J. Am. Chem. Soc. **1996,** *118,* 4490−4491

Conduction and Valence Band Edges of Porous Silicon Determined by Electron Transfer

Julie M. Rehm,[†] George L. McLendon,[‡] and
Philippe M. Fauchet*,[§]

Department of Chemistry, University of Rochester
Rochester, New York 14627
Department of Chemistry, Princeton University
Princeton, New Jersey 08544
Department of Electrical Engineering and
Department of Physics & Astronomy
University of Rochester, Rochester, New York 14627

Received November 20, 1995
Revised Manuscript Received February 12, 1996

Many models have been proposed to explain the visible photoluminescence (PL) mechanism in porous silicon (PSi). The two models which have received the most experimental and theoretical support are the pure quantum confinement model and an extended version of the quantum confinement model called the smart confinement model.[1−3] The pure quantum confinement model attributes the visible PL to quantum-confined Si structures, while the smart confinement model attributes the larger band gap and the PL efficiency to quantum-confined Si structures but proposes that recombination of electrons and holes occurs in a surface state. Both models agree that PSi has a wider band gap than does bulk silicon. However, the magnitude of the valence band (VB) and conduction band (CB) shifts from bulk values is not known. Recent photoemission, X-ray, and electron spectroscopy studies[4,5] support calculations which suggest that as the band gap opens, the VB shift is significantly larger than the CB shift in PSi.[6] The absolute magnitude of the VB and CB shifts in PSi samples with a PL peak of 2 eV are examined in this study using dynamic electron transfer (ET) quenching as an empirical probe of the VB and CB levels. Bulk crystalline Si electrode potentials were used for PSi: $E_{VB}° = 0.40$ V and $E_{CB}° = -0.70$ V vs NHE.[7] All electrode potentials reported here were measured in acetonitrile vs NHE.

Red-emitting PSi samples were prepared electrochemically under ~100 mW/cm^2 of tungsten light in a 25:25:50 solution of H_2O:HF:EtOH using a constant current density of 20 mA/cm^2 for 15 min. The ⟨100⟩ n-type wafers had a resistivity of <0.1 Ω cm. The wafers were removed from the HF solution, rinsed with Millipore water, and allowed to dry in air. Time-resolved measurements were made using an excimer pumped dye laser ($\lambda_{ex} = 530$, $\lambda_{em} = 650$ nm).[8] The PL peak energy is 2 eV (630 nm).

The quenchers are listed in Table 1 with their electrode potentials in acetonitrile vs NHE. They were purchased from Aldrich and used without further purification. For each quencher, PSi PL steady-state spectra and lifetimes were measured (a) in pure benzene, (b) in quencher solution, and (c) in pure benzene again. All reported quenching was reversible.

Table 1. List of CB and VB Quenchers with Electrode Potentials in Acetonitrile vs NHE

adsorbate	potential (V) vs NHE in acetonitrile
CB Quenchers	
1,4-dinitrobenzene	−0.80
4-nitrobenzonitrile	−1.00
4-nitrophenyl acetate	−1.10
4-nitrotoluene	−1.19
4-nitroanisole	−1.25
4-nitro-*o*-xylene	−1.40
2-nitro-*m*-xylene	−1.60
VB Quenchers	
ferrocene	0.40
1,1-ferrocenedimethanol	0.63
ferrocenecarboxylic acid	0.74
1,2,4,5-tetramethoxybenzene	1.00
1,2,4-trimethoxybenzene	1.22
1,4-dimethoxybenzene	1.54
hexamethylbenzene	1.80
1,2,4,5-tetramethylbenzene (durene)	2.00
1,4-dimethylbenzene (*p*-xylene)	2.20

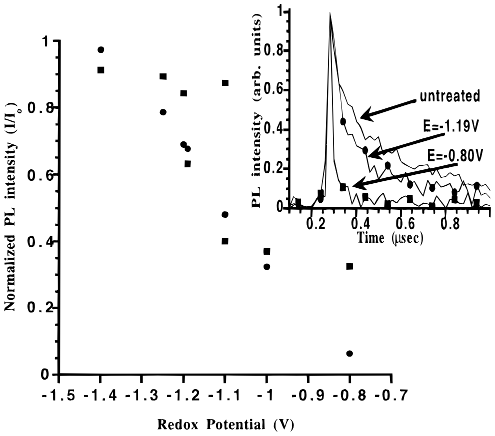

Figure 1. Plot of normalized intensity [I/I_0 = (treated PL/untreated PL)] for PSi vs redox potential (V) for CB quenchers. Circles are the results of steady-state measurements, while squares represent the integral under the time-resolved data shown in the inset. Solid, dotted, and dashed lines in the inset represent time profiles for a sample in benzene, 4-nitrotoluene ($E = -1.19$ V), and 1,4-dinitrobenzene ($E = -0.80$ V), respectively.

If dynamic ET occurs between a redox active molecule and the VB or CB of PSi, the PL intensity will be quenched and the lifetime will decrease. If the quencher redox level lies above (below) the conduction (valence) band edge of PSi, then an energy barrier to transfer electrons (holes) from PSi to the quencher is created, oxidation (reduction) of PSi does not occur, and carrier recombination remains unaffected. Thus, the PL intensity and temporal response will depend sharply on quencher potential only when ET is allowed.

A plot of the normalized PL intensity vs redox potential (V) for the CB quenchers is given in Figure 1. When the redox potential reaches a value of −1.20 ± 0.2 V, a drop-off in the quenching ability of the adsorbate occurs. The effect of the CB quenchers on the temporal response is illustrated in the inset of Figure 1. For the CB quenchers, the PL lifetime shortens as oxidation of PSi becomes easier; 1,4-dinitrobenzene with a redox potential of −0.80 V decreases the PL lifetime significantly, whereas 4-nitrotoluene with a redox potential of −1.19 V has very little effect on the PL lifetime. All CB quencher solutions were 1×10^{-2} M in benzene. Steady-state PL spectra support this trend.[8]

[†] Department of Chemistry, University of Rochester.

[‡] Princeton University.

[§] Department of Electrical Engineering and Department of Physics & Astronomy, University of Rochester.

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S0002-7863(95)03879-0 CCC: $12.00

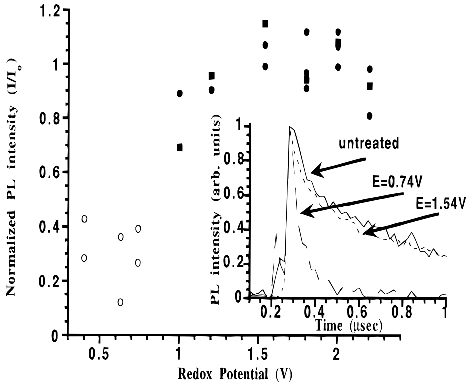

Figure 2. Plot of normalized intensity [I/I_0 = (treated PL/untreated PL)] for PSi vs redox potential (V) for VB quenchers. Circles are the results of steady-state measurements, while squares represent the integral under the time-resolved data shown in the inset. Solid symbols represent substituted benzene compounds, and open symbols represent ferrocene compounds. Solid, dotted, and dashed lines in the inset represent time profiles for a sample in benzene, 1,4-dimethoxybenzene (E = 1.54 V), and ferrocenecarboxylic acid (E = 0.74 V), respectively.

A plot of the normalized PL intensity vs redox potential (V) for the VB quenchers is given in Figure 2. According to theory, the shift in the VB should be twice as large as the shift in the CB. The CB quenching data shows a shift of 0.50 V, which suggests that the VB shift should be 1.00 V. Since the bulk Si VB energy level is 0.40 V, this implies that we should observe a drop-off in quenching at 1.40 V. This is in agreement with the data shown in Figure 2. When the redox potential reaches a value of 1.40 ± 0.2 V, the quenching ability of the adsorbate drops off. The effect of the VB quenchers on the temporal response is illustrated in the inset of Figure 2. For the VB quenchers, the PL lifetime shortens as reduction of PSi becomes easier; ferrocenecarboxylic acid with a redox potential of 0.74 V decreases the PL lifetime much more than 1,4-dimethoxybenzene, which has a redox potential of 1.54 V. All VB quencher solutions were 2×10^{-3} M in benzene. Steady-state spectra support this trend.[8]

These results suggest that the energy level for the CB is near −1.20 ± 0.2 V (vs NHE in acetonitrile) and the energy level for the VB is near 1.40 ± 0.2 V (vs NHE in acetonitrile). The electrode potentials reported in Table 1 were measured in acetonitrile; however, benzene was the solvent used in the experiments described above. In principle there would be a correction for the difference in solvation between acetonitrile and benzene. In practice this correction is difficult to calculate because the molecule is adsorbed to the surface of the semiconductor. How to estimate the solvation cavity size, surface charge effects, and image dipole effects remains unclear. The situation is further complicated by the fact that the exciton binding energy (E_B) is large for small Si crystallites; 0.15 eV $< E_B <$ 1.40 eV for crystallites with radius 20 Å $< R <$ 4 Å.[9] Since it is difficult to provide a reliable estimate for the correction, we used the reported electrode potentials in acetonitrile. However, we know that the band gap of 2.60 eV reported here is a lower bound value. This is due to two effects: (1) the correction due to solvation differences between benzene and acetonitrile, using a Born solvation correction, effectively opens the band gap (as much as 1 V), and (2) the value of 2.60 eV could underestimate the real value of the band gap by an amount comparable to the exciton binding energy.[21]

In these experiments, it is important to distinguish between energy transfer and electron transfer. Recent studies by Sailor and co-workers identified an energy transfer pathway for quenching by aromatic organic molecules, in which low-lying triplet states provided a mechanism for energy transfer.[10] For the substituted benzenes examined here, the lowest triplet lies above the emitting energy of PSi, thus ruling out an energy transfer mechanism. However, the lowest triplet energy for the ferrocene compounds is such that an energy transfer mechanism cannot be ruled out. Nevertheless, the data taken with the ferrocene compounds (open symbols in Figure 2) follow the clear trend of the data taken with the substituted benzene compounds (closed symbols in Figure 2).

Many theories have been proposed to describe how the band gap energy of PSi changes as a function of crystallite size.[11−15] The band gap energy calculated by theory is larger than the PL peak energy observed experimentally, especially at small sizes. Experiments show that the peak PL energy of PSi depends only weakly on size.[16−18] The experiments described here also provide evidence that for our samples the band gap is much larger than the PL peak energy; the sum of the VB and CB shifts gives a total band gap energy of ≥2.60 eV, whereas the measured peak PL energy is ca. 2.0 eV. Our result is consistent with the data of Van Buuren and co-workers[19] and Kux and co-workers[20] if they are extrapolated to larger band gaps or smaller crystallites. Since the peak PL energy is well below the band gap, we conclude that quantum confinement alone is not sufficient to explain the PL. Quantum confinement plays an important role in widening the band gap and accounts for increased PL efficiency, but it does not seem capable to explain the large Stokes shift between the band gap and PL peak. A model which includes surface states in quantum confined silicon nanocrystals or the "smart confinement" model[2,3] seems more appropriate because it provides a natural mechanism for the Stokes shift.

Acknowledgment. The authors thank Professor Nathan Lewis for helpful discussions and for providing prepublished values for the flat band potentials for bulk Si. This work is supported in part by the Science and Technology Center for Photoinduced Charge Transfer which is funded by the National Science Foundation under Grant CHE-9120001.

Supporting Information Available: Steady-state PL spectra of PSi after exposure to CB and VB quenchers (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9538795

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[21] For the reasons discussed in the text, the band gap deduced by using benzene as the solvent may be subject to corrections that are difficult to calculate but can only increase the value of the band gap. Our value of 2.6 eV for the band gap cannot underestimate the true band gap by more than ∼0.2 eV since the steady-state luminescence experiments were performed with an excitation wavelength of 450 nm (photon energy of 2.75 eV). If the band gap were larger than 2.75 eV, electron−hole pairs would not be generated, and no luminescence could be detected.