

# Effects of SO<sub>2</sub> and I<sub>2</sub> on the Photoluminescence of Oxidized Porous Silicon

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The photoinduced visible light emission from lightly oxidized porous silicon can be reversibly quenched by both sulfur dioxide molecules and iodine molecules. Possible mechanisms for these processes are compared to the better understood mechanism for Brønsted base quenching of porous silicon photoemission. Supporting evidence was obtained through infrared spectroscopy, electron paramagnetic resonance spectroscopy, and surface chemistry. The feasibility of fashioning a SO<sub>2</sub> sensor using oxidized porous silicon is also discussed.

## Introduction

Initially synthesized about 40 years ago, porous silicon has only recently attracted attention in the literature, primarily due to reports that it both photoluminesces<sup>1</sup> and electroluminesces<sup>2</sup> in the visible portion of the optical spectrum. Much of the latest materials interest in porous silicon has been related to the possibility of generating a device having applications in the areas of display technology and information storage. Apart from this, porous silicon shows very interesting surface chemistry, this chemistry sometimes having profound effects on the ability of porous silicon to emit visible light and thereby offering the new opportunity that porous silicon may have applications in the area of sensors.<sup>3,4</sup> Here the observation that the photoluminescence of oxide coated porous silicon (OPS) is rapidly and reversibly quenched on a selective basis by gas-phase sulfur dioxide and by gas-phase iodine is studied. Mechanistic evidence is presented that links the quenching phenomenon to the reversible creation of a paramagnetic defect during exposure of the porous silicon to these molecular quenchers.

It has been documented that exposure of freshly etched porous silicon to many analytes results in reversible quenching of the observed photoluminescence (PL). While it is true that several different photophysical processes result in photoluminescence quenching, often the only available information is emission spectra, so quenching mechanisms remain poorly understood. A few mechanistic hypotheses have been advanced. For example, quenching by aromatic ring systems has been correlated with an energy-transfer mechanism.<sup>5–8</sup> Static

quenching by amines has been associated with a surface chemisorption process.<sup>9,10</sup> Certain metal ions are reported to quench via a charge-transfer mechanism.<sup>11–13</sup> A quenching mechanism has been advanced in which the dipoles of the solvent molecules induce quenching via an image charge hole trap mechanism.<sup>6</sup> Other quenching mechanisms have also been noted on freshly etched porous silicon. However, when there is a sufficient amount of insulating surface oxide present, the quenching mechanisms associated with freshly etched porous silicon are no longer observed to operate.<sup>14,15</sup> Rather, in the presence of a surface oxide coating, a more selective quenching is observed by gas-phase and aqueous Brønsted bases.<sup>16</sup> This quenching, which we refer to as Brønsted quenching, is mechanistically unrelated to solvent, energy-transfer, or charge-transfer quenching. Experimental evidence demonstrates that PL loss occurs when the base removes an acidic proton from near the Si/SiO<sub>x</sub> interface.<sup>15,17</sup> Interfacial proton loss results in the creation of a trap state in the bandgap,<sup>18,19</sup> facilitating electron–hole recombination. Replacement of the interfacial proton restores PL to the

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OPS sample. In this report, Brönsted quenching is compared mechanistically to the PL quenching observed in the presence of sulfur dioxide and iodine.

### Experimental Section

**Porous Silicon.** Electrochemically etched porous silicon was fashioned from B doped p-type single-crystal silicon with a resistivity of 2–10  $\Omega$  cm (obtained from El-Cat Semiconductor). The etching solution was a 1:1:1 volume ratio of HF (48%), ethyl alcohol, and distilled water. Etch time was 10 min, under constant current of 10 mA, with an area of  $\sim 1.1$  cm<sup>2</sup>. A two-compartment cell was used, the compartments separated by a silicon wafer 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 fashioned using an etching solution consisting of 10 mL of distilled water, 10 mL of H<sub>2</sub>SO<sub>4</sub> (96%), 2 mL of HF(48%), and  $\sim 0.25$  g of NaNO<sub>2</sub>.<sup>20</sup> The etching vessel was a 50 mL polyethylene beaker, with fast stirring using a Teflon stir bar. During the 15 min etch, NO<sub>2</sub> gas evolution is observed. At the end of the 15 min the beaker is filled completely with distilled water and filtered with large amounts of distilled water, followed by 50 mL of glacial acetic acid to enhance PL. Normally 0.50 g of Si powder (60 mesh, Aldrich chemicals) was etched. Alternately, ground single-crystal silicon was used to fashion powdered samples on single-crystal substrate.

**Oxidation of Porous Silicon.** Oxidation of porous silicon was allowed to occur thermally by storing powder or wafers on the benchtop, exposed to air. Oxidation generally took 1–2 weeks and was tested by dropping ethanol on the surface, while observing the PL with a hand-held UV lamp (365 nm excitation). No significant quenching of PL by ethanol indicated the growth of a satisfactory oxide coating. Oxidation was also performed photochemically, by placing the wafer in a solution of 1:1 ethanol and 3% HCl under a 365 nm UV lamp for 15 min.

**Instrumentation.** Photoluminescence quenching was observed using either a Perkin-Elmer LS-50 luminescence spectrometer, or an SLM 8000C luminescence spectrometer with an Ar<sup>+</sup> laser excitation source. The laser beam was defocused, with power  $< 5$  mW/cm<sup>2</sup>. Large changes in PL intensity were also observed by eye using a hand-held UV lamp (365 nm) as the excitation source.

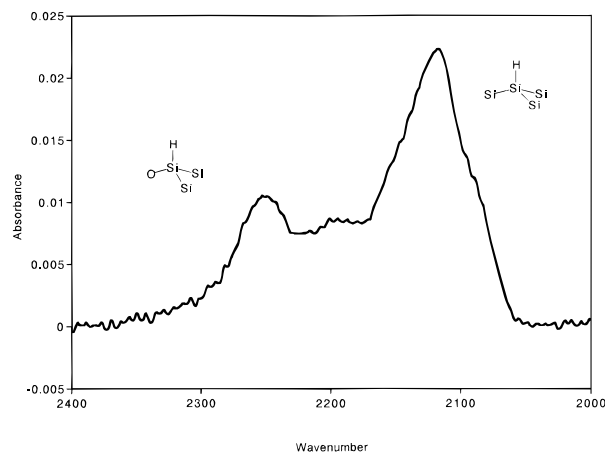
Transmittance Fourier transform infrared spectroscopy was performed using Nicolet 730 or Nicolet 800 FTIR spectrometers. Transmittance spectra were obtained against a background of HF-treated single-crystal silicon or air.

Electron paramagnetic resonance (EPR) 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). EPR spectra of porous silicon in the presence of sulfur dioxide gas were obtained by simply filling the EPR tube with SO<sub>2</sub> gas and capping it. Sufficient amounts of the gas remained in the tube to maintain the quenched state of photoluminescence for the duration of the EPR experiment. For EPR spectra of porous silicon in the presence of iodine, a small piece of solid I<sub>2</sub> was placed in the EPR tube along with the porous silicon sample. The room-temperature sublimation produced enough gas-phase I<sub>2</sub> in the EPR tube to result in quenching of the PL. EPR spectra of OPS quenched by Brönsted bases were obtained by adding a solution of 10<sup>-1</sup> M diethylamine in hexane to the EPR tube containing the OPS sample.

### Results and Discussion

We have recently reported that the PL from the oxidized porous silicon surface can be quenched by

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**Figure 1.** Infrared spectrum of partially oxidized porous silicon, showing hydride peaks associated with both oxidized silicon and oxide free silicon.

exposure to gaseous sulfur dioxide,<sup>15,21,22</sup> and we now report that iodine is another effective quencher of PL from OPS. Iodine quenching of porous silicon PL has been reported previously by Sailor and co-workers on freshly etched (hydride terminated) porous silicon.<sup>23</sup> In the Sailor system, a surface iodide is present and used as an intermediate in surface modification. The quenching is irreversible, and partial PL can be restored only by further chemical modification of the surface resulting in removal of the iodide. We report that if the porous silicon surface is allowed to oxidize before exposure to I<sub>2</sub>, then the quenching by I<sub>2</sub> becomes reversible. Removal of the I<sub>2</sub> source results in rapid (seconds) restoration of the PL to its original intensity. Like the Brönsted quenching noted above, both iodine and sulfur dioxide quenching require the presence of some surface oxide, but the oxidation of the porous silicon surface need not be complete. Infrared spectroscopy (Figure 1) shows prominent peaks in both the 2100 and 2250 cm<sup>-1</sup> regions. The former stretches are indicative of silicon mono-, di-, and trihydride stretches in which the silicon atom is bonded to other silicon atoms and not to oxygen. When the porous silicon surface has oxidized, silicon hydrides in the 2100 cm<sup>-1</sup> region have shifted to 2250 cm<sup>-1</sup> which attests to a bonding of the silicon atom to oxygen. When complete oxidation has taken place no substance has been shown to evoke a reversible quenching response.<sup>14,15,23</sup>

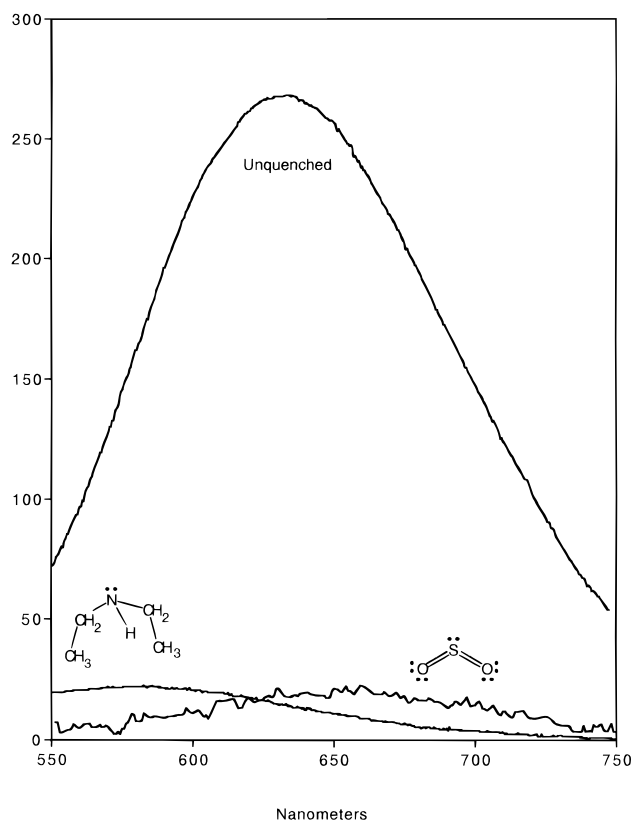
**Comparison of Brönsted and Sulfur Dioxide PL Quenching.** The sulfur dioxide molecule is usually described as a Lewis acid,<sup>24</sup> where previously only bases were known to quench OPS photoemission due to the requirement of proton removal from the surface. Its many lone pairs would make the classification of sulfur dioxide as a Lewis base permissible, but a comparison of some phenomenological aspects of the quenching by standard bases with quenching by sulfur dioxide indicates that assignment of basic character to SO<sub>2</sub> does not explain the observed quenching. For example, after

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**Figure 2.** Photoluminescence spectrum of porous silicon. The lower traces show weak emission from base quenched porous silicon and sulfur dioxide quenched porous silicon, with respective blue- and red-shifts of the emission maxima.

quenching with a base, subsequent exposure to a Brönsted acid will restore PL to its original intensity. To restore strong luminescence to SO<sub>2</sub>-quenched OPS, only removal of the sulfur dioxide source is necessary. Partial quenching of the OPS luminescence by Brönsted bases resulted in a blue-shifting of ~40 nm in the emission maximum. Similar treatment with sulfur dioxide (Figure 2) results in a pronounced red-shift of emission maximum. Plots of PL intensity versus time during exposure to SO<sub>2</sub> and to a Brönsted base show kinetics that are more rapid for quenching by sulfur dioxide.<sup>21</sup>

Further experimentation demonstrated that the Brönsted PL quenching interaction and the sulfur dioxide quenching interaction operated independently of one another, most likely at different sites on the surface. This conclusion was reached in part by observing that PL could be quenched by a gas-phase base and then further quenched by SO<sub>2</sub>. Corroborating evidence was obtained in a second quenching experiment, in which brightly luminescent oxidized porous silicon was placed in water that was then sparged with SO<sub>2</sub> gas. In water, SO<sub>2</sub> behaves as an acid and the pH of the solution dropped to ~2. Despite the fact that an aqueous solution of pH 2 normally has a restorative effect on the PL of Brönsted-quenched porous silicon due to the abundance of protons, a marked PL loss was observable by eye. To restore PL, the sample could be removed from the aqueous solution and blown dry in air. The quenching is due to hydrated SO<sub>2</sub>, and not to the aqueous HSO<sub>3</sub><sup>-</sup> ion, as NaHSO<sub>3</sub>(aq) does not bring about a PL quenching response. Under these strongly acidic conditions, extraction of a surface proton by sulfur

dioxide (i.e., SO<sub>2</sub> acting as a base) can be ruled out because of the quantity of protons in solution. Since quenching is observed, some other SO<sub>2</sub>-surface interaction must be responsible for PL loss.

**Comparison of Brönsted Base and Iodine Quenching.** The iodine molecule, like the sulfur dioxide molecule, is most often considered an acid according to the Lewis definition.<sup>24</sup> In formation of the I<sub>3</sub><sup>-</sup> ion, for example, the I<sub>2</sub> molecule has accepted a pair of electrons from I<sup>-</sup>, thereby acting as a Lewis acid. It can be considered a base if it were to coordinate through a lone pair on one of the iodines. As stated earlier, the wavelength of PL from base-quenched oxidized porous silicon is blue-shifted from its original position and can be restored to its original position and intensity if the sample is exposed to a proton source. After I<sub>2</sub> quenching, the emission maximum red-shifts and the only requirement for full PL restoration is removal of the I<sub>2</sub> source. The implication of these observations is that, like SO<sub>2</sub>, I<sub>2</sub> operates by a quenching mechanism that differs from that used to explain base quenching of oxidized porous silicon. The fact that SO<sub>2</sub> and I<sub>2</sub> have red-shifting of the PL wavelength maximum in common and neither require protons for restoration hints at a stronger connection between the mechanisms responsible for SO<sub>2</sub> and I<sub>2</sub> quenching than either mechanism might have with the mechanism for base quenching.

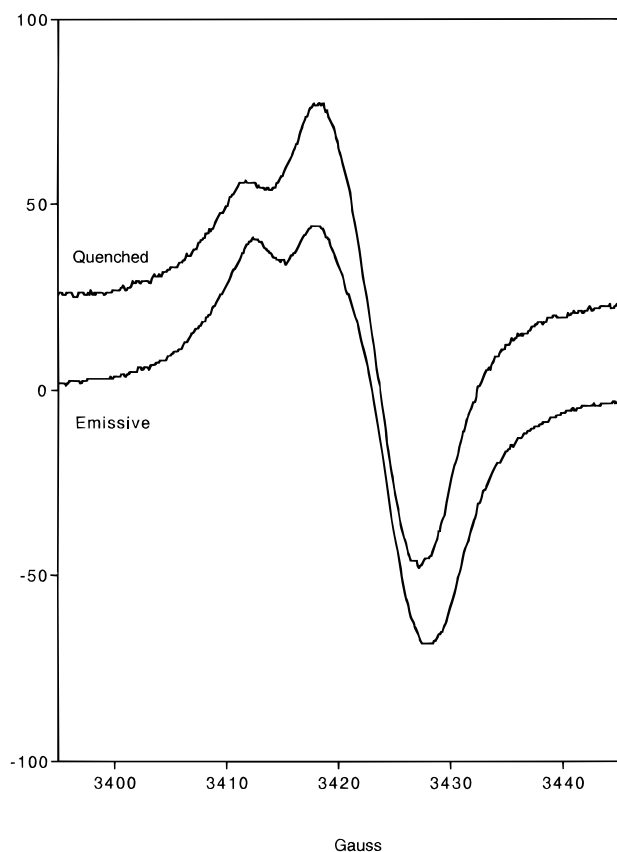
**EPR Spectroscopy.** In earlier reports it was demonstrated that a correlation can be made between PL and dangling bond density of OPS.<sup>15,25</sup> Using either gas-phase amines or amines in a hexane solution, in situ changes in the electron paramagnetic resonance spectrum of oxidized porous silicon can be observed. For experimental convenience, samples used for EPR spectroscopy differed from conventional OPS samples. Instead of the usual electrochemical etch on single-crystal silicon wafers, a stain etch on polycrystalline powder generated a high surface area porous silicon sample that could be studied at room temperature using standard EPR tubes. The EPR signal from powder oxidized porous silicon (Figure 3, emissive) consists of two major components near  $g = 2$ . The lower field component corresponds to the bulk K1 defect at  $g = 2.0079$ .<sup>26</sup> This defect is due to silicon atoms adjacent to dislocations in plastically deformed silicon. The higher field component at  $g = 2.0054$  is close to the  $g$  value of several features, all of which may be contributing to the signal. Polycrystalline silicon, microcrystalline silicon, and amorphous silicon all produce a  $g = 2.0054(\pm 5)$  signal and are likely to be present in our samples.<sup>18</sup> The higher field signal is most likely composed of contributions from all of these different defects and also from defects similar to the  $P_{b0}$  defect introduced upon oxidation of silicon surfaces having a wide variety of crystal faces.<sup>27</sup> A  $P_{b0}$  defect is an unpaired electron in a p-like orbital on a central silicon atom which is bonded to three other silicon atoms. The defect is the result of lattice mismatch at the silicon/silicon dioxide interface.

When exposed to amines, the PL intensity of OPS is dramatically reduced, while the higher field component

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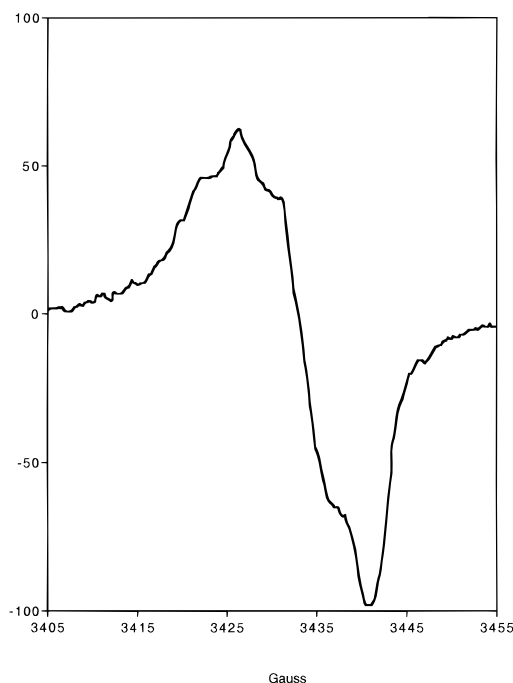
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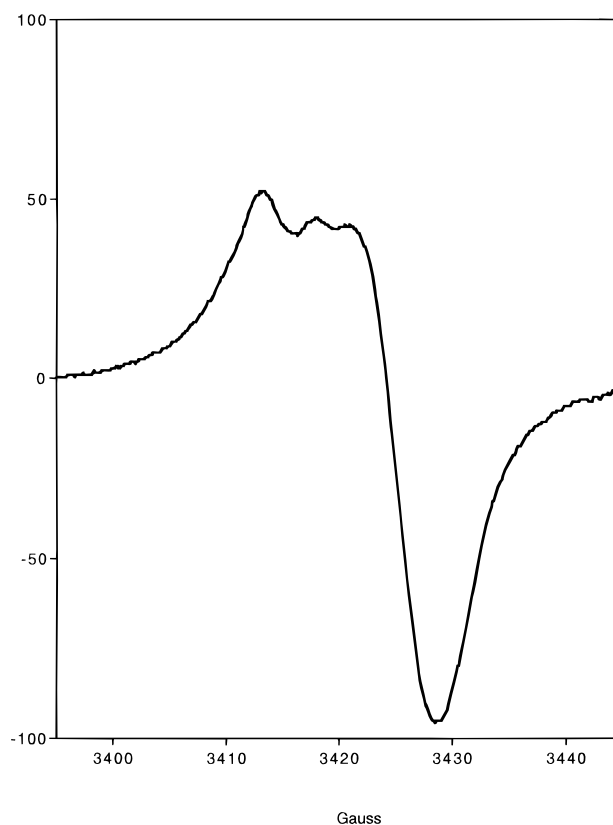


**Figure 3.** Emissive trace: EPR spectrum of a typical stain-etched polycrystalline porous silicon. Strong PL is shown by the powder. Quenched trace: EPR spectrum of stain-etched polycrystalline porous silicon exposed to diethylamine. The higher field component has increased in magnitude relative to the lower field component of the signal. Little or no PL is observed in samples exposed to amines.

of the EPR signal grows in intensity. The lower field signal remains unchanged (Figure 3, quenched). If the amines are allowed to evaporate, the signal returns to its original shape and magnitude, and the PL returns to its original intensity.<sup>15</sup> Sulfur dioxide gas passed through the EPR tube also generates a response in the EPR. Similar to bases, the absolute number of dangling bonds on the silicon surface appears to increase in the presence of SO<sub>2</sub>. Unlike the bases, which alter the relative magnitude of the two components, a third component grows in at a higher field than the two components already present (Figure 4). Definite assignment of this signal to a defect is made difficult by its close proximity to the original higher field signal. For the same reason it is also difficult to determine if both original signals remain unchanged after exposure to SO<sub>2</sub> or if they are changing along with the appearance of the new signal. As with sulfur dioxide, iodine vapor causes a change in the EPR spectrum of porous silicon (Figure 5). The OPS spectrum in the presence of I<sub>2</sub> is similar to that observed in the presence of SO<sub>2</sub> in that a third component appears, separate from the two components present in the original porous silicon spectrum. For I<sub>2</sub> however, resolution of the third peak as a separate entity is superior than for SO<sub>2</sub>, so it is more apparent by inspection that the new signal grows in without significant alterations to the shape and magnitude of the untreated porous silicon EPR spectrum.

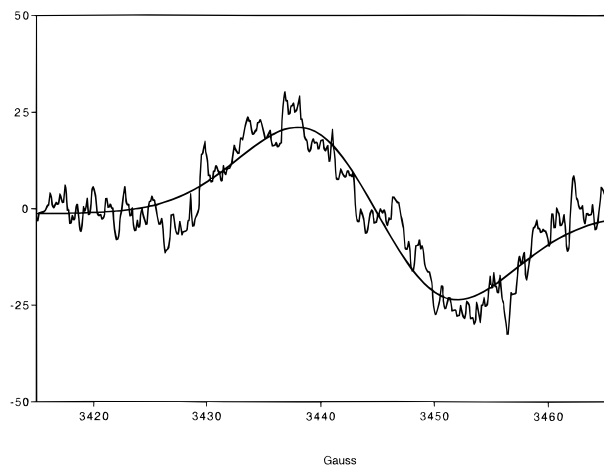


**Figure 4.** EPR spectrum of stain-etched polycrystalline porous silicon exposed to sulfur dioxide. Weak or no PL is exhibited by OPS in an SO<sub>2</sub> atmosphere. A third component in the EPR spectrum can be seen clearly, centered at a slightly higher magnetic field than the two components of luminescent porous silicon.



**Figure 5.** EPR spectrum of stain-etched polycrystalline porous silicon exposed to iodine vapors. Weak PL or no PL is exhibited by OPS samples. Three signals contributing to the spectrum are readily apparent. No obvious splitting by the spin  $^{1/2}$  iodine nucleus is observed.

Many of the problems associated with identification of the paramagnetic species can be corrected by using



**Figure 6.** EPR spectrum of stain-etched single-crystal porous silicon powder after sulfur exposure to sulfur dioxide. The solid line is fit to the derivative signal with a single Gaussian. The signal is centered at  $g = 2.0035$ .

ground single-crystal silicon instead of polycrystalline silicon to generate OPS samples. As anticipated, the K1 bulk signal at  $g = 2.0079$  is no longer observed, since this defect is associated with grain boundaries. In the absence of the K1 signal, it is easier to determine the  $g$  value of new signals that appear during PL quenching by sulfur dioxide. The  $g = 2.0054$  signal associated with amorphous silicon and microcrystalline silicon defects disappears as well. In brightly luminescent samples, it is difficult to resolve out a signal arising from porous silicon surface defects at  $g = 2.0054$ , but the new signal due to quenching with  $\text{SO}_2$  is readily apparent. This signal from  $\text{SO}_2$  quenched OPS is shown to be well fit by a single Gaussian (Figure 6) and has  $g = 2.0035$ . Because the sample is powdered, it is not known if there is any  $g$  value anisotropy in the spectrum. There are no EPR signals associated with porous silicon reported at  $g = 2.0035$  to the best of our knowledge. It is known that the location of  $P_b$  defects in the EPR spectrum of amorphous silicon shift toward lower  $g$  value with additional O and N atoms bonded to the silicon.<sup>28</sup> We therefore speculate that the signal is due to an increased number  $P_{b1}$  defects on many crystalline faces. The  $P_{b1}$  defect is similar to the  $P_{b0}$  defect, the difference being that the Si atom on which the unpaired electron resides is bonded to two silicon atoms and one oxygen atom as illustrated in Scheme 1.

The mechanism by which  $\text{SO}_2$  and  $\text{I}_2$  selectively increases the number of such sites remains unclear, but experiments thus far have yielded several important clues. First, it is apparent that neither molecule undergoes irreversible redox chemistry during its interaction with the OPS surface. After quenching with  $\text{SO}_2$  or  $\text{I}_2$  porous silicon restoration will occur under flowing argon as long as the source of  $\text{SO}_2$  or  $\text{I}_2$  is removed, so it is unlikely that it has been permanently oxidized or reduced. The formation of the  $\text{I}^-$  anion or  $\text{SO}_4^{2-}$  anion on the OPS during quenching would prohibit fast restoration in air, although other reversible redox couples such as  $\text{SO}_2/\text{SO}_2^-$  and  $\text{I}_2/\text{I}_2^-$  cannot be ruled out based on this argument. However, studies by Rehm indicate that electron acceptor quenchers are

effective only if  $E^\circ_{\text{R}} \leq -0.8$  V vs NHE. Given that  $E^\circ_{\text{R}}(\text{SO}_2/\text{SO}_2^-) = -0.288$  V vs NHE and  $E^\circ_{\text{R}}(\text{I}_2/\text{I}_2^-) = +0.210$  V vs NHE, charge-transfer quenching in these cases must be ruled out on thermodynamic grounds.

As demonstrated by the restoration of PL under flowing argon and unlike the base-quenched surfaces, no protons are required for PL recovery, so the proton abstraction model that describes base quenching does not fit the observed phenomena. Other sulfur-containing molecules such as phenyl disulfide, phenyl sulfone, and thiophene are not quenchers of OPS. Elemental bromine, however, does exhibit reversible quenching behavior similar to that of iodine. There are remarkably few similarities between  $\text{SO}_2$  and the halogens, which might suggest the nature of the PL quenching mechanism. Both molecules are electrophilic and oxophilic, but other such species such as  $\text{BF}_3$ ,  $\text{TiCl}_3$ , and  $\text{SnCl}_4$  are nonquenchers of oxidized porous silicon. It is also known, at least for  $\text{I}_2$ , that the quenching species is not directly interacting with the paramagnetic silicon atom. Direct interaction between a spin  $^{7/2}$  iodine nucleus and the paramagnetic silicon center would result in a splitting of the EPR signal into a multiplet and this is not observed (Figure 6). This might be indicative of a mechanism involving an intermediary which causes the paramagnetic defect to appear on silicon through the interaction of the intermediary with  $\text{SO}_2$  or  $\text{I}_2$ . For Brønsted base quenching the intermediary is a proton, whose presence or absence is responsible for the creation of an interfacial hole-trap state that provides a route for efficient nonradiative recombination.<sup>15</sup> For the  $\text{SO}_2/\text{I}_2$  quenching system, protons are ruled out as the intermediary, but no other strong candidate has emerged.

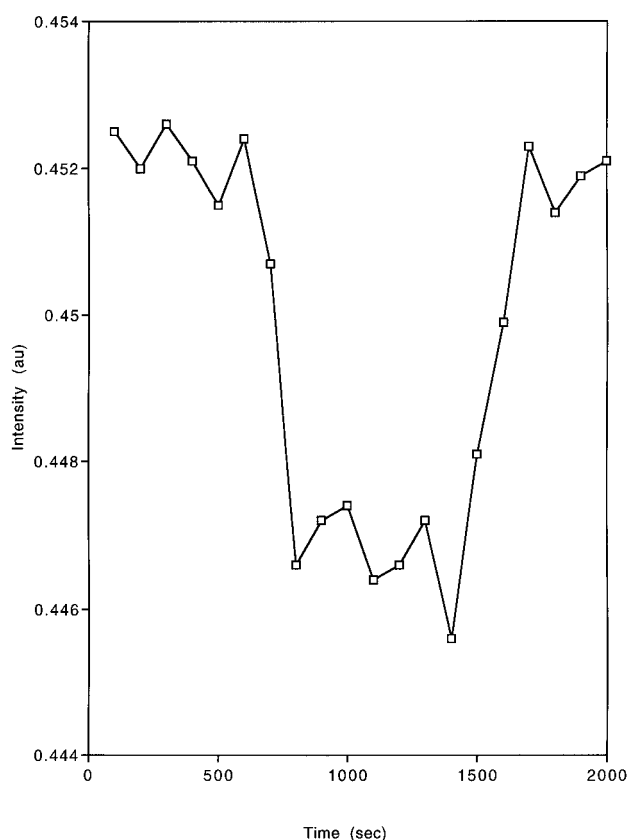
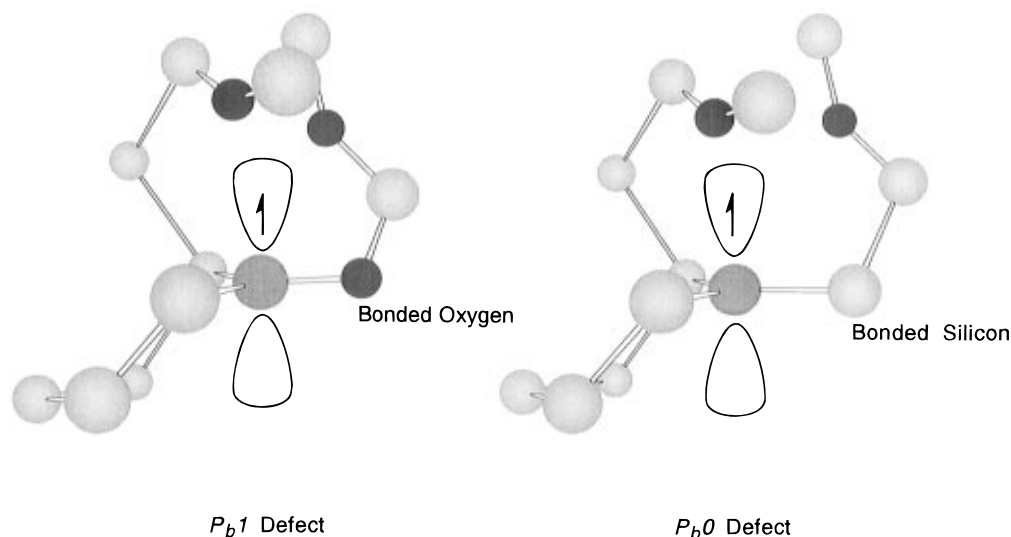
**Porous Silicon Sensors.** The phenomenon of PL quenching lends itself to interesting sensor applications. Sulfur dioxide is a molecule of environmental concern, because  $\text{SO}_2$  pollution is a primary contributor to acid rain formation, making its detection and elimination important. In sulfur dioxide/argon atmospheres of greater than 10%  $\text{SO}_2$ , luminescence quenching of OPS can be clearly seen by the naked eye. The reproducibility of quenching/restoration cycles over time has been previously reported.<sup>21</sup> Using a spectrofluorimeter to detect small changes in PL intensity, the limit of detection of sulfur dioxide in argon was found to be 440 ppb.<sup>3</sup> This concentration produced a reproducible 1.2% change in the observed photoluminescent intensity, which was detected on a background photoluminescence signal having a signal-to-noise ratio of 4:1 using signal-averaging conditions. As a typical example, quenching induced by an argon atmosphere containing 890 ppb is shown in Figure 7. Similar  $\text{SO}_2$  selective quenching is observed when an air carrier is substituted for argon.

Taking into consideration that stack gases typically release sulfur dioxide at concentrations of 100–4000 ppm,<sup>29</sup> it is apparent that the sensitivity of OPS to the  $\text{SO}_2$  molecule is sufficiently high that application in environmental monitoring is a realistic possibility. Exposure of the sulfur dioxide active OPS surface to high concentrations of the typical atmospheric and industrial waste gases ( $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{NO}_x$ ) does not evoke a quenching response. Thus,  $\text{SO}_2$  detection by porous silicon does not suffer from the interference

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Scheme 1



**Figure 7.** Argon sulfur dioxide mixture (890 ppb  $\text{SO}_2$ ) flows through cell containing oxidized luminescent porous silicon. Emission intensity shows a significant drop after  $\text{SO}_2$  flow begins (time = 600 s) and subsequent restoration after  $\text{SO}_2$  flow is shut off (time = 1400 s).

by the expected gas-phase species. This makes it an excellent candidate for in line  $\text{SO}_2$  monitoring with no pre-separation of gas necessary.

There are several problems to solve before a porous silicon-based  $\text{SO}_2$  sensor could be realistically employed. At present, the surface reactivity toward sulfur dioxide lasts for several weeks. Over that period of time the layer of oxidized silicon grows thicker, and the quenching response grows weaker until eventually exposure to  $\text{SO}_2$  results in no quenching. Preliminary experi-

ments involving chemical modification of the OPS surface show that the  $\text{SO}_2$  response is maintained. Since such treatments are known to inhibit the oxidation of silicon surfaces,<sup>30</sup> it is probable that long-term stabilized interfaces can be synthesized.

### Conclusions

The differences observed between base quenching and  $\text{SO}_2$  quenching indicate that the silicon surface- $\text{SO}_2$  interaction is distinct from the Brønsted base interaction and that  $\text{SO}_2$ -induced PL quenching does not easily fit a mechanism involving abstraction of a surface proton. There are sufficient similarities in  $\text{SO}_2$  and  $\text{I}_2$  quenching to suggest that they operate by similar mechanisms. It can be concluded that like bases, the interaction of  $\text{SO}_2$  and  $\text{I}_2$  with the surface of porous silicon results in the reversible creation of a paramagnetic species which introduces a new nonradiative pathway for relaxation of photoexcitation. In the case of the bases, it appears that the presence of the paramagnetic silicon center (the  $P_{b0}$  defect) is related to absence of a proton. For sulfur dioxide and iodine, experiment suggests that the paramagnetic species involved in the PL quenching mechanism is different from that related to Brønsted quenching, a possibility being the  $P_{b1}$  center. The exact interaction between the OPS surface and the  $\text{I}_2$  or  $\text{SO}_2$  molecule and how it brings about the changes in the EPR spectrum remains obscure.

Several characteristics of  $\text{SO}_2$  quenching contribute to the desirability of porous silicon as a potential reusable in-line detector. The reversibility of the PL loss means the porous silicon sensor is continually active. The selectivity of porous silicon for  $\text{SO}_2$  sensing eliminates the need for separation of gases before detection. Clarification of the  $\text{SO}_2$  quenching mechanism will lead to optimal sensitivity and device lifetime and may suggest new applications for porous silicon as a sensor.

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