

# Rôle for organic molecules in the oxidation of porous silicon

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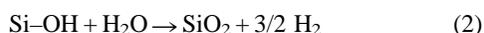
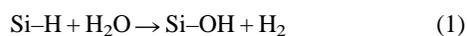
**A simple rapid solution-based method for forming the oxide layer at porous silicon is described which uses amphiphilic molecules to wet the hydrophobic porous structure.**

Porous silicon (PS) has received much interest in recent years owing to its remarkable luminescent properties allied with the possible compatibility of the material with existing semiconductor processing techniques.<sup>1</sup> However, it is well known that as-prepared PS exhibits weak and unstable photoluminescence (PL) as a consequence of the slow oxidation of the hydrogen-terminated silicon surface in air.<sup>2</sup> As a result, numerous post-formation treatments of PS have been reported which aim to stabilize the PL through the formation of a passivating oxide layer.<sup>3</sup> Some of these treatments involve mild oxidation by immersion of the PS in organic solvents prior to thermal oxidation but little explanation has been given as to the mechanism of this initial oxidation.

Here we report on a simple, rapid chemical procedure for the formation of the oxide layer at porous silicon using a dilute aqueous solution of the surfactant, hexadecyltrimethylammonium bromide. These findings are discussed in terms of the influence of the wetting properties of porous silicon on the mechanism of oxide formation. The consequences of this have significant implications for the recent efforts towards the development of covalent modifications of porous silicon surfaces.<sup>4,5</sup>

Porous silicon was formed by galvanostatic anodisation of a p-doped Si(100) wafer in a 50:50 solution of 48% aqueous HF and ethanol in a Teflon cell, with a current density of 19 mA cm<sup>-2</sup> for 4 min. The PS was then rinsed in de-ionised water (Millipore, 18 MΩ) to remove ethanol, immersed in 48% aqueous HF to ensure removal of any remaining oxide and finally rinsed in de-ionised water (20 s) and dried in a N<sub>2</sub> stream. An FTIR spectrum indicated that samples so prepared were hydrogen-terminated with little, or no oxide, present. These samples were then immersed in 1 mM aqueous solution<sup>†</sup> of hexadecyltrimethylammonium bromide (CTAB) and comparisons were made with samples treated with de-ionised water. Oxidation of the PS in de-ionised water and CTAB solution was followed using FTIR spectroscopy and Fig. 1 shows the spectra for a CTAB-treated sample. In each case the spectra show loss of intensity of Si-H<sub>x</sub> modes (Si-H<sub>x</sub> stretching modes around 2100 cm<sup>-1</sup> and the SiH<sub>2</sub> scissors mode at 910 cm<sup>-1</sup>) and an increase in intensity of bands due to Si-O (1135, 1075, 878 cm<sup>-1</sup>) and O<sub>x</sub>Si-H (2250, 2220 cm<sup>-1</sup>).<sup>6</sup> The CTAB-treated PS also showed some evidence for adsorption of surfactant with bands observed in the C-H stretch region.

Oxidation in de-ionised water was very slow, taking place over a few days, whereas the reaction in CTAB solution was extremely rapid accompanied by visible gas evolution, assumed to be hydrogen on the basis of the expected reactions (1) and (2).<sup>7</sup>



Figs. 2 and 3 show plots of the integrated intensity of the Si-O modes and Si-H stretch modes vs. log (immersion time/min),

respectively, and give clear evidence for a correlation between loss of Si-H and gain of Si-O modes. In addition to the significantly increased rate in CTAB solution it is also evident that almost twice as much oxidation occurs compared to water. Moreover, the total surface area of the CTAB-treated sample was 13% less than the control, as evidenced by the integrated intensity of the Si-H<sub>x</sub> stretch modes prior to oxidation. This

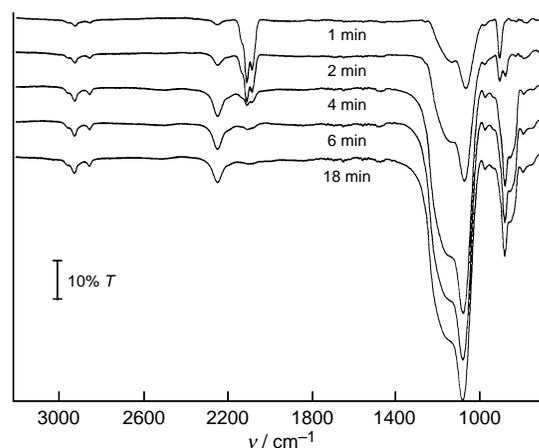


Fig. 1 Transmission FTIR spectra for CTAB-treated porous silicon

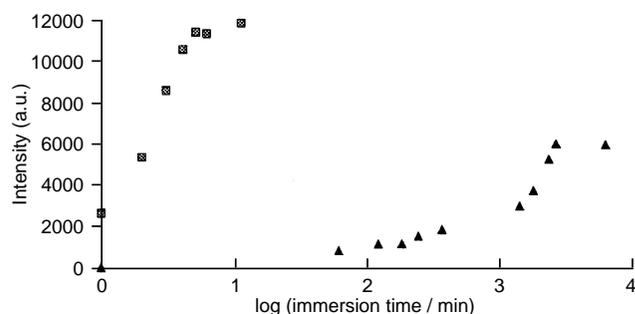


Fig. 2 Plot of integrated intensity of the Si-O modes vs. log(immersion time/min) for water (▲) and CTAB-treated porous silicon (■)

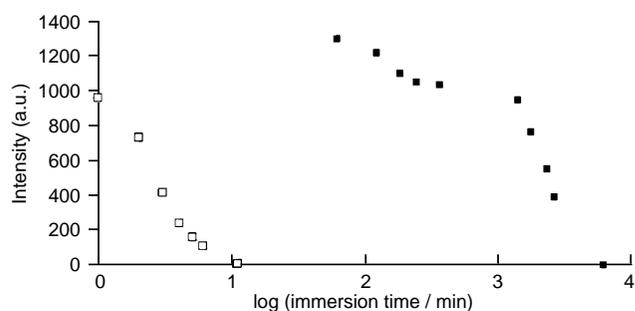


Fig. 3 Plot of integrated intensity of the Si-H stretching mode vs. log(immersion time/min) for water (■) and CTAB-treated porous silicon (□)

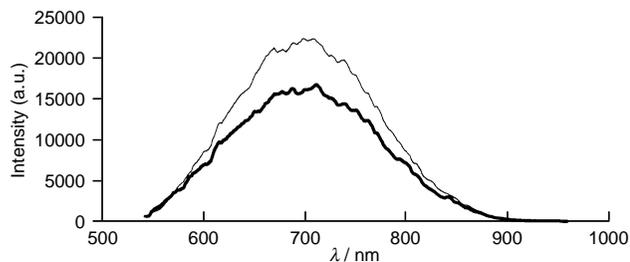


Fig. 4 PL spectra of porous silicon before (—) and after treatment with CTAB (---)

shows that a greater percentage of the hydrogen-terminated surface is accessible to water molecules in the presence of CTAB.

PL spectra<sup>‡</sup> of both as-prepared and CTAB-treated samples show a maximum at ~680 nm, typical of porous silicon (Fig. 4). Despite evidence from the IR spectra that no material is lost on CTAB-treatment, a small decrease in PL intensity is observed.<sup>§</sup>

The very significant enhancement of the oxidation by CTAB can be explained by considering the nature of the porous layer. Studies have shown that PS layers consist of silicon columns attached to the crystalline substrate with pore sizes in the nanometre range. The surface is highly hydrophobic with a large surface area (100–400 m<sup>2</sup> cm<sup>-3</sup>).<sup>1</sup> The rapid oxidation observed in the CTAB-treated sample is explained as being due to a lowering of the surface tension ( $\gamma$ ) of the liquid phase. Water can only oxidize the PS if it is in intimate contact with it. Immersion wetting of the PS is therefore a prerequisite to oxidation. Wetting will occur when:<sup>8</sup>  $\gamma_{\text{PS/air}} > \gamma_{\text{PS/H}_2\text{O}} + \gamma_{\text{H}_2\text{O/air}}$ .

Owing to the high surface tension of water ( $\gamma_{\text{H}_2\text{O/air}} = 72.75$  mN m<sup>-1</sup>) and the hydrophobic nature of the PS surface, water does not spontaneously wet PS. The addition of CTAB lowers both  $\gamma_{\text{PS/H}_2\text{O}}$  and  $\gamma_{\text{H}_2\text{O/air}}$  thereby ensuring more complete wetting. Water molecules are therefore able to penetrate more effectively the porous structure leading to increased oxidation.

This finding has a considerable bearing on the post-preparation treatments and also for the more recent interest in the development of synthetic routes for the formation of molecular films at PS.<sup>4,5</sup> Specifically, the choice of solvent or reactant must take these effects into account. Most organic solvents have a significantly lower surface tension than water and may wet the PS surface more effectively on immersion.<sup>9</sup> Even nominally dry solvents will, if hygroscopic, absorb water from the surroundings thus enabling water, dissolved in the solvent, to penetrate, and oxidize, the PS.

Indeed, proof of this was demonstrated by immersion of PS in solvents under dry nitrogen using conventional Schlenk techniques to minimize contamination by water. Immersion in dry acetonitrile (distilled over CaH<sub>2</sub>) for 30 min reveals considerable oxidation as observed by IR spectroscopy, equivalent to 4 h immersion in de-ionised water. Similar results were obtained with ethanol and ether, whereas no oxidation was observed with hexanes. The extent of oxidation is therefore clearly associated with the solvent's affinity for water.<sup>¶</sup> These data reaffirm the acknowledged fact that under standard Schlenk line conditions adventitious water is present in sufficient quantity for oxidation to occur.<sup>10</sup>

These results suggest that the use of hygroscopic solvents in the chemical modification of PS is to be avoided if oxidation is undesirable. It is noteworthy that a recent report on the derivatization of PS using alcohols stresses the need for

anhydrous conditions in the formation of alcohol-derived molecular films.<sup>5</sup>

In conclusion, the effect of organic molecules on the oxidation of hydrogen-terminated porous silicon is highly dependent on their hygroscopic nature and ability to lower the PS surface tension. This may be exploited for the rapid formation of an oxide layer. These findings are also relevant to chemists developing synthetic strategies for the covalent modification of PS.

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## Footnotes and References

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† This concentration is close to the critical micelle concentration of CTAB ( $9.2 \times 10^{-4}$  M) ensuring a minimum in surface tension for the liquid phase at minimum CTAB concentration.<sup>11</sup>

‡ Photoluminescence spectra were recorded using an EG&G Princeton Applied Research Peltier cooled photodiode array system (150 ms exposure time, 0.7 nm spectral resolution). Excitation was at 488 nm using a Spectra-Physics model 2010 argon ion laser and measured at room temp. (20–21 °C).

§ A recent review<sup>1</sup> has emphasised that the effect of oxidative treatments on PS luminescence intensity and peak wavelength varies between laboratories. Reports of both intensity decreases and increases and red or blue shifts have been made. A decrease in PL intensity on oxidation may be explained as due to the production of a strained SiO<sub>2</sub> layer containing defects which act as nonradiative recombination centres.<sup>12</sup>

¶ Properties of solvents.<sup>9</sup>

Solvent	$\gamma^a$ /mN m <sup>-1</sup>	Solubility <sup>b/g</sup> (100 ml) <sup>-1</sup>
H <sub>2</sub> O	72.75	— <sup>c</sup>
MeCN	29.1	— <sup>c</sup>
EtOH	22.3	— <sup>c</sup>
Et <sub>2</sub> O	17.0	1.3
C <sub>6</sub> H <sub>14</sub>	18.4	$1.1 \times 10^{-2}$

<sup>a</sup> At 20 °C. <sup>b</sup> Of water at 25 °C. <sup>c</sup> Completely soluble.

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