Reversible Luminescence Quenching of Porous Si by Solvents

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It has recently been discovered that electrochemical and chemical etching of silicon for extended periods of time results in a material that photoluminesces in the visible region of the spectrum.[1,2] The etching process produces microporous Si, and the visible photoluminescence (PL) has been attributed to quantum size effects arising from isolated nanometer-size Si features (bulk Si, with a bandgap at 1.1 eV, is very weakly luminescent in the near-infrared region of the optical spectrum).[1-4] Highly luminescent porous Si has generated a great deal of interest from a fundamental level and also because of the unique role that Si plays in modern technology. In this work, we report that the PL observed from porous Si is reversibly quenched on exposure to organic solvent molecules, indicating that the PL of this material is extremely surface sensitive.

Luminescent porous silicon samples were prepared by galvanostatically etching n-Si (P-doped, 0.642 Ω·cm resistivity, (100) orientation) in a 50/50 ethanol/HF solution at a low current density (5 mA/cm^2) for 30 min, followed by a 25-s etch at 50 mA/cm^2. The wafers were illuminated with a 300-W W lamp during the etch. The samples were rinsed with ethanol, dried under a stream of N_2, and placed in a glass vacuum chamber. The chamber was evacuated to 50 mTorr and backfilled with N_2 three times before analysis. Wafers for vapor analysis were left under vacuum, and wafers for neat solvent analysis were handled under purified N_2 (<2 ppm O_2 and H_2O) and exposed to the solvents using conventional vacuum line or Schlenk and syringe techniques.[5] All solvents were purified and deoxygenated according to published procedures,[6] and the solvents used in vapor exposure studies were freeze-pump-thaw degassed three times prior to use. The PL of the porous Si samples was monitored using 442-nm He/Cd laser excitation (defocussed, 5 mW/cm^2) and a $^1/_4$-m monochrometer/CCD detector setup. For both neat solvent and vapor studies, the PL intensity dropped to a lower value within 10 s of exposure and remained stable at that level until the solvent was removed. The amount of PL quenching by each solvent (I/I_0) was determined as the ratio of PL intensity immediately before and 1 min after exposure to the solvent.

Figure 1 presents the emission spectra of a luminescent porous Si layer before and after exposure to ca. 160 Torr of tetrahydrofuran (THF) vapor. Immediately after exposure to the solvent, the emission centered at 670 nm decreased by a factor of 4 and shifted to 630 nm. The emission spectrum recovered to the original intensity within seconds of evacuation of the excess solvent vapor, although λ_{max} at this point was shifted slightly from the original value. Repeated THF exposure/evacuation cycles reproduced the latter two spectra. Exposure to gaseous diethyl ether, methylene chloride, toluene, *o*-xylene, benzene, and methanol also resulted in reversible quenching and a blue shift in λ_{max}. Exposure to water vapor resulted in no detectable decrease in emission.

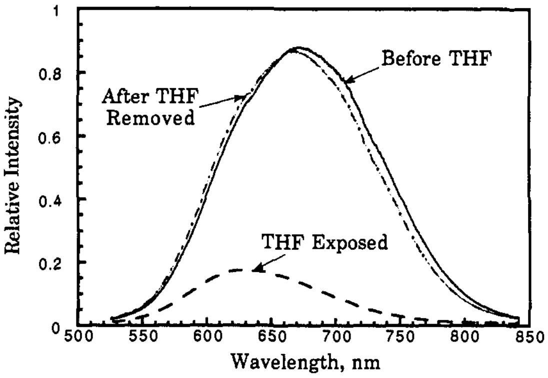

Figure 1. Emission spectra of luminescent porous Si sample before THF exposure (—), after 1 min of THF exposure (---), and after removal of THF under dynamic vacuum (-·-). Excitation source was the 442-nm line of a He/Cd laser (5 mW/cm^2).

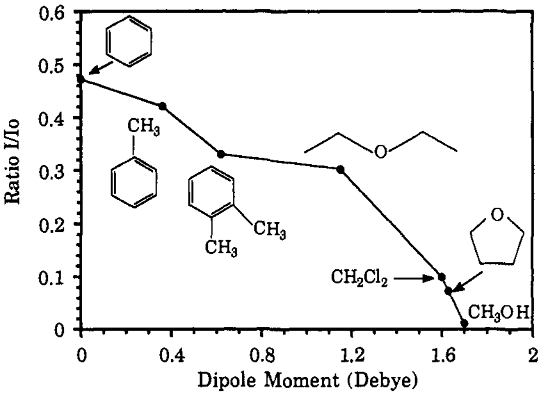

Figure 2. Correlation of the porous Si luminescence quenching ratio I/I_0 of the liquid solvents to their (gas phase) dipole moments.[11] The values determined for I/I_0 in (solvent) are as follows: 0.47 (benzene); 0.42 (toluene); 0.33 (*o*-xylene); 0.30 (diethyl ether); 0.11 (methylene chloride); 0.074 (tetrahydrofuran); 0.013 (methanol).

Transmission infrared spectra taken on the electrodes before solvent exposure confirm the presence of Si-H stretches at 2120 cm^{-1}, consistent with previous observations that porous Si is produced with a hydrogen-terminated surface.[7,8] The infrared spectrum of the porous Si surface after exposure to solvent vapor was the same as the unexposed surface for all solvents studied.

For porous Si samples exposed to neat liquid solvents, the degree of PL quenching (I/I_0) scaled with solvent dipole moment, as shown in Figure 2. The blue shift of λ_{max} also scaled with dipole moment, with the more polar solvents showing the largest shifts (up to 60 nm) as well as the greatest degree of PL quenching. It was found that the value of I/I_0 for a given solvent was somewhat dependent on the etching procedure used to prepare the porous Si surface, although the relative ranking of the quenching ratios was invariant with electrode preparation. PL quenching ratios of CD_3OD and CD_2Cl_2 are identical (within the reproducibility limits of the measurement) to those of the corresponding nondeuterated solvents, implying that vibrational coupling is not important to the quenching mechanism. Luminescence of CdS and Cd_3As_2 colloids has been found to be enhanced on exposure to simple amines, and this has been attributed to the elimination of recombination states at the semiconductor surface via adsorbate binding.[9] In addition, interaction of gas-phase amine and solvent molecules has been found to enhance PL at single-crystal CdSe surfaces.[10] Adsorbate binding

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(1) Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1046-1048.

(2) Lehmann, V.; Gosele, U. *Appl. Phys. Lett.* **1990**, *58*, 856-858.

(3) Bsiesy, A.; Vial, J. C.; Gaspard, F.; Herino, R.; Ligeon, M.; Muller, F.; Romestain, R.; Wasiela, A.; Halimaoui, A.; Bomchil, G. *Surf. Sci.* **1991**, *254*, 195-200.

(4) Canham, L. T.; Houlton, M. R.; Leong, W. Y.; Pickering, C.; Keen, J. M. *J. Appl. Phys.* **1991**, *70*, 422-430.

(5) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986; pp 13-40.

(6) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986; pp 84-92.

(7) Ito, T.; Kiyama, H.; Yasumatsu, T.; Watabe, H.; Hiraki, A. *Physica B* **1991**, *170*, 535-539.

(8) Gupta, P.; Colvin, V. L.; George, S. M. *Phys. Rev. B* **1988**, *37*, 8234-8243.

(9) Dannhauser, T.; O'Neil, M.; Johansson, K.; Whitten, D.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 6074-6076.

(10) Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1988**, *110*, 4914-4918.

(11) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1990; pp 9.6-9.9.

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in these bulk samples has been suggested to affect PL intensity by changing the depletion region width and/or the surface recombination velocity. All solvents that we have investigated *reduce* the emission intensity of porous Si, indicating that the solvent interactions increase nonradiative recombination in this particular material. An interpretation consistent with the observed data is that the dipoles attract either electrons or holes to surface traps. On very small particles, the carrier recombination rate should be dependent on the product of the electron and hole concentrations (the number of dopant atoms present in a 10-nm diameter piece of 0.642 Ω·cm n-Si is less than 1, so in a photoexcited nanoparticle the carrier concentrations are comparable). Thus, trapping of either electrons or holes at the surface should reduce luminescence intensity. Although this interpretation explains the correlation to solvent dipole moment, the observation that nonpolar molecules such as benzene also cause significant PL quenching indicates that the above interpretation is overly simplified. In addition, the fact that there is no detectable PL quenching on exposure to water vapor is surprising. This may be due to the inability of H_2O to preferentially align on the hydrophobic hydrogen-terminated Si surface. Current experiments are aimed at understanding the mechanism of PL quenching in more detail. The extreme sensitivity of the luminescent porous Si surface presents the potential for application of this material in chemical sensors.

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Aqueous Basicity of the Carboxylate Lone Pairs and the C–O Barrier in Acetic Acid: A Combined Quantum and Statistical Mechanical Study

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The stereoelectric effects at carboxyl oxygen are of importance in the understanding of the mechanism of organic and enzymatic reactions as well as molecular recognition processes.[1] Consequently, there has been a continuous effort in both theoretical and experimental investigations.[2-8] Gandour pointed out 10 years ago that the syn-oriented carboxylate is preferred in enzymatic catalysis because of its much higher basicity than the anti form.[2]

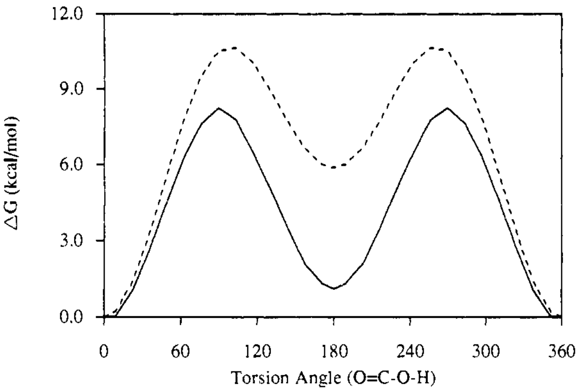

Figure 1. Computed rotational energy function (- - -) and potential of mean force in aqueous solution (—) for CH_3COOH at 25 °C. Torsional angle is in degrees.

However, recent studies of model systems indicate that there is only minimal syn-stabilization in these compounds in solution.[3,4] These effects have also been thoroughly investigated by Houk and Wiberg and their co-workers using ab initio molecular orbital methods.[6,7] Nonetheless, little is known about the solvent contribution to this phenomenon.[8b] To assess the solvent effects on the relative basicity of carboxylate lone pairs in water, we have carried out Monte Carlo simulations using a combined quantum mechanical (QM) and molecular mechanical (MM) potential to compute the potential of mean force (pmf) of the C–O rotation in acetic acid. Although such potentials have been applied in energy minimization and relative free energy calculations,[9-11] they have not been used for determination of a complete pmf in solution.

The combined QM/MM potential for a condensed-phase system as defined by Field et al.[10] is partitioned into a QM region consisting of the solute and an MM region of solvent molecules. The total energy of the system is obtained from the QM particle electronic Hamiltonian ($\hat{H}_{QM}$), the QM/MM interaction Hamiltonian ($\hat{H}_{QM/MM}$), and MM potential functions,[10,11] while the pmf is determined via statistical perturbation theory (eq 1) by computing free energy changes along the reaction coordinate,[12] θ;

$$\Delta G(\theta_0 \rightarrow \theta_1) = -kT \ln \langle e^{-\Delta E(\theta_0 \rightarrow \theta_1)/kT} \rangle_0 \qquad (1)$$

where $\langle\ \rangle_0$ represents the ensemble average with the Hamiltonian $\hat{H}(\theta_0)$, and $\Delta E(\theta_0 \rightarrow \theta_1)$ is the energy difference between states θ_0 and θ_1. $\Delta E(\theta_0 \rightarrow \theta_1)$ is given by eq 2 and is evaluated using the method described previously:[11]

$$\Delta E(\theta_0 \rightarrow \theta_1) = \Delta E_{pol}(\hat{H}_{QM}[\theta_0 \rightarrow \theta_1]) + \Delta E_{tor}(\theta_0 \rightarrow \theta_1) + \Delta E(\hat{H}_{QM/MM}[\theta_0 \rightarrow \theta_1]) + \Delta E^{vdW}_{QM/MM}(\theta_0 \rightarrow \theta_1) \qquad (2)$$

Here, the terms on the right-hand side of eq 2 are, respectively, differences in solute polarization, gas-phase torsional energy, and solute–solvent electronic and solute–solvent van der Waals energies.[11] The electric polarization energy for the solute is defined as follows:

$$E_{pol}(\hat{H}_{QM}(\theta)) = \langle \Phi | \hat{H}_{QM}(\theta) | \Phi \rangle - \langle \Phi^\circ | \hat{H}_{QM}(\theta) | \Phi^\circ \rangle \qquad (3)$$

where Φ° and Φ are, respectively, the wave functions for QM particles in the gas phase and in aqueous solution. Applying eq

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(1) (a) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183. (b) Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman: New York, 1985.

(2) Gandour, R. D. *Bioorg. Chem.* **1981**, *10*, 169.

(3) (a) Huff, J. B.; Askew, B.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5908. (b) Marshall, L. R.; Parris, K.; Rebek, J., Jr.; Luis, S. V.; Burguete, M. I. *J. Am. Chem. Soc.* **1988**, *110*, 5192. (c) Tadayoni, B. M.; Parris, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 4503. (d) Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245. (e) Tadayoni, B. M.; Rebek, J., Jr. *Bioorg. Med. Chem. Lett.* **1991**, *1*, 13.

(4) (a) Zimmerman, S. C.; Cramer, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 5906. (b) Cramer, K. D.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 3680. (c) Zimmerman, S. C.; Korthals, J. S.; Cramer, K. D. *Tetrahedron* **1991**, *47*, 2649. (d) Menger, F. M.; Ladika, M. *J. Am. Chem. Soc.* **1988**, *110*, 6794.

(5) (a) Hocking, W. H. *Z. Naturforsch.* **1976**, *31A*, 1113. (b) Bjarnov, E.; Hocking, W. H. *Z. Naturforsch.* **1978**, *33A*, 610.

(6) (a) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935. (b) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872.

(7) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 1870. (b) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 4505.

(8) (a) Gao, J.; Garner, D. S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4784. (b) Briggs, J. M.; Nguyen, T. B.; Jorgensen, W. L. *J. Phys. Chem.* **1991**, *95*, 3315.

(9) (a) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1986**, *7*, 718. (b) Weiner, S. J.; Seibel, G. L.; Kollman, P. A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 649. (c) Hwang, J.-K.; King, G.; Greighton, S.; Warshel, A. *J. Am. Chem. Soc.* **1988**, *110*, 5297. (d) Rullmann, J. A. C.; Bellido, M. N.; van Duijnen, P. T. *J. Mol. Biol.* **1989**, *206*, 101. (e) Bash, P. A.; Field, M. J.; Davenport, R. C.; Petsko, G. A.; Ringe, D.; Karplus, M. *Biochemistry* **1991**, *30*, 5826.

(10) (a) Bash, P. A.; Field, M. J.; Karplus, M. *J. Am. Chem. Soc.* **1987**, *109*, 8192. (b) Field, M. J.; Bash, P. A.; Karplus, M. *J. Comput. Chem.* **1990**, *11*, 700.

(11) Gao, J. *J. Phys. Chem.* **1992**, *96*, 537.

(12) Zwanzig, R. W. *J. Chem. Phys.* **1954**, *22*, 1420.

0002-7863/92/1514-1912$03.00/0