Inorg. Chem. **1998,** *37,* 3355−3360

Dimethyl Sulfoxide as a Mild Oxidizing Agent for Porous Silicon and Its Effect on Photoluminescence

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Received December 18, 1997

Dimethyl sulfoxide acts as a mild room-temperature oxidant of luminescent porous silicon. The oxidation reaction is accompanied by a loss in photoluminescence intensity from the silicon nanocrystallites, indicating that the oxide formed under these conditions is electronically defective. The rate of oxidation is reduced if the reaction is carried out in the presence of the radical traps 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) or cumene. In addition, photoluminescence intensity is preserved if the DMSO oxidation reaction is carried out in the presence of high concentrations of BHT. The BHT is proposed to form a more electronically passive oxide layer by hydrogenating the surface radicals (dangling bonds) generated during the oxidation reaction.

Introduction

Porous Si is comprised of a high surface area network of Si nanocrystallites.[1−3] The most commonly used hypothesis to explain light emission in the visible range from porous Si is the confinement of charge carriers in quantum-sized nanocrystallites.[4,5] Current interest in porous Si has been stimulated by its potential for application in optoelectronics, displays, and chemical or biological sensors.[6] The stability of the photoluminescence properties of porous Si is a serious issue for these applications. It has been found that very stable material can be generated by a rapid thermal oxidation in an oxygen atmosphere at high temperatures,[7−9] although there is an increasing desire to find milder oxidation reactions that do not isolate the luminescent chromophore behind an electronically insulating thick SiO_2 layer.[10] A number of groups have reported room-temperature chemical oxidation of porous Si with hydrogen peroxide,[11−13] nitric acid,[11] or halogens.[14] The chemical oxidations have been shown, in some cases, to provide good electronic surface passivation, to allow chemical functionalization, and to improve the stability against environmental aging, without burying the sample in a thick oxide layer.[3,15] In this paper, we report that dimethyl sulfoxide acts as a mild self-limiting oxidizing agent for porous Si which generates a stable oxide layer at room temperature. The oxidation reaction is proposed to produce radical surface traps (dangling bonds) which reduce the intensity of the steady-state photoluminescence spectrum significantly. We additionally show that these surface radicals can be passivated by treatment with butylated hydroxytoluene (BHT) or cumene, which presumably delivers a hydrogen atom to the Si surface radical. The radical traps serve two functions: they suppress the rate of oxidation, and they generate a more electronically passive oxide.

Experimental Section

Sample Preparation and Treatment. Luminescent porous Si samples were prepared by galvanostatic photoetch of polished crystalline *n*-Si (phosphorus doped; 0.58 Ω-cm resistivity; (100) orientation) supplied by International Wafer Service. The etching solution was prepared by adding an equal volume of pure ethanol (Quantum Chemicals) to an aqueous solution of HF (48 wt %; Fisher Scientific). The etching cell was constructed of Teflon and was open to air. Si wafers were cut into squares with a diamond scribe and mounted in the bottom of the Teflon cell with a Viton O-ring seal, exposing 1.1 cm^2 of the Si surface. Electrical contact was made to the backside of the Si wafer with a strip of heavy Al foil. A loop of Pt wire was used as a counterelectrode. Samples were illuminated during the etch with a 300-W tungsten lamp in order to supply a photocurrent for the corrosion reaction. Samples were etched at an anodic current density of 50 mA/cm^2 for 5 min. After the etching, the samples were rinsed in 95% ethanol or methylene chloride, dried under a stream of dry $N_2(g)$, and then dried in vacuo for 30 min prior to use. From this point on, standard inert atmosphere (nitrogen) techniques were used to avoid introduction of air or water.[16]

Anhydrous dimethyl sulfoxide (Aldrich Chemical Co., 99.8%) was freeze−pump−thaw degassed three times and handled under dry N_2.

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S0020-1669(97)01587-5 CCC: $15.00

2,6-Di-*tert*-butyl-4-methylphenol (BHT, 99+%) and cumene (99%) were used as received from Aldrich Chemical Co. Phenol (99+%) was used as received from ACROS Chemicals. BHT was deuterated at the 1-hydroxy position (D-BHT) by dissolution of 3 g of BHT in 12 mL of CH_3CH_2OD (Aldrich Chemical Co., 99 atom % D at the hydroxyl position) and evaporation of the ethanol solvent. The extent of incorporation of D was checked by ^1H NMR in d_6-benzene and was found to be 95%. All solutions were handled under dry $N_2(g)$ in a glovebox or by using conventional Schlenk and syringe vacuum line techniques.[16] The DMSO oxidation reactions were carried out (under dry $N_2(g)$) in the same spectroelectrochemical cell used for the electrochemical etching.[15] After the reaction, the dimethyl sulfoxide solvent was removed from the cell, and the porous Si surface was rinsed thoroughly with toluene (Aldrich Chemical Co., 99.8%) or methylene chloride (Aldrich Chemical Co., 99.6%) before spectroscopic analysis.

Photoluminescence Measurements. Steady-state photoluminescence spectra were obtained with an Acton 0.275-m monochromator, a 450-nm cutoff filter, and a UV-enhanced Princeton Instruments liquid nitrogen-cooled charge coupled device (CCD) detector. The excitation source was the 435-nm emission line (filtered through two identical narrow-band-pass interference filters) from an Oriel 250-W Hg arc lamp. Incident power at the sample was always below 1.25 mW/cm^2, and the photoluminescence measurements were performed with the samples exposed to air. The excitation source was blocked between photoluminescence measurements to avoid possible photoinduced degradation of the porous Si samples.[17−20] The reported photoluminescence intensities were corrected for fluctuations in excitation source intensity and for variations in optical alignment by comparison with an external standard Cu:ZnS green phosphor, whose spectrum was run immediately before collection of the sample spectrum, using the same collection geometry. The intensity values of each sample spectrum were divided by the value of the integrated intensity of each corresponding phosphor standard spectrum.

Infrared Spectroscopic Measurements. Fourier transform infrared spectra were collected on a Nicolet Magna 550 operating in transmission mode. Spectral resolution was 4 cm^{-1}, and typically, 128 interferograms were acquired per spectrum. The sample chamber was flushed with dry N_2.

Gas Chromatographic Measurements. A Hewlett-Packard 5890 Series II Plus gas chromatograph with a GasPro GSC column (porous layer open tubular, PLOT) and a flame photometric detector (FPD) was used to detect the dimethyl sulfide product of the DMSO reactions. The head gas from a DMSO/porous Si reaction was transferred from the reaction vessel to a sampling chamber on a vacuum line, and the sample was then introduced directly into the GC inlet through a gastight valve. Under these conditions, dimethyl sulfide comprised 98.2% of the collected gas.

Results and Discussion

Oxidation of Porous Si with Dimethyl Sulfoxide. After the electrochemical etch, the surface of the resulting porous Si layer is H-terminated and is characterized by infrared absorptions assigned to SiH, SiH_2, and SiH_3 $\nu_{(Si-H)}$ stretching modes at 2085, 2110, and 2140 cm^{-1}, respectively,[21−23] an Si−H_2 scissor mode at 915 cm^{-1}, and no detectable surface oxide absorptions (Figure 1). The photoluminescence from this sample is strong and centered around 650 nm (Figure 2). Treatment of the sample in liquid dimethyl sulfoxide for 40 min results in an oxidized surface which displays bands in the infrared spectrum characteristic of a $\nu_{(Si-O)}$ stretching vibration at 1100 cm^{-1} (Figure 1). In addition to the Si−O stretching band, new bands assigned to $\nu_{(OSi-H_x)}$ are observed around 2260 cm^{-1}. These higher energy Si−H_x vibrations are characteristic of Si−H species that have oxygen atoms bound to the Si atom.[23] Figure 1 also shows that the loss in intensity of the $\nu_{(Si-H_x)}$ band is offset by increased intensity in the $\nu_{(OSi-H_x)}$ band. A plot of the areas of the $\nu_{(Si-H_x)}$, $\nu_{(OSi-H_x)}$, and $\nu_{(Si-O)}$ bands as a function of DMSO reaction time is presented in Figure 3A. The plot shows that the area of the $\nu_{(Si-H_x)}$ peak decreases, while the areas of the $\nu_{(OSi-H_x)}$ and $\nu_{(Si-O)}$ bands increase during the course of reaction, but that the combined area of the $\nu_{(OSi-H_x)}$ and $\nu_{(Si-H_x)}$ bands stays roughly constant. Thus, although the amount of oxide grows, the total concentration of H species on the

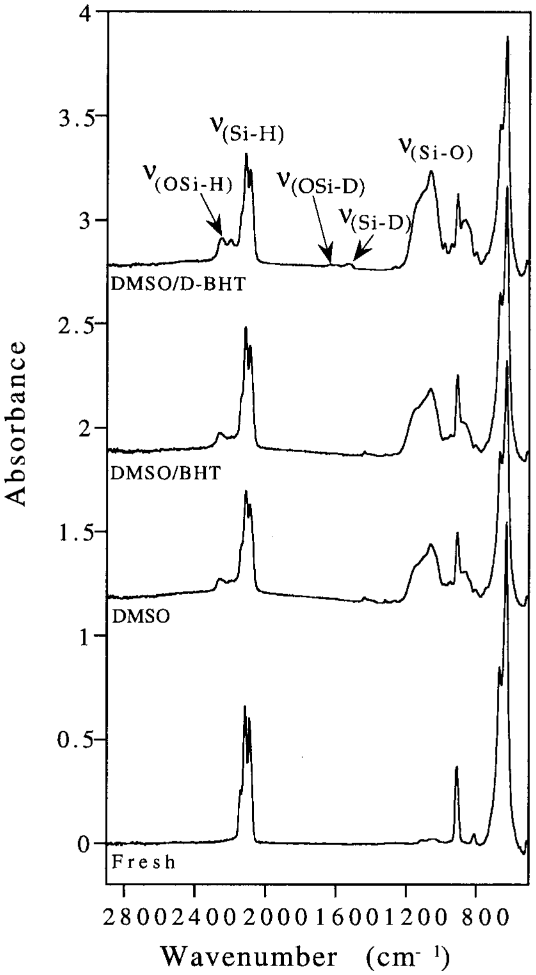

Figure 1. Transmission FTIR spectra of porous Si samples showing the important vibrational assignments. As-formed (fresh) porous Si displays bands associated with surface hydrides. The spectrum of the sample treated with dimethyl sulfoxide for 40 min (DMSO) displays oxide-related bands in the 2260 and 1100 cm^{-1} region, indicating a significant amount of oxidation has occurred. The spectrum of the sample exposed to DMSO containing 3.2 M BHT for 75 min (DMSO/BHT) displays the same oxide-related peaks with comparable intensities, indicating that the rate of the oxidation reaction has been reduced by the added BHT. If D-BHT is used in the reaction, deuterium is incorporated into the surface as Si−D (DMSO/D-BHT). The DMSO/D-BHT sample was treated with the DMSO/D-BHT solution for 300 min, and the concentration of D-BHT was 2.2 M. The top three spectra are offset along the *y*-axis by 1.2, 1.8, and 2.75 au for clarity.

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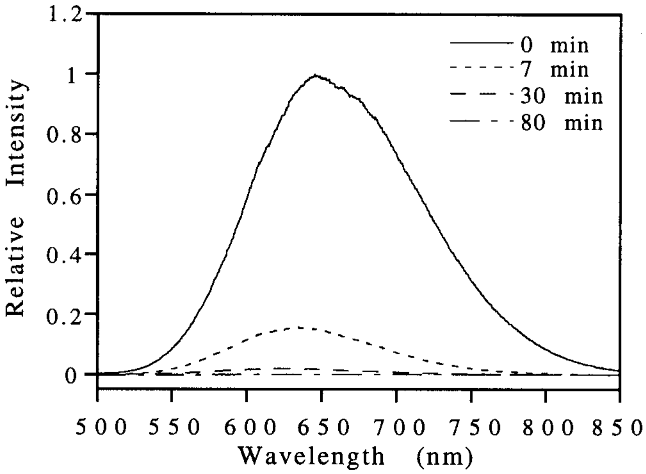


Figure 2. Photoluminescence (PL) spectra (435-nm excitation) from a porous Si sample after soaking in DMSO for the indicated times. The PL spectra were obtained after removing the samples from DMSO, rinsing them thoroughly with CH_2Cl_2, and drying them under a stream of dry nitrogen. Intensities are all normalized to an external standard phosphor spectrum as described in the Experimental Section.

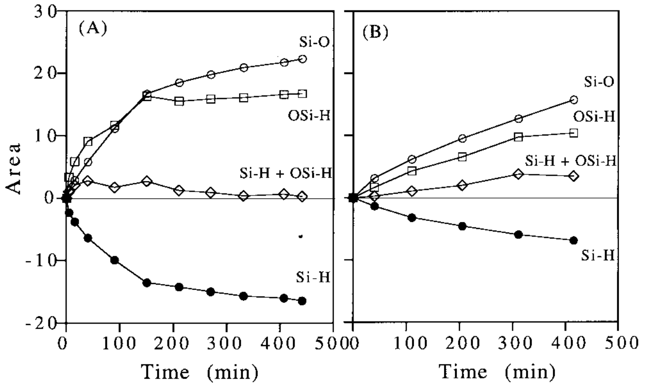


Figure 3. Evolution of the areas of the infrared absorption peaks associated with the stretching vibrations of Si–O (open circles), OSi–H (squares), Si–H + OSi–H (diamonds), and Si–H (solid circles) species during the course of a DMSO reaction (A) or a DMSO/3.2 M BHT reaction (B). The areas were measured by integration; the Si–O band was integrated between 990 and 1236 cm^{-1}, the Si–H band was integrated between 2048 and 2160 cm^{-1}, the OSi–H band was integrated between 2309 and 2160 cm^{-1}, and the Si–H + OSi–H band was integrated between 2048 and 2309 cm^{-1}. The O–Si areas (open circles) were divided by 4 in A and B for clarity of presentation. At each time interval, the sample was removed from the DMSO solution, rinsed with methylene chloride (sample A) or toluene followed by methylene chloride (sample B), and blow-dried in a stream of dry N_2 before measurement of the spectrum.

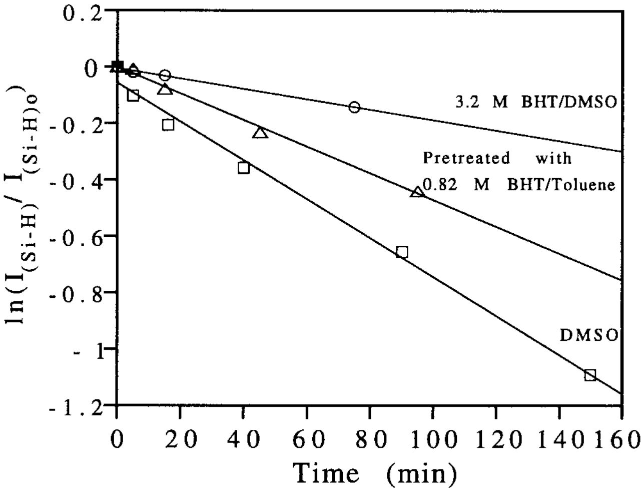
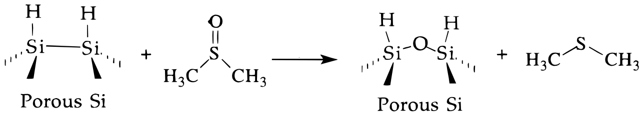


Figure 4. First-order rate law plots of the loss of intensity of the $\nu_{(\mathrm{Si-H}_x)}$ band in the infrared spectrum, showing the rate of porous Si oxidation by DMSO (squares). The rate of oxidation is suppressed if the porous silicon sample has been pretreated with a 0.82 M solution of the radical trap BHT in toluene (triangles). The rate of oxidation is even further suppressed if 3.2 M BHT is included in the DMSO solution during the oxidation reaction (circles). Data are presented as $\ln(I_{(\mathrm{Si-H})}/I_{(\mathrm{Si-H})_0})$ vs time, where $I_{(\mathrm{Si-H})}$ is the integrated intensity of the band assigned to $\nu_{(\mathrm{Si-H}_x)}$ in the infrared spectrum (between 2048 and 2160 cm^{-1}), and $I_{(\mathrm{Si-H})_0}$ is the value of $I_{(\mathrm{Si-H})}$ at time $t = 0$ min.

porous Si surface remains almost constant during the reaction, suggesting that H atoms are not removed from the surface during the oxidation process. The rate of disappearance of the Si–H vibrational bands between 2048 and 2160 cm^{-1} follows a first-order rate law dependence at reaction times greater than 5 min, with an apparent rate constant of $(1 \pm 0.3) \times 10^{-2}$ min^{-1} (Figure 4). The reaction rate is significantly larger at earlier times ($t < 5$ min), which is attributed to the presence of a small number of more reactive surface Si atoms. The fit of the rate data to a second-order rate law (1/area of the $\nu_{(\mathrm{OSi-H}_x)}$ and $\nu_{(\mathrm{Si-H}_x)}$ bands vs time) is much worse than the first-order fit.

The data are interpreted to indicate that oxidation of porous Si by dimethyl sulfoxide occurs by cleavage of Si–Si, rather than Si–H bonds (eq 1). This is reasonable considering the difference in bond enthalpies between Si–H (76 kcal/mol) and Si–Si (53 kcal/mol); surface Si–Si bonds are expected to be weaker than surface Si–H bonds.[24]



(1)

The oxidation process significantly degrades the photoluminescence of porous Si. The intensity of the steady-state photoluminescence spectrum of DMSO-oxidized porous Si is reduced to around 1–2% of the original (freshly etched) porous Si after 30 min of exposure to DMSO (Figure 2). The data indicate that DMSO oxidation introduces interfacial defects which act as nonradiative traps. This result is somewhat surprising, considering that thermally grown SiO_2 usually is an excellent electronically passive layer in Si microelectronic circuits and thermal or chemical oxidation reactions have been employed to stabilize photoluminescence of porous Si.[8,9] However, there are also examples of chemically or photochemically grown oxides that degrade photoluminescence from porous Si.[10,17,19,20,25–27] As in the present work, the degradation is most often attributed to the introduction of nonradiative surface states.

Although the thickness of the oxide layer produced by DMSO oxidation could not be quantitatively determined, a relative measure of oxide thickness can be estimated by comparison of the intensity of the Si–O band relative to the intensity of the Si–H bands in the infrared spectrum. Using this criterion, the oxide thickness on a sample after 90 min of room-temperature

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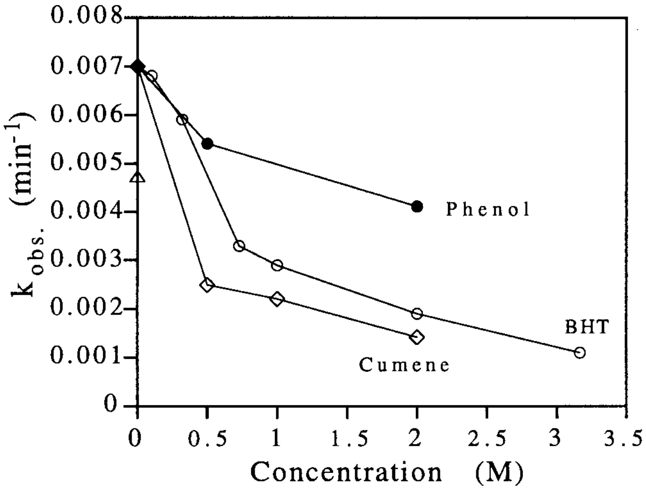
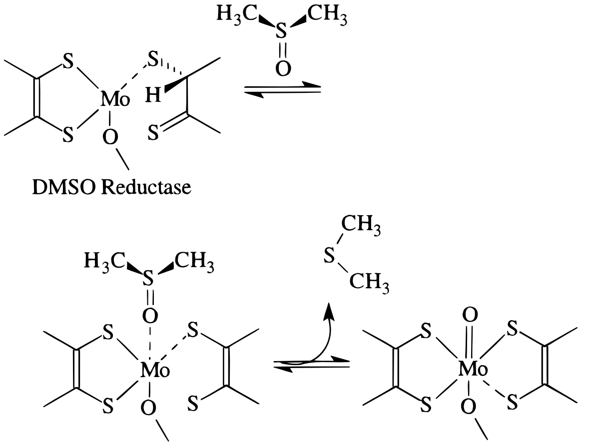


Figure 5. Plot of the pseudo-first-order rate constants (k_{obs}) for porous Si oxidation in DMSO as a function of concentration of the radical trapping reagents phenol (solid circles), BHT (open circles), and cumene (diamonds). The initial rate of oxidation in pure DMSO is somewhat less if the porous Si sample has been treated with BHT prior to exposure to DMSO (triangle).

DMSO exposure is comparable to that of a sample which has been thermally oxidized in air at 100 °C for 15 min.

Effect of Added Radical Traps on the Rate of Oxidation. The above data indicate that dimethyl sulfoxide is a mild chemical oxidant for porous Si. In organic and biological oxidations, DMSO is known to deliver an O atom to the substrate.[28] For example, DMSO reductase converts DMSO to dimethyl sulfide, generating a molybdenum oxo species in the process (eq 2).[29] In the present system, it is postulated that decomposition of DMSO oxidizes silicon and produces radicals at the porous Si surface. Experiments designed to test this hypothesis were performed using the radical-trapping reagents 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT), phenol, and cumene. BHT is a well-known radical scavenger that produces a very stable, structurally hindered phenoxy radical.[30] In DMSO solutions that contain BHT, the infrared data indicate that the rate of surface oxidation is reduced (Figures 1, 3, and 4). When a 2.2 M DMSO solution of D-BHT is used, slight incorporation of deuterium is observed in the infrared spectrum as $\nu_{(\mathrm{Si-D})}$ and $\nu_{(\mathrm{OSi-D})}$ stretching vibrations at 1537 and 1633 cm^{-1}, respectively (Figure 1). The rates of oxide growth and (Si$-$H$_x$) loss are reduced in the presence of BHT, and a plot of the apparent first-order rate constant for Si$-$H$_x$ disappearance versus concentration of BHT clearly shows that the rate of oxidation decreases with increasing [BHT] (Figure 5). The plot of Figure 5 is not linear, indicating that the effect of added BHT cannot be interpreted as a simple second-order process. In addition, in the presence of BHT, there is a net increase in total surface hydride coverage (Si$-$H$_x$ and OSi$-$H$_x$) during the course of the DMSO oxidation reaction (Figure 3B). The fact that the total H atom concentration increases as the oxidation reaction proceeds suggests that the dimethyl sulfoxide reaction produces radical species on the surface of porous Si which then abstract H atoms from the BHT donor. This interpretation is also consistent with the observation that surface Si$-$D species appear on the porous Si surface when deuterated BHT is used (Figure 1). If a freshly etched porous Si sample is pretreated with a solution of BHT in toluene and then exposed to pure DMSO, the rate of oxidation is also suppressed (Figure 4), indicating that the residual surface radicals generated during the electrochemical etch that produces porous Si also play a role in the DMSO oxidation reaction.



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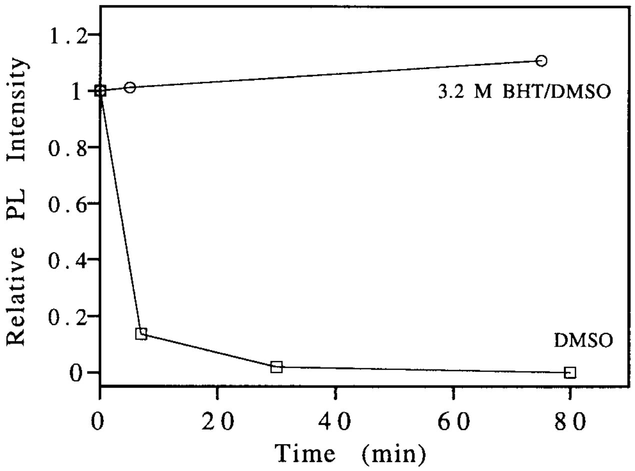

Figure 6. Integrated intensity of the steady-state photoluminescence spectrum from two porous silicon samples exposed to DMSO as a function of time. The squares represent a sample that was exposed to pure liquid DMSO, and the circles represent a sample that was exposed to DMSO containing 3.2 M BHT. The intensities were integrated between the wavelength values of 500 and 800 nm, and the samples were excited with 435-nm light. Measurements were all made in air after removing the sample from the DMSO solution, rinsing with CH_2Cl_2, and drying under a stream of N_2. To allow an accurate comparison, the spectra were all normalized to the intensity of a standard phosphor as described in the Experimental Section.

The effect on the rate of oxidation of porous Si by DMSO in the presence of other radical scavengers was also investigated. The rate of oxidation is suppressed if either BHT, cumene, or phenol are present in the DMSO during treatment (Figure 5). Phenol suppresses the oxidation rate the least, consistent with the poor ability of this reagent to retard radical reactions.[31]

Effect of Added Radical Traps on Photoluminescence. The intensity of photoluminescence from porous Si is preserved if the DMSO oxidation reaction is carried out in the presence of BHT. Thus, a plot of the integrated photoluminescence intensity from porous Si as a function of DMSO exposure time shows a rapid drop when pure DMSO is used, but it is

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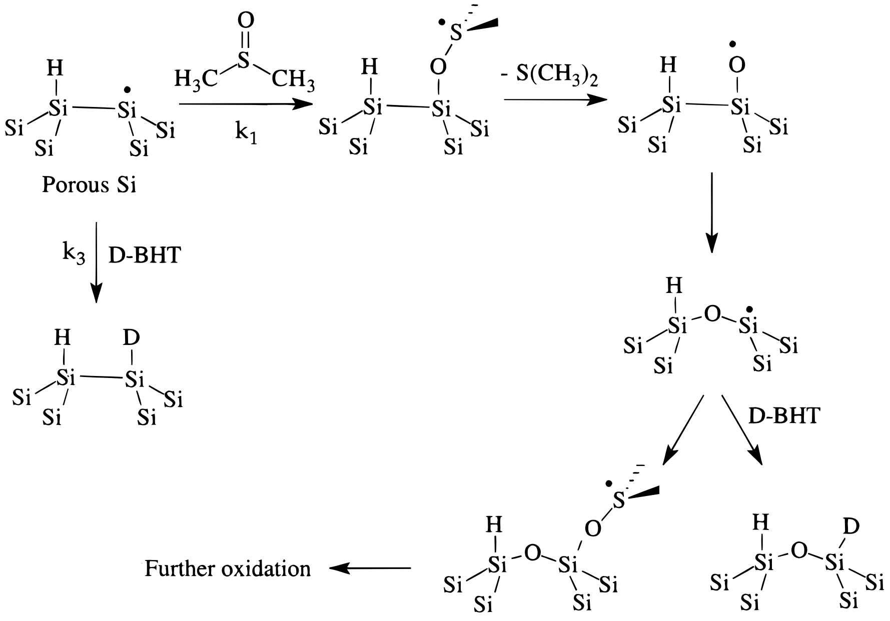
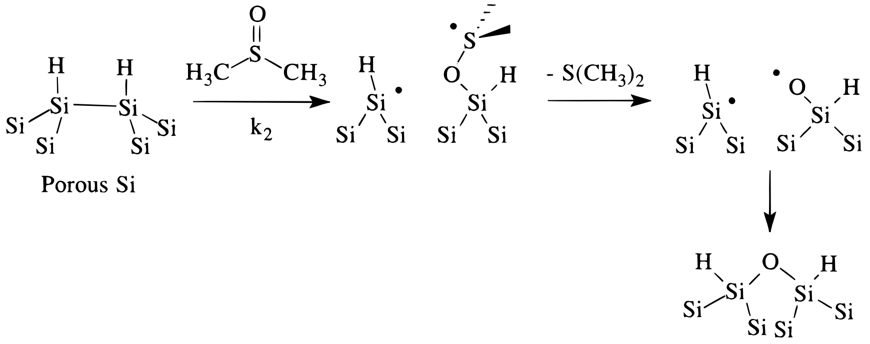
Scheme 1



Scheme 2



essentially constant when the DMSO solution contains 3.2 M BHT (Figure 6). The data are consistent with the interpretation that BHT acts to hydrogenate surface dangling bond states during oxide formation. These surface radicals are expected to be very efficient nonradiative recombination centers, causing a significant drop in photoluminescence intensity as they are generated during the DMSO-oxidation reaction. Hydrogenation of the surface radicals passivates them and leads to preservation of the photoluminescence intensity. The intensity of photoluminescence from a freshly etched porous Si sample increases slightly if the sample is treated with BHT in toluene, suggesting that the radicals present on native porous Si also act as recombination centers, as has been concluded from previous EPR studies.[26,27,32,33] Similarly, the intensity of photoluminescence from DMSO-oxidized porous Si increases slightly after treatment with a toluene solution of BHT, consistent with the hypothesis that DMSO oxidation generates radical centers in the oxide which can be passivated by hydrogenation. The radical species are also thought to be important to the mechanism of oxidation, as outlined below.

Proposed Oxidation Mechanisms and the Effect on Photoluminescence. A reaction mechanism consistent with the above observations is outlined in Schemes 1 and 2. It is proposed that there are two oxidation pathways available, both involving cleavage of a Si−Si surface bond. The pathways involve two different types of Si−Si surface bonds; one type containing a Si dangling bond (radical) state (Scheme 1) and the other a normal hydrogenated surface Si−Si bond (Scheme 2). Oxidation by DMSO is expected to occur faster at the radical center (Scheme 1) than at the hydrogenated Si−Si center (Scheme 2). Both pathways ultimately produce dimethyl sulfide, which was identified as the main volatile product of the reaction by gas chromatography, and a surface silicon oxide species.

In the radical pathway of Scheme 1, a surface silicon radical is attacked by DMSO, transferring an O atom to the surface and producing dimethyl sulfide. The surface-bound O atom radical rapidly rearranges, adding across a Si−Si bond and regenerating the surface silicon radical. Thus, the radical pathway is catalytic. Termination of the radical reaction can occur by a H atom transfer from solvent, impurities, or added BHT. The observation that pretreatment of porous Si with BHT suppresses the observed rate of oxidation by DMSO is consistent with this interpretation.

The second pathway (Scheme 2) involves attack by DMSO across a normal Si−Si bond, eliminating dimethyl sulfide and generating a surface-bound O radical and a surface-bound Si radical. Recombination of the two radical species generates the silicon oxide. If, instead of radical−radical recombination,

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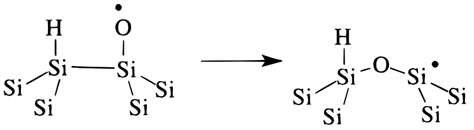
the O surface radical attacks a Si−Si bond, a new Si radical can be formed, eq 3.


(3)

To be consistent with the observed data, the rate constant for the reaction of DMSO with a surface radical, k_1, should be larger than the rate constant for the reaction of DMSO with a normal surface Si−Si bond, k_2 (the observed rate constants measured in this work correspond to $k_1 + k_2 - k_3[\mathrm{BHT}]$, where k_3 is the rate constant for the radical trapping reaction with BHT). In addition, it is assumed that the number of Si−Si bonds with a radical nature is a small fraction of the total available Si−Si bonds at the surface. In the presence of BHT or if the surface has been pretreated with BHT, the radicals on the porous Si surface abstract a H atom from BHT to make a Si−H surface species, resulting in a net slower rate of oxidation.

The above radical generation process also accounts for the observation that DMSO oxidation produces very nonluminescent porous Si unless BHT is added to the reaction mixture. As has been observed previously, the intensity of photoluminescence from porous Si is inversely proportional to the concentration of surface radicals,[26,27] implying that the surface radical states are highly efficient nonradiative recombination centers. Presumably, radicals present in the oxide layer near the Si/oxide interface also act as recombination centers. As outlined in Scheme 1, BHT removes these radicals in the growing oxide layer, resulting in material that is more luminescent than material that would be obtained if BHT were not included in the reaction mixture.

Acknowledgment. This work was funded by the U.S. Department of Energy, Basic Energy Sciences program. The authors thank Dr. Joseph MacNeil and William C. Trogler for the GC measurements and helpful discussions and one of the reviewers for suggesting the experiment in which BHT is added to a porous Si sample after DMSO oxidation.

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