must also be considered a possibility for the oxidized porous silicon case. Alternately

* Author to whom correspondence should be addressed.

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we have suggested that a base near the surface abstracts a proton from within the SiO_2H_2 layer.^{2,17}

Energy transfer quenching mechanisms for freshly etched PS have also been advanced and supported in the literature;^{8,11} however the aromatic or polar molecules that usually exhibit this behavior show no quenching of oxidized porous silicon. The lack of energy transfer quenching is attributed to the presence of the oxide as a physical barrier separating the emitting silicon wire/particle and the quenching species.⁹ It is known that the rate of energy transfer falls off very quickly with distance ($1/r^6$) while charge transfer or electrostatic interactions can have effects over much greater distances.¹⁸ For this reason mechanisms involving energy transfer from PS to a base are considered unlikely.

Experimental Section

Porous Silicon. Electrochemically etched porous silicon was fashioned from B-doped p-type single-crystal silicon with a resistivity of 2–10 Ω cm (obtained from El-Cat Semiconductor). The etching solution was a 1:1:1 volume ratio of HF (48%), ethyl alcohol, and distilled water. A ~ 1.1 cm² area of Si was etched using a constant current of 10 mA for 10 min. A two-compartment cell was used, the compartments separated by the single-crystal silicon sample held in place by two O-rings. Two platinum electrodes were used, one in each compartment. In this configuration, an anode and a cathode can be induced on opposite sides of the Si wafer by applying a bias across the electrodes, the induced anode being where formation of porous silicon takes place.

Chemically etched porous silicon powder was synthesized using an etching solution consisting of 10 mL of distilled water, 10 mL of H_2SO_4 (96%), 2 mL of HF (48%), and ~ 0.25 g of NaNO_2 .¹⁹ The etching vessel was a 50 mL polyethylene beaker, with fast stirring using a Teflon stir bar. During the 15 min etch, NO_2 gas evolution was observed. At the end of the 15 min the beaker was filled completely with distilled water and the product was filtered and washed with large amounts of distilled water, followed by 50 mL of glacial acetic acid to enhance PL. Normally 0.5 g of Si powder (60 mesh, Aldrich Chemicals) was carried through the etch process.

Oxidation of PS. Oxidation of PS was allowed to occur thermally by storing powder or wafers on the bench top, exposed to air. Oxidation generally took 1–2 weeks and was tested by dropping ethanol on the surface, while observing the PL with a UV lamp (365 nm excitation). No significant quenching of PL by ethanol indicated the growth of a satisfactory oxide coating. Oxidation was also performed chemically, by placing the wafer in a solution of 1:1 ethanol and 3% HCl, irradiating with a 365 nm source for 15 min.

Deuteration. Porous silicon was quenched using a sodium bicarbonate solution and was restored to comparable PL intensity using DCl. This treatment was not intended to have the effect of replacing all surface hydrogen with deuterium; it was utilized to selectively replace the acidic protons present on or below the surface of oxidized porous silicon.

Instrumentation. Photoluminescence quenching was observed using either a Perkin-Elmer LS-50 luminescence spectrometer or an SLM 8000C luminescence spectrometer with an Ar^+ laser excitation source. The laser beam was defocused to power < 5 mW/cm². Titrations were performed in the sample chamber of the SLM, with a calibrated pH meter and constant stirring. The porous silicon was usually immersed in a solution of 0.10 M hydrochloric acid, and PL and pH were monitored as bases were added slowly with a buret. Photoluminescence vs pH profiles were obtained for a variety of bases, including sodium bicarbon-

ate, sodium hydroxide, sodium oxalate, and dibasic sodium phosphate. In the case of two end point curves, the hydrochloric acid solution was replaced with a mixture of hydrochloric acid and formic acid and titrated with sodium hydroxide. The open circuit voltage of porous silicon electrodes was measured using a digital volt meter while performing a standard titration using a 0.1 M HCl solution and a 0.1 M sodium bicarbonate titrant.

Transmittance fourier transform infrared spectroscopy (FTIR) was performed using Nicolet 730 or Nicolet 800 FTIR spectrometers. Transmittance spectra were obtained against a background of either HF-etched single-crystal Si or air.

Electron paramagnetic resonance spectroscopy was performed using a Bruker ESP300 X-band EPR spectrometer. Porous silicon samples used for EPR were chemically etched from Si powder (60 mesh, 99.999%, Aldrich Chemicals). Liquid phase measurements were taken in a quartz 3 or 5 mm EPR tube. Gas phase quenching was performed in an open-ended EPR tube using glass wool to support the PS sample. Diethylamine vapors were passed through the tube to quench the PL. Leaving the tube open to atmosphere after it was quenched allowed restoration of PL to occur on a time scale of hours. To obtain a ratio of peak heights, spectra were deconvoluted using two Gaussians.

Results and Discussion

Weak, aqueous, Brönsted bases are observed to reversibly quench the PL from *oxidized* PS layers while molecules that quench the PL of *fresh* PS, such as organic solvents, are not effective quenchers of oxidized PS.¹⁵ Subsequent exposure to Brönsted acids restores the PL to its original intensity. The quenching and restoration can be cycled many times.

Lewis/Brönsted Base Quenching. In order to probe whether the quenching interaction is the result of a Lewis base or a Brönsted base, the following experiments were conducted. After quenching oxidized PS PL with diethylamine vapor, AlCl_3 which is a strong Lewis acid in diethyl ether, an aprotic solvent, did not restore PL. It should be noted that diethyl ether has no quenching effect on the oxide-coated PS. The addition of an excess of strong Lewis acid is expected to result in complex formation between the acid and the amine. Having thus eliminated any possible interactions between the base and an electrophilic site on the surface, restoration would occur if Lewis base “docking” was involved in the quenching mechanism. Since no restoration was observed to occur, removal of the base must not be the only requirement for PL restoration. For oxidized surfaces, this is supportive of the Brönsted base abstraction model discussed in the Introduction over the docking hypothesis but is not definitive. To further probe this interaction, porous silicon was exposed to a solution of Proton Sponge (1,8-bis-(dimethylamino)naphthalene) in toluene. Due to its geometry, Proton Sponge is a powerful base and a very weak nucleophile. It was observed that Proton Sponge is a strong quencher of the PL. Although it has been shown that toluene³ and naphthalene¹¹ have quenching effects on fresh porous silicon, control experiments indicate that on the oxidized surface quenching is not observed for either molecule. This demonstrates that a Brönsted base interaction can induce quenching since Proton Sponge cannot ligate to the oxidized surface.

Deuteration. The observed acid–base response demonstrates that protons are obviously important to the quenching process of oxidized porous silicon PL, but they are not directly associated with the luminophore. This conclusion was supported by a series of experiments performed on porous silicon after quenching the PL with bicarbonate solution and restoring the PL using DCl instead of HCl. Replacement of the surface

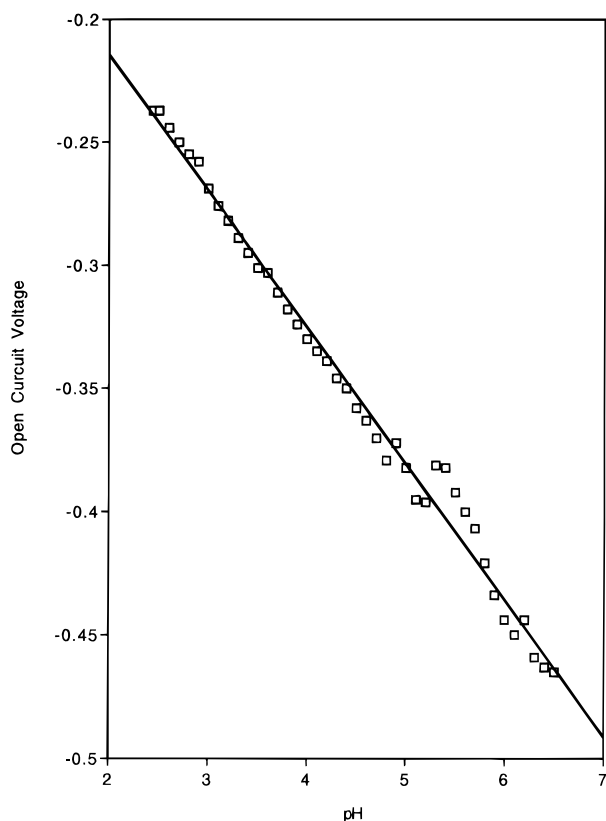


Figure 2. Porous silicon electrode whose open circuit voltage vs SCE is measured during a titration of HCl and NaHCO₃. The electrode behaves like a proton sensitive ion selective field effect transistor (ISFET).

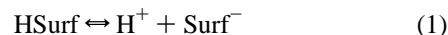
proton with a deuteron resulted in no observable change in emission, excitation, or decay properties.¹⁵ An excited state molecular luminophore would be strongly influenced by deuteration if the surface proton under consideration were a terminating functionality on the molecular luminophore.

FTIR Spectroscopy. While the noted quenching and restoration experiments unambiguously indicated that removal of an interfacial proton leads to PL quenching, they do not identify the chemical nature of the abstracted proton. There are many environments in which hydrogen can be found on oxidized silicon surfaces, including silicon hydroxides and silicon hydrides to name the most abundant. Intuitively, hydrides must be ruled out because the pK_a of a surface hydride is much too high for a base such as diethylamine (a strong PL quencher) to remove the hydrogen. Silicon hydroxides also are not normally acidic enough for diethylamine to abstract the proton, but some silicon surface hydroxides are acidic and therefore cannot be dismissed outright as a possible source of protons. However, the absorbance FTIR spectrum of PS indicates no significant changes from the unquenched state to the quenched state in Si—H, Si—OH, or Si—O—Si (2100 and 2250 cm⁻¹ for hydrides, 3450 cm⁻¹ for hydroxides, and 1100 cm⁻¹ for silicon oxide structures) related peaks. A hydrogen source alternative to a surface hydride or hydroxide is the proton that is nonspecifically associated with the SiO_xH_y surface layer encapsulating the silicon wires and/or particles. Such protons are not easy to observe directly, but their acidic nature on silica gel surfaces is well-known.²⁰ The best description of the proton's environment would be to say it resided in the oxide layer and not precisely on the surface. *These protons seem to best fit the observations regarding the high reversibility of the quenching chemistry, as well as the lack of bondmaking and bondbreaking observed in FTIR spectrum of quenched vs unquenched surfaces.*

Field Effect Transistors. Ion-selective field effect transistors (ISFETs) are sensitive to the concentration of a particular ion and undergo a change in the open circuit voltage as the ion in question diffuses into the interfacial region of the electrode. An oxide-coated silicon electrode interface, for example, shows a change in the open circuit voltage with changes in pH of the electrolyte solution. This is due to the association or dissociation of protons within the native oxide on the silicon surface. These protons sample a wide variety of chemical environments, making them hypothetically similar in nature to the protons proposed to be responsible for quenching of PL from PS. In order to test this idea, a set of titrations were performed, and the open circuit voltage of a porous silicon electrode immersed in the reaction vessel was monitored as the pH was changed. Figure 2 shows that the voltage changes linearly with pH. That porous silicon exhibits ISFET behavior for protons, much the same as a single-crystal silicon electrode, is strong evidence for diffusion of protons into the surface oxide of PS, supporting the conclusions drawn from FTIR spectroscopy.

Titration. Protons associated with a particular surface site would have a specific pK_a while mobile protons or protons generally associated with the surface would not exhibit a specific pK_a . Figure 3, part a, shows both the photoluminescence intensity of a porous silicon sample immersed in an HCl solution and the solution pH as a function of the volume of added basic sodium oxalate solution.

Assuming that a generalized acid dissociation can be written



then the equilibrium statement takes on the form

$$K_a = \frac{[\text{H}^+][\text{Surf}^-]}{[\text{HSurf}]} \quad (2)$$

where $[\text{H}^+]$ is the concentration of solution protons, $[\text{HSurf}]$ is the fractional interfacial coverage of acid, and $[\text{Surf}^-]$ is the fractional coverage of conjugate base. From the mass balance equation

$$[\text{HSurf}] + [\text{Surf}^-] = C \quad (3)$$

where C is a constant, $[\text{Surf}^-]$ can be expressed as a function of $[\text{HSurf}]$ and substituted into eq 2. On the basis of the data in Figure 3, part a, it is concluded that $[\text{HSurf}]$ is proportional to the PL intensity. Upon combining eq 2 and 3 and the proportionality constant between $[\text{HSurf}]$ and PL intensity, one obtains

$$\text{PL} = \frac{C'}{(K_a/[\text{H}^+]) + 1} \quad (4)$$

where C' is the proportionality constant between PL and $[\text{HSurf}]$ multiplied by the constant labeled C in eq 3.

Fitting the pH and PL data from the titration data given in Figure 3, part a, to eq 4 provides a surface acid pK_a of 3.47. If, however, PL is plotted against pH as shown in Figure 3, part b, it is obvious that the PL curve generated by inserting the measured pH values into eq 4 is of a different functional form than that of the actual data, and the pK_a determined by this method is of questionable value. Figure 3, part b also shows that PL appears to be linearly related to solution proton concentration. This was investigated further by performing a second titration, this time immersing the sample in a mixture of HCl and HCOOH and titrating it with NaOH. A mixture of two acids was used in this experiment to ascertain whether the

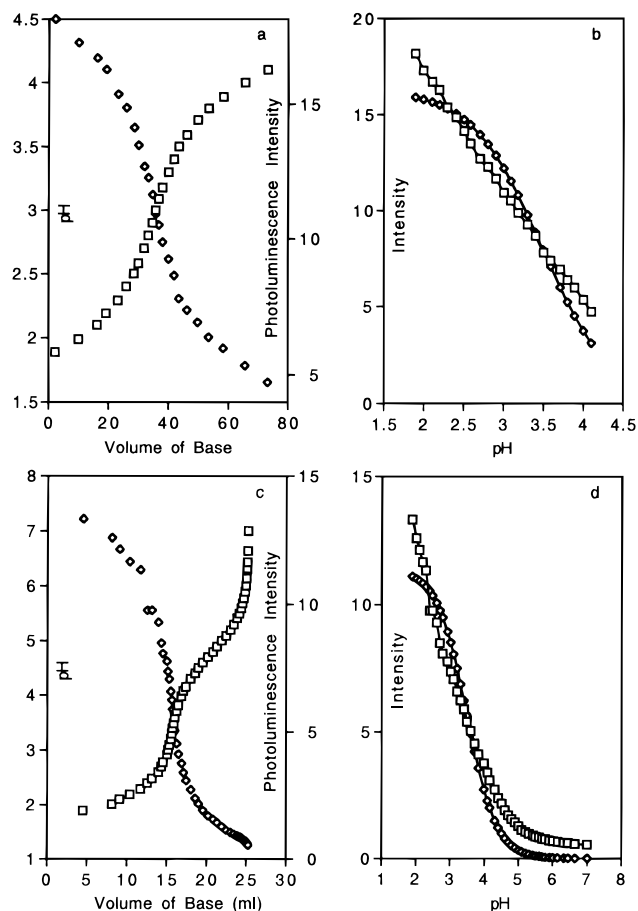


Figure 3. (a) Titration and related variation in PL of a HCl solution contained in an immersed sample of PS. Sodium oxalate was used as the titrant. The PL quenching mirrors the changing pH. (b) Titration data presented in part a, directly correlating PL intensity (squares) with changing pH. The relationship appears linear. Equation 4 is used to generate the curved trace (diamonds), demonstrating that a Henderson–Hasselbalch analysis for a monoprotic acid does not produce a fit to the data. (c) Titration, monitoring PL intensity of PS immersed in the titration vessel during a titration of an HCl and HCOOH mixture. The PL quenching again mirrors the changing pH; both end points are clearly visible. (d) Analysis of the titration data provided in part c, showing (squares) PL plotted against changing pH. The relationship is clearly nonlinear. The curve generated by eq 4 (diamonds) as before does not fit with the data, suggesting that a monoprotic surface acid model is an insufficient description of the surface acid system.

PL remained linear with pH, independent of the solution acids used to change the pH. In Figure 3, part c, two titration end points are clearly seen. The PL provides a similar response exhibiting two end points. Equation 4 was again used to determine a surface pK_a , having a value of 3.48. Even though the calculated pK_a value is similar in both titrations, from the pH vs PL plot in Figure 3, part d, it is evident that the relationship among pH, PL, and pK_a is not well described by eq 4. Figure 3, part d also shows that PL and pH are not necessarily linearly related.

Figure 3, parts a–d, demonstrates that a monoprotic surface acid moiety with a specific pK_a is an oversimplification of the system and that models based on a single-surface-confined acidic species do not describe the oxidized PS interface well. It therefore must be concluded that protons are nonspecifically associated with the surface, sampling a wide variety of environments with a corresponding variety in acidity. The PL is controlled in a nonlinear fashion by solution pH, and protons diffuse into and out of the PS surface by mass action between the silicon surface oxide and the solution. This conclusion is in agreement with the infrared analysis discussed earlier, which

suggested that no specific surface species is releasing protons upon exposure of PS to a base. The PL intensity variation with pH coupled with the H^+ responsive ISFET behavior already demonstrated also gives a direct link between the presence of protons in nonspecific sites within the oxide layer and the observed photoluminescence quenching.

Alkali/Alkaline-Earth Metals. One consequence of removing a proton from the surface is that there is a loss of a positive charge near the surface. To ascertain whether protons simply supplied some density of charge necessary for PL, oxidized PS was exposed to nonbasic metal salts in aqueous solution. Exposure of the surface to such salts (LiCl, NaCl, KCl, $CsNO_3$, $BeCl_2$) in either the emitting (protonated) state or quenched (deprotonated) state resulted in no obvious change in PL, in agreement with results obtained by Andsager.⁶ However, subsequent attempts to restore the PL to base-quenched, metal cation treated surfaces with acids failed. Once treated with such a salt, the restoration back to an emitting state with acid was very slow or was prevented completely depending on the salt.

Cesium cations were found to be the strongest inhibitor while the effect of Be^{2+} was least perturbing. The alkali metal cations on the surface might occupy whatever surface sites are normally occupied by protons, thereby preventing restoration, or they might occupy a site near the surface, preventing a proton from diffusing into the oxide layer. If the charge on a proton was responsible for quenching, then an alkali cation in the same location should restore the PL. If the protons induced structural changes in the oxide layer leading to changes in PL intensity, then cations in similar sites should also induce PL changes. On the basis of this reasoning, it was concluded that cations do not occupy the same sites as protons, but rather blocked the proton pathways into the oxide layer.

EPR Spectroscopy. Researchers had shown previously that strongly emitting PS samples have correspondingly lower numbers of paramagnetic defects compared to those of non-emitting oxidized samples.^{21,22} While being suggestive of a link between PL emission and paramagnetic defects, the evidence obtained thus far is not conclusive. In prior studies, in order to effect the transformation from emitting to nonemitting porous silicon, emitting samples needed to be removed from the instrument and be subjected to extreme oxidation conditions before being returned to the EPR spectrometer for further experiments. Such treatments resulted in nonemissive samples with more paramagnetic defects, but EPR spectral features such as g -value and g -anisotropy also exhibited significant changes. In addition, this method of PL quenching is irreversible; thus, it cannot be ruled out that some chemical or structural change unrelated to the number of paramagnetic defects caused the observed quenching.

A typical chemically etched, chemically oxidized porous silicon powder EPR spectrum is shown in Figure 4, part a (trace A). All samples show two features in the EPR spectrum near $g = 2$. Assignment of the peaks is complicated by use of polycrystalline silicon as the starting material. Additionally, the use of chemical etching which causes at least some amorphization^{23,24} of the sample further complicates the spectrum. The signal components are assignable, however, as follows. The lower field component of the signal has $g = 2.0079$, which is within experimental error of the bulk K1 defect.²⁵ This paramagnetic defect is due to silicon atoms adjacent to dislocations in plastically deformed silicon. This signal is not observable by EPR in high-quality single-crystal silicon, but can be observed in the polycrystalline Si powders used in our PS samples. It has been shown that when single-

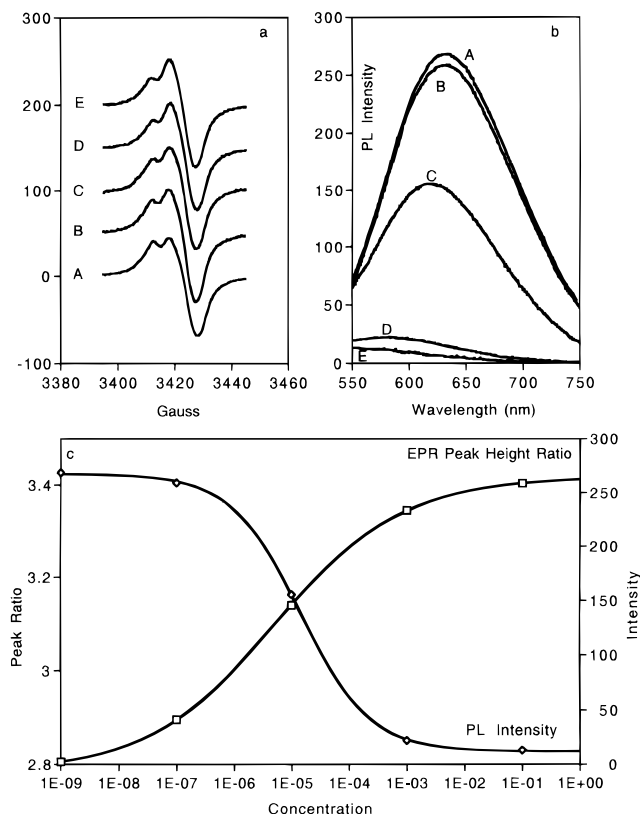


Figure 4. (a) EPR spectra showing an increase in the $g = 2.0054$ feature with increasing amine concentration in hexane. A = 10^{-9} M diethylamine. B = 10^{-7} M diethylamine. C = 10^{-5} M diethylamine. D = 10^{-3} M diethylamine. E = 10^{-1} M diethylamine. (b) Photoluminescence intensity of a porous silicon sample immersed in the same diethylamine solutions used in part a. (c) The ratio of the peak heights of the $g = 2.0054$ and $g = 2.0079$ features of the EPR spectra plotted against concentration (diamonds) has the same shape (sigmoidal) as the maximum PL intensity plotted against concentration (squares).

crystal silicon is used in place of a polycrystalline substrate for chemical generation of PS the $g = 2.0079$ feature does not appear.²³

The higher field component of the porous silicon spectrum has $g = 2.0054$, close to the g -value of several features, all of which may be contributing to the signal. Polycrystalline Si, microcrystalline Si, and amorphous Si broken bond defects all have $g = 2.0054(\pm 5)$, and a summation of P_b centers on many different crystalline faces has also been assigned to $g = 2.005$.²⁶ P_b centers, reported to be present in PS samples by many groups,²⁷⁻³⁰ are silicon atoms at the interface between Si and SiO_2 layers which are bonded to three other Si atoms via sp^2 hybridization. P_b defects have a single unpaired electron in the remaining valence orbital. The hybridization of the half-filled orbital has been characterized as close to a pure p-orbital. These defects are usually a result of lattice mismatch between silicon bulk and silicon oxide and are protected from further chemical reaction by the oxide layer. It is probable that P_b defects on many different crystalline faces of the porous silicon surface result from wet oxidation. Since a chemical etch on polycrystalline silicon was used for sample preparation, and samples were subsequently oxidized chemically, the $g = 2.0054$ signal is assigned to a combination of bulk defects and interfacial P_b defects.

Upon exposure to gas phase amine or an amine-hexane solution, the $g = 2.0054$ defect grows in intensity (Figure 4, part a, trace E), indicative of an increase in the concentration of the P_b defect. It is possible that the concentration of bulk amorphous silicon defects or the concentration of bulk poly-

crystalline defects is increasing, but it seems more reasonable that the surface interaction with a base will affect a nearby interfacial defect rather than a remote, bulk one. The assumption is bolstered by the static nature of the bulk K1 defect in the presence of base. Like PL quenching, the change in the EPR signal is reversible. If the gas phase amine is removed, the spectrum returns to its original size and shape.

A set of EPR spectra were taken using hexane solutions of increasing diethylamine concentration. The results are shown in Figure 4, part a, where it is obvious that the size of the higher field component signal increases with amine concentration. Observing the EPR tube with a UV lamp, we noticed that the intensity of photoemission decreased notably from 10^{-7} M diethylamine up to 10^{-1} M diethylamine solution, in which no PL was visible to the naked eye. A parallel experiment (Figure 4, part b), which used the same solutions employed in the EPR experiment, was carried out to quantify the PL quenching. The data shown in Figure 4, parts a and b, clearly indicate a correlation between diethylamine concentration, PL intensity, and EPR signal intensity. Figure 4, part c, demonstrates that the functional form of the maximum photoluminescence intensity plotted against amine concentration and the ratio of the peak heights of the two components of the EPR signal also plotted against amine concentration is the same. Thus, a direct connection between the PL and the EPR response is apparent, linking a physical change in the porous silicon structure with the observed PL.

A number of control experiments were performed to show that only when quenching of PL is unambiguously caused by a base is there an observable change in the EPR spectrum. Upon exposure of the freshly etched (i.e., nonoxide coated) porous silicon to diethylamine, PL intensity was observed to decrease. No change was observed in the EPR signal. On a similarly fresh sample, ethanol, which is known to quench freshly etched porous silicon, also resulted in a quenching of photoemission with no change in the EPR spectrum. This control shows that oxidation is important to the defect-induced quenching of porous silicon emission. After the porous silicon has been lightly oxidized, ethanol no longer causes quenching of PL and still shows no change in the EPR signal. The diethylamine case on lightly oxidized porous silicon, in which PL decreases and EPR increases, can be unambiguously attributed to base quenching. No PL quenching is observed when either ethanol or diethylamine is used as the quencher once the surface has been heavily oxidized. The EPR spectrum of heavily oxidized PS is unaffected by the presence of diethylamine. Similarly, the EPR spectrum of the nonporous silicon powder starting material does not change upon exposure to any quenching species. Both the $g = 2.0079$ peak and the $g = 2.0054$ peak are present in the polycrystalline spectrum, but the relative intensities are altered significantly with etching to form the porous product.

It can be unambiguously concluded that PS PL quenching must operate by more than one mechanism. On the freshly etched, oxide free surfaces, ethanol and diethylamine and a number of other species quench PL reversibly.³ The method of restoration in all these cases is removal of the quencher, whereas on oxidized samples a proton source is also required. The surface of fresh porous silicon is primarily hydride terminated. There are no acidic protons on a perfect silicon hydride surface to be extracted, and such protons were shown (via the Proton Sponge experiment reported here) to be important to the base-quenching mechanism. When the freshly etched PS surface is exposed to quenching species such as ethanol and diethylamine, changes in defect concentration in the structure play no role, as shown by static nature of the EPR

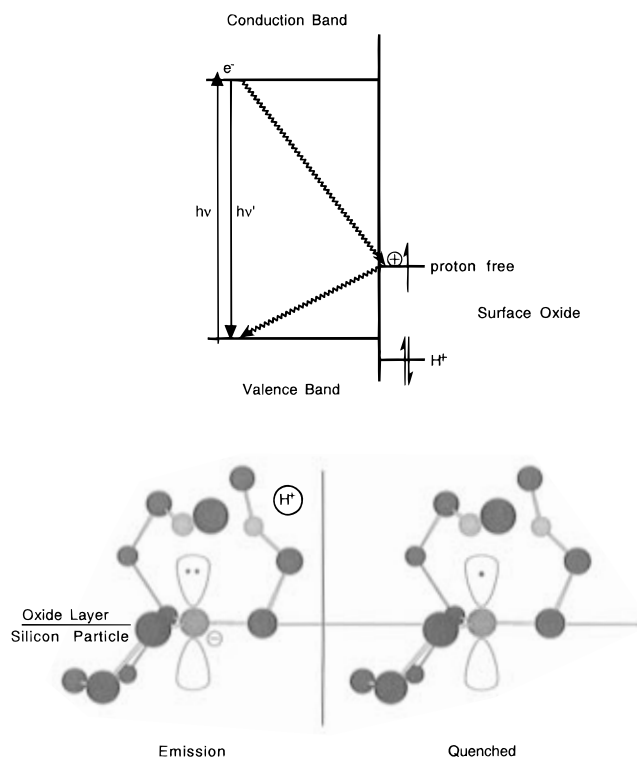


Figure 5. (Top) Energetic model of porous silicon luminescence quenching. When the oxide layer is protonated, there is efficient radiative recombination. When the oxide layer is deprotonated, non-radiative recombination dominates via surface state trapping at the paramagnetic surface site. (Left) A molecular model of the protonated oxide layer showing an anionic surface trap stabilized via a Coulombic interaction with a nonbonded proton. Light gray spheres symbolize the oxygen sites in the SiO_2 layer while Si is represented by the black spheres. The dark gray site represents a sp^2 -hybridized silicon trap site. Nonlocalized radiative recombination dominates the relaxation process in this case. (Right) A model of the deprotonated oxide layer showing a P_b paramagnetic defect (trigonal, sp^2 -hybridized silicon) at the Si/SiO_2 interface. Nonradiative recombination via this trap site is the dominant relaxation process, and photoluminescence is quenched.

spectra. Possible mechanisms for this quenching have been proposed elsewhere.^{3–11} Once a light oxide has formed, solvents cease to have a general quenching effect, but strong PL quenching by bases is still observable. With the formation of an oxide, acidic protons become available for abstraction. The PL quenching is accompanied by significant changes in the EPR spectrum. Hence, it must be concluded that at least two different quenching mechanisms are operating, depending on the degree of surface oxidation.

Photoluminescence Quenching Mechanism

Since a wide variety of aqueous bases are able to produce PL-quenching effects, the mechanism has to be one involving very general interaction between quenching molecules and the oxidized PS surface. The reversible change in the EPR signal, along with the knowledge that protons moving into and out of the SiO_xH_y layer gate the photoluminescence, led to the hypothesis of a quenching mechanism, represented schematically at the top of Figure 5, that functions as follows: protons penetrate into the silicon oxide layer and interact Coulombically with a neutral silicon radical (P_b defect) near the $\text{Si}-\text{SiO}_x$ interface. The presence of the proton lowers the energy of the silicon p-orbital such that it is no longer an effective hole trap, and a second electron fills the orbital. Thus, the hole initially associated with the defect becomes delocalized in the bulk of the silicon nanocrystallite. In the lower left portion of Figure

5, a portion of the silicon/silicon oxide interface is shown, with a cage-like silicon dioxide structure protecting a P_b site from chemical reaction. A nearby proton is also shown. There is no covalent bonding between what is now a silicon anion and the proton, otherwise there would be an observable change in the hydride stretching region of the FTIR. It is a weak, long range interaction, but sufficient to allow the presence of a second electron into the surface state. When a base is present outside the oxide layer, a proton gradient is established, causing H^+ to diffuse out of the layer. When the protons are removed, the interfacial state reverts to a hole trap (a silicon p-orbital occupied by a single electron) maintaining charge neutrality and creating a dangling bond at the silicon/silicon oxide interface. Figure 5 also models (on the lower right) the situation in the absence of a proton near the interfacial defect, showing the familiar paramagnetic P_b state. Since the energy of an interfacial defect of this type is known to be in the bandgap of silicon,³¹ we propose that this hole trap is the dominant PL killer. Metal cations do not penetrate into the SiO_x layer, but rather get stuck near the surface so as to block protons from entering into the layer. This conclusion is supported by the lack of PL restoration after exposure of PS to cations. As the oxide layer grows thicker over time (several months of exposure to air), base quenching is observed to cease. In this case, the base cannot establish a pH gradient through the SiO_xH_y layer. Like the PL, the EPR signal remains constant even in the presence of base with sufficient oxidation over time.

It is important to note that, on freshly etched PS, the proposed dangling bond creation and destruction mechanism does not apply because there is no oxide layer to prevent a covalent interaction between protons and dangling on the surface Si atoms. Quenching of freshly etched (hydride passivated) PS must therefore operate by some other mechanism. This is shown decisively by the lack of changes in the EPR signal when the PL of fresh PS is quenched by ethanol or even by diethylamine, a molecule used extensively in this work as a base quencher.

Conclusion

The changes in the EPR signal give important information on the mechanism of base quenching and directly illustrate how unpaired electrons affect PL, but also illuminates the roles of oxygen and hydrogen. There has been some disagreement about whether the presence of hydrogen or oxygen is necessary for the emission of visible light. Researchers have created PS surfaces that are nearly hydride free,²¹ while others have taken pains to produce surfaces that are nearly oxide free.³² The implication of this is that neither oxides specifically nor hydrides specifically are required to emit light. While silicon–heteroatom bonds may have a role in the PL mechanism, they certainly serve in pacifying the surface by tying up dangling bonds which will quench the PL. The thermally and chemically oxidized samples used in this work are examples where both oxygen and hydrogen are necessary to completely pacify the surface. In freshly etched PS there is very little oxygen, but surface passivation by hydrogen is complete, resulting in strong light emission. Thus, bases will not quench PL of freshly etched PS by proton abstraction (although a molecule that is a base might quench by some other mechanism).^{4,5} PS samples that have undergone rapid thermal annealing at temperatures greater than $\sim 750^\circ\text{C}$ have surfaces with very little hydrogen, but surface passivation by oxygen is complete, again showing strong PL.²¹

In summary, we have given a detailed description of the mechanism by which selective quenching of oxidized porous silicon by bases operates. IR spectroscopy shows that bonds are not created or destroyed in the process. Proton Sponge

quenching indicates that removal of a proton rather than attack by a nucleophile is responsible for quenching. Protons act as a gate to photoluminescence, but deuteration of the surface demonstrates that they are not the luminophore responsible for light emission.^{2,15,17} EPR spectroscopy reveals that dangling bonds are created and destroyed in the base-quenching process. EPR also proves that multiple quenching mechanisms exist, since freshly etched porous silicon quenched by bases or solvents show no changes in dangling bond density and therefore operate by some other mechanism.

Currently, we are finding the proposed mechanism useful with regard to the applications of porous silicon quenching in analytical areas and the development of sensors based on porous silicon surface modification.

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