reduced to Bouguer anomalies. Ocean depths within the map region do not exceed 100 m and average ~20 m; the distinction between free-air reductions in the offshore data and Bouguer reductions for land stations, therefore, is of little consequence and imparts no meaningful complications to the analysis of the data.

7. H. Akima, *Assoc. Comput. Mach.* **4**, 160 (June 1978); *Rocky Mountain J. Math.* **14**, 41 (winter 1984).
8. This spacing rule can be expressed as $D_N = (\sqrt{2})^{N-1}D_1$ where D_N is the diameter of the Nth ring and D_1 is the diameter of the inner ring. R. J. Pike, *Lunar Planet. Inst. Tech. Rep.* **449**, 46 (1981); ——— and P. D. Spudis, *Earth Moon Planets* **39**, 129 (1987); P. D. Spudis, *Geology of Multiring Basins* (Cambridge Univ. Press, Cambridge, 1993); ——— and V. L. Sharpton, *Lunar Planet. Sci.* **XXIV**, 1339 (1993).
9. R. A. F. Grieve, P. B. Robertson, M. R. Dence, *Geochim. Cosmochim. Acta* **15** (suppl.), 37 (1981); S. K. Croft, *Geochim. Cosmochim. Acta*, *ibid.*, p. 227.
10. The transient crater refers to the deep bowl-shaped cavity produced early in the impact process by excavation plus downward displacement of the target rocks. In large events, more than several kilometers in diameter, this crater form is gravitationally unstable and collapses to form a broader, shallower final crater.
11. H. J. Melosh, *Impact Cratering: A Geologic Process* (Oxford Univ. Press, New York, 1989).
12. P. D. Spudis, B. R. Hawke, P. G. Lucey, *J. Geophys. Res.* **89**, C197 (1984).
13. M. Pilkington and R. A. F. Grieve, *Rev. Geophys.* **30**, 161 (1992).
14. J. L. Pindell, *Tectonics* **4**, 1 (1985); K. Burke, *Annu. Rev. Earth Planet. Sci.* **16**, 201 (1988); S. A. Hall and I. Najmuddin, *GSA Abstr. Programs* **24**, 14 (1992); J. A. Dunbar and D. S. Sawyer, *Tectonics* **6**, 739 (1987).
15. K. Burke and A. J. Whiteman, *Implications of Continental Drift to the Earth Sciences* (Academic Press, London, 1973), vol. 2, p. 735.
16. E. Lopez Ramos, *Geologia de Mexico* (University of Mexico, Mexico City, ed. 2, 1979), vol. 2.
17. W. K. Hartmann, *Icarus* **4**, 157 (1965); *Geochim. Cosmochim. Acta* **12** (suppl.), 155 (1980); G. W. Wetherill, *Science* **228**, 877 (1985).
18. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208**, 1095 (1980).
19. We thank the Defense Mapping Agency, National Oceanic and Atmospheric Administration, and Instituto Nacional de Estadistica, Geografica e Informatica for providing the gravity data used in this analysis. S. Hokanson drafted Fig. 1. D. Black and B. Schuraytz (Lunar and Planetary Institute) and two anonymous referees provided helpful reviews. This work was conducted through a collaborative research agreement between the Lunar and Planetary Institute and the Instituto de Geofisica, Universidad Nacional Autónoma de México. The Lunar and Planetary Institute is operated by Universities Space Research Association under contract (NASW 4574) with the National Aeronautics and Space Administration. Parts of this work were funded through the National Aeronautics and Space Administration Magellan Guest Investigator and Venus Data Analysis programs (to V.S.) and the Dirección General de Apoyo al Personal Académico, Universidad Nacional Autónoma de México, project number IN106891 (to L.M.). This is Lunar and Planetary Institute contribution number 814.

6 May 1993; accepted 27 July 1993

Chemical Modification of the Photoluminescence Quenching of Porous Silicon

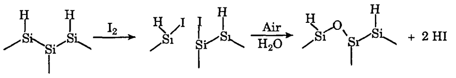
Jeffrey M. Lauerhaas and Michael J. Sailor*

The photoluminescence of porous silicon can be quenched by adsorbates, and the degree of quenching can be tuned by chemical derivatization of the porous silicon surface. Thus, as-prepared porous silicon has a hydrophobic, hydrogen-terminated surface, and the photoluminescence is strongly quenched by ethanol and weakly quenched by water. Mild chemical oxidation (iodine followed by hydrolysis) produces a hydrophilic porous silicon surface. Photoluminescence from this hydrophilic material is quenched to a lesser extent by ethanol and to a greater extent by water, relative to the original surface. This demonstrates that the visible luminescence from porous silicon is highly surface-sensitive, and the surface interactions can be tuned by specific chemical transformations.

The observation of visible photoluminescence (PL) from porous Si has attracted attention for a wide range of applications, including electrooptic (*1*), solar energy conversion (*2*), photodetector (*3*), and chemical sensor devices (*4*–*7*). Chemical sensors could take advantage of changes in the PL wavelength and intensity that occur in the presence of different chemical adsorbates. For nonreactive molecular adsorbates, the quenching of PL intensity scales roughly with the dipole moment of the chemical species (*5*, *6*), so that molecules with large dipole moments like methanol or ethanol quench the PL of porous Si to a large extent (typically >99% loss of PL intensity). The reversible quenching phenomenon has been interpreted as the stabilization of surface traps by alignment of molecular dipoles on the porous Si surface (*5*, *6*). An exception to the correlation is water, which does not appreciably quench the PL of porous Si despite its large dipole moment. This observation has been attributed to the hydrophobic nature of the porous Si surface; water does not wet the hydrogen-terminated surface of porous Si, so dipole alignment does not occur.

We tested this postulate by derivatizing the surface of porous Si with hydrophilic O and OH groups. The surface modification reduced the surface hydrophobicity of porous Si, and the PL quenching effect of water was enhanced relative to ethanol. These results clearly show that PL from porous Si is highly dependent on the nature of the interaction of physisorbed molecules with the surface. The chemical "tunability" of this quenching response may be useful in the development of Si-based sensors with a specific adsorbate binding response.

The Fourier-transform infrared (FTIR) spectrum of a freshly etched porous Si wafer (*8*) shows a hydrogen-terminated surface with little to no surface oxide present (Fig. 1A). The proposed reaction (Scheme 1) of I_2 and air



Scheme 1

with porous Si involves an initial attack by I_2 at Si–Si bonds (*9*, *10*), which is consistent with the observation that the Si–H and Si–H_2 infrared stretching modes are not reduced significantly on I_2 exposure (Fig. 1B) (*11*). X-ray photoelectron spectroscopy (XPS) of the surface revealed the presence of an iodide species (I $3d_{5/2}$ at 619.9 ± 0.3 eV; Si $2p$ at 102.2 ± 0.3 eV). There was an immediate loss of >99% of the integrated PL intensity on I_2 exposure. Oxidation of the I_2-treated porous Si material in air results in new peaks characteristic of Si–O (at 1100 cm^{-1}), O–Si–H (at 2225 cm^{-1}), and OH (at 3480 cm^{-1}) species (*12*) (Fig. 1C) and recovery of 30% of the original PL intensity (*13*). Initial oxide growth occurs much more rapidly on a porous Si wafer that has been pretreated with I_2 (*10*, *14*). Oxide is detectable by FTIR and XPS [O (SiO_2) 1*s* at 533.0 ± 0.3 eV] on I_2-treated wafers within 5 min of being exposed to air, whereas an untreated porous Si sample requires 122 min in air to grow a comparable oxide thickness. Contact angle measurements on the samples show that the chemically oxidized surface is more hydrophilic than as-formed (H-terminated) porous Si (H_2O drop, advancing contact angles were 112° and 131°, respectively).

The PL intensity of as-formed porous Si was strongly quenched by ethanol vapor (97.4 ± 0.1% drop in integrated intensity, average of nine runs, 95% confidence interval) and weakly quenched by water vapor (11 ± 3%) (Fig. 2A). In contrast, the material that was made more hydrophilic by surface oxidation (Fig. 2B) was

---

Department of Chemistry, University of California at San Diego, La Jolla, CA 92093.

*To whom correspondence should be addressed.

quenched to a greater degree by water vapor (44 ± 2%) and to a lesser degree by ethanol (88 ± 3%), relative to the original hydrophobic material. Benzene quenched the PL of the hydrophobic and hydrophilic surfaces to the same degree, within our experimental error (38 ± 6% for H-terminated material and 38 ± 4% for O-terminated material). The adsorbate-quenching experiments were reversible; the same quenching ratios were obtained on multiple exposure-evacuation cycles on the same wafers. Porous Si with a thicker (thermally grown) oxide layer showed very little quenching response toward any of these adsorbates.

The data can be interpreted within the context of a surface trapping model. Presumably, the adsorbed polar molecules stabilize electrons or holes at the porous Si surface, where nonradiative or subbandgap emission processes dominate the recombination rate (*15*). This phenomenon is thus somewhat analogous to polar solvent enhancement of nonradiative decay rates observed in many molecular fluorophore systems (*16*). For freshly etched, hydrophobic porous Si, the hydrophobic CH_3 end of ethanol aligns with surface Si–H groups, creating a net dipole moment and a corresponding stabilization of surface charge. When the surface is made partially hydrophilic by treatment with I_2 and air, the OH group of ethanol can hydrogen bond to surface O groups, resulting in a decrease in the net dipole moment. In a similar manner, water does not align on freshly etched porous Si, because the surface is hydrophobic. When the surface is made more hydrophilic, H_2O hydrogen-bonding interactions can produce the net dipole and the concomitant increase in the nonradiative or subbandgap emission channel. Benzene, because it has zero dipole moment, cannot stabilize surface traps through polar interactions; therefore, it quenches both materials to the same extent, regardless of the nature of the porous Si surface (Fig. 2).

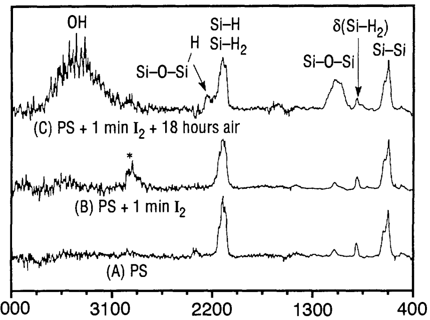
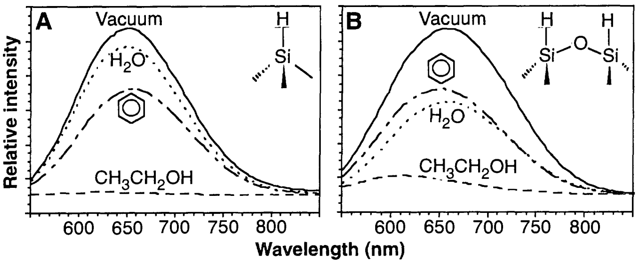


Fig. 1. Transmission FTIR spectra of (A) freshly etched porous Si (PS), (B) I_2-exposed porous Si (PS + 1 min I_2), and (C) I_2-exposed porous Si exposed to air (PS + 1 min I_2 + 18 hours air). Vibrational mode assignments are as shown in the top spectrum. Asterisk specifies hydrocarbon impurity.

The fact that benzene has no dipole moment but still quenches the PL of porous Si suggests that a second mechanism is important. Measurements of PL lifetime support the existence of a separate nonradiative channel for nonpolar adsorbates. We measured PL decay data from a porous Si sample in vacuum or exposed to benzene or ethanol vapors with a pulsed N_2 laser (337 nm) and a gated charge-coupled device detector setup (100-ns time resolution). The highly nonexponential decay curves for porous Si in vacuum and benzene vapor had the same $t_{1/2}$ (2.9 ± 0.4 and 3.5 ± 0.3 μs, respectively) and scaled identically in time, whereas the PL decay from ethanol-exposed porous Si was much shorter ($t_{1/2}$ = 0.98 ± 0.03 μs). Thus, at least two nonradiative mechanisms are operative in the solvent-induced quenching of PL from porous Si: polar molecules like ethanol decrease the long (microsecond) component of the emission lifetime, whereas the nonpolar quencher benzene does not.

The significant surface sensitivity of porous Si demonstrated in this report indicates that the simple quantum confinement model provides an inadequate description of the photophysics of this material. Although the energetics of electron-hole pair generation may be determined by spatial electron or hole confinement, an adequate model to describe the recombination processes in luminescent porous Si should account for the accessibility of surface-related decay processes.

Fig. 2. PL spectra of samples exposed to vacuum (———) and ethanol (— —), water (· · · · ·), and benzene (— – —) vapors. (**A**) A freshly etched porous Si wafer, and (**B**) a chemically modified porous Si wafer.



REFERENCES AND NOTES

1. A. Halimaoui *et al.*, *Appl. Phys. Lett.* **59**, 304 (1991); P. M. M. C. Bressers, J. W. J. Knapen, E. A. Meulenkamp, J. J. Kelly, *ibid.* **61**, 108 (1992); L. T. Canham, W. Y. Leong, M. I. J. Beale, T. I. Cox, L. Taylor, *ibid.*, p. 2563; Z. Chen, G. Bosman, R. Ochoa, *ibid.* **62**, 708 (1993); N. Koshida and H. Koyama, *ibid.* **60**, 347 (1992); F. Kozlowski *et al.*, *Thin Solid Films* **222**, 196 (1992); F. Namavar, H. P. Maruska, N. M. Kalkhoran, *Appl. Phys. Lett.* **60**, 2514 (1992); A. Richter, P. Steiner, F. Kozlowski, W. Lang, *IEEE Electron Dev. Lett.* **12**, 691 (1991); H. Zimmermann, F. H. Cocks, U. Gosele, *Mater. Chem. Phys.* **32**, 310 (1992).
2. G. Smestad, M. Kunst, C. Vial, *Sol. Energy Mater. Sol. Cells* **26**, 277 (1992).
3. L. Z. Yu and C. R. Wie, *Electron. Lett.* **28**, 911 (1992); J. P. Zheng, K. L. Jiao, W. P. Shen, W. A. Anderson, H. S. Kwok, *Appl. Phys. Lett.* **61**, 459 (1992).
4. R. C. Anderson, R. S. Muller, C. W. Tobias, *Sens. Actuators* **A21–A23**, 835 (1990).
5. J. M. Lauerhaas, G. M. Credo, J. L. Heinrich, M. J. Sailor, *J. Am. Chem. Soc.* **114**, 1911 (1992).
6. ______, *Mater. Res. Soc. Symp. Proc.* **256**, 137 (1992).
7. R. L. Smith and D. C. Scott, *IEEE Trans. Biomed. Eng.* **BME-33**, 83 (1986).
8. Luminescent porous Si samples were prepared by galvanostatically etching *n*-Si [0.832-ohm·cm resistivity, (100) orientation, P-doped] as previously described (*5*). After preparing the porous Si layer, we rinsed the samples with ethanol, dried them under a stream of N_2, and placed them in a vacuum chamber. The chamber was evacuated to 50 mtorr and backfilled with N_2 three times.
9. S. J. Band and I. M. T. Davidson, *Trans. Faraday Soc.* **66**, 406 (1970); C. Chatgilialoglu, D. Griller, M. Lesage, *J. Org. Chem.* **54**, 2492 (1989); H. Sakurai, K. Sasaki, A. Hosomi, *Tetrahedron Lett.* **21**, 2329 (1980).
10. D. Seitz and L. Ferreira, *Synth. Commun.* **9**, 931 (1979).
11. After we prepared the porous Si layer, the samples were rinsed with ethanol, dried under a stream of N_2, and placed in a vacuum chamber. The chamber was evacuated to 50 mtorr and backfilled with <1 torr of I_2(g) for 1 min. The chamber was then evacuated to 50 mtorr for 15 min.
12. Y. Kato, K. Ito, A. Hiraki, *Jpn. J. Appl. Phys.* **27**, L1406 (1988); A. Nakajima, T. Itakura, S. Watanabe, N. Nakayama, *Appl. Phys. Lett.* **61**, 46 (1992); W. Theiss *et al.*, *Appl. Surf. Sci.* **63**, 240 (1993); G. Mauckner, K. Thonke, R. Sauer, *J. Phys.: Condens. Matter* **5**, L9 (1993); Y. H. Xie *et al.*, *J. Appl. Phys.* **71**, 2403 (1992).
13. For surface oxidation, the wafer was exposed to <1 torr of I_2(g) for 1 min, the chamber was evacuated to 50 mtorr for 15 min, and the sample was then air-oxidized at room temperature for 18 hours. We monitored PL spectra in a glass exposure chamber using a 442-nm He/Cd laser (defocused, 5 mW/cm^2) and a 1/4-m monochromator/CCD detector setup.
14. M. E. Jung and M. A. Lyster, *J. Org. Chem.* **42**, 3761 (1977).
15. T. Dannhauser, M. O'Neil, K. Johansson, D. Whitten, G. McLendon, *J. Phys. Chem.* **90**, 6074 (1986); G. J. Meyer, G. C. Lissensky, A. B. Ellis, *J. Am. Chem. Soc.* **110**, 4914 (1988).
16. J. V. Caspar, B. P. Sullivan, E. M. Kober, T. J. Meyer, *Chem. Phys. Lett.* **91**, 91 (1982); T. A. Perkins, W. Humer, T. L. Netzel, K. S. Schanze, *J. Phys. Chem.* **94**, 2229 (1990); H. H. Thorp, C. V. Kumar, N. J. Turro, H. B. Gray, *J. Am. Chem. Soc.* **111**, 4364 (1989).
17. We thank D. A. Buttry, S. M. George, and M. B. Robinson for helpful discussions, J. Heinrich for experimental assistance, D. Harvey for use of the infrared spectrometer, and the Office of Naval Research and the NSF (DMR 9220367) for funding.

4 May 1993; accepted 20 July 1993