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Dynamics of porous silicon formation by etching in HF + V\textsubscript{2}O\textsubscript{5} solutions

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Formation of porous silicon by etching of silicon wafers with vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) dissolved in hydrofluoric acid (HF) has been studied with infrared spectroscopy and electron microscopy. V\textsubscript{2}O\textsubscript{5} creates VO\textsuperscript{2+} in solution, which initiates the reaction by injecting holes into the silicon valence band. Much is known about the mechanism of etching that leads to flat Si surfaces; however, the transition to pore formation is not well understood. The rate of film growth depends linearly on the V\textsubscript{2}O\textsubscript{5} concentration in aqueous solutions but has a nonlinear dependence on the formal HF concentration. Addition of ethanol greatly decreases the etch rate and changes the pore morphology from a mixture of {100} + {110} planes to predominantly {100} planes. A plot of thickness versus etch time evolves from a quadratic to a linear dependence, whereas the surface area depends linearly on the etch time. These observations are consistent with a model in which pores with a uniform diameter nucleate randomly then lengthen linearly in time. The pore density increases at short times and then reaches a saturation value. The probability that the collision of a VO\textsuperscript{2+} ion with the surface leads to etching of a Si atom (reactive sticking coefficient) is ∼3 \times 10\textsuperscript{-8}.

Keywords: surface chemistry; reaction dynamics; laser/surface interactions; etching; nanostructures

1. Introduction

Porous silicon (por-Si) is of great technological interest in optics [1–4], sensors [5–9], electronics [10–13], biomaterials [14–16], diagnosis and treatment of disease [17], and energy storage/generation devices [18–20]. The most common method of preparation is anodic [21]. Stain etching is an electroless form of por-Si formation [22] that involves the addition of an oxidant to an acidic fluoride solution. Though stain etching has been known for over 50 years, very little is known about the mechanism by which it creates nanocrystalline microporous silicon or about the etch kinetics.

Stain etching involves exposing Si to an aqueous mixture of acidic fluoride and an oxidant. Almost exclusively, the oxidant used is nitric acid (or another nitrate or nitrite). Robbins and Schwarz [23–25] and Turner [26] were the first to develop mechanisms of ‘chemical etching’ of silicon. Robbins and Schwarz primarily studied the electropolishing regime in which the Si wafer is etched to reveal a more or less flat surface. Turner recognized the electrochemical nature of the process and that a pitted or porous solid can be made if—rather than being uniform—the anodic and cathodic processes are localized to specific separate sites. The nanostructured nature of the film was confirmed by the study of Beale et al. [27]. They did not address the chemical aspects of etching; rather, they focused on structure and ‘confirmed’ the Turner mechanism. However, they insisted that the anodic and cathodic sites occurred in the same region of the sample (at the pore tips) in direct opposition to Turner’s model. Furthermore, they did not explain how pores formed, only how pores propagated after they formed.

The Robbins–Schwarz–Turner mechanism consists of two steps, (1) oxidation of the Si surface to produce SiO\textsubscript{2}, and (2) chemical removal of the SiO\textsubscript{2} layer (or patches) by HF attack:

\[
\text{Si} + 2\text{H}_2\text{O} + n\text{h}^+ \xrightarrow{\text{Step 1}} \text{SiO}_2 + 4\text{H}^+ + (4 - n)\text{e}^- \xrightarrow{\text{Step 2} + \text{6HF}} \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}. \tag{1}
\]

The role of the nitric acid is to inject holes (h\textsuperscript{+}) via

\[
\text{HNO}_3 + 3\text{H}^+ \rightarrow \text{NO} + 2\text{H}_2\text{O} + 3\text{h}^+, \tag{2}
\]

which, according to Turner, leads to oxide formation and, importantly, the production of gas bubbles from NO(g). As pointed out by Kooij et al. [28], Turner neither specified the relative contributions of electrons and holes, nor did he consider whether the production of H\textsubscript{2} occurred as a direct result of the etching reaction or through a coupled chemical reaction. Kooij et al. demonstrated unequivocally, first, that holes were

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required for Si dissolution and, second, that H₂ was generated by a coupled chemical reaction. Furthermore, 80% of the gas released during etching in HF + HNO₃ was H₂ while the remaining 20% was composed mainly of N₂O. Consumption of the electrons liberated in the process can occur via reduction of H⁺ to form H₂. This ensures charge neutrality, though it does not have to occur in the same region of the sample as etching, and can also generate bubbles.

Föll and co-workers [29–31] have developed a current burst model along the lines of the Robbins–Schwarz–Turner mechanism. In it, four processes—direct Si dissolution, oxide layer formation, chemical oxide removal and formation of a H-terminated surface—are thought to occur. The chemistry and kinetics of these processes are not explicitly treated; instead they are represented by different time constants, which are further convoluted with temporal and spatial correlations. An oxide film is assumed to form exclusively at the pore tips after which it is removed by chemical etching. The electrochemical process that causes oxidation of the pore tips is directed toward the tips by several effects (quantum confinement and characteristic length scales of the space charge region, pore tip radius, and diffusion), which control the flow of the carriers (holes) that are responsible for the initiation of etching. Quantum confinement influences carrier transport in accord with the model of Lehmann and Gösele [32,33]. The current burst model gives a plausible explanation of pore propagation of anodically etched macropores once pores are formed but it does not explain how pores nucleate and form in the first place. This model also relies on H-termination not being intrinsically part of direct dissolution and for the adsorption of H atoms onto Si(100) to be slower than on Si(111). The first point is in direct opposition to the commonly accepted Gerischer model of direct dissolution [34–36]. There is no experimental evidence for the second point. It is also decidedly unclear whether the current burst model is applicable to microporous silicon formed by stain etching in which carrier generation and transport is fundamentally different than in anodic etching. During stain etching, carrier injection must occur via a surface process involving adsorption of the oxidant. Anodic etching proceeds after generation of carriers in the bulk followed by transport to the surface. Nonetheless, the development of the current burst model has again demonstrated the importance of understanding carrier transport and how the length scales involved in the processes controlling carrier transport are decisive in the formation and propagation of pores.

In developing their mechanism, no surface-sensitive techniques were used by Robbins, Schwarz and Turner. The formation of the surface oxide was never demonstrated. This mechanism calls for SiO₂ films or patches to form—not isolated adsorbed OH units, not individual adsorbed O atoms. No conclusive evidence for oxide film formation during por-Si production has been obtained in the ensuing years. The most recent X-ray photoelectron spectroscopy data indicate the absence of an oxide layer when Si is etched in HF + HNO₃ solutions [37,38]. No reasoning for how a perfectly isotropic reaction such as chemical removal of SiO₂ can lead to por-Si formation, which requires a great deal of anisotropy and a self-limiting reaction, was ever given. The above reaction is woefully inadequate to explain stain etching and por-Si formation completely, that is, to explain the atomic removal of silicon atoms, the nucleation of pores, the propagation of pores and the evolution of film morphology.

The Robbins–Schwarz–Turner mechanism is virtually unchallenged in the literature. That was true until 2006 when Nahidi and Kolasinski [39] critiqued the role of the oxidant and whether a surface oxide forms. They preferred removal of Si atoms according to the Gerischer mechanism [34,35], which does not involve the formation of a surface oxide, is initiated by a hole in a bulk electronic state localized at the surface, and proceeds by the attack of fluoride species such as F⁻, HF and HF₂⁻. This allowed them to predict that other oxidants should produce por-Si and opened up a richer seam of potential stain etchants. An extensive series of experiments by Steinert et al. [37,38,40,41] on Si etching in HF + HNO₃ solutions supports an etch mechanism that does not involve a surface oxide. While stain etching is fast, simple, inexpensive, and can be performed on substrates of arbitrary shape, nitrate-based etchants have a bad reputation because of inhomogeneous films and irreproducible results. An annoyance is that the etchants often exhibit variable induction times that can be 15 min or more. Much of this variability can be explained by the work of Steinert et al., who have shown the importance of the formation of N(III) intermediates.

Kolasinski and co-workers [39,42,43] have shown that bubble generation can be suppressed at least partially and uniform films can be made by using an oxidant that involves a metal ion, e.g. the Fe(III), Ce(IV), V(V) and Mn(VII) oxidation states. An advantage of these new stain etchants is that ethanol can be added to act as a surfactant in an attempt to further reduce problems with bubbles. This is not true of HNO₃-based stain etchants, which can lead to explosive mixtures with ethanol [39].
Here we report on studies that aim to develop the HF + V₂O₅ etchant further. We vary the etch parameters of concentration, etching time and the addition of ethanol. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to interrogate the surface area, chemical composition and crystallography of the exposed pore walls. Scanning electron microscopy is used to determine film thickness. We report the dependence of growth kinetics on these etch parameters and show that film formation is consistent with the model of Brumhead et al. [44], which was used to describe anodic por-Si formation.

2. Experimental
All samples were etched from Si(100), Czochralski grown, B doped, p-type prime grade wafers with 14–22 Ω·cm resistivity and 500–550 μm thickness. All etching was performed at room temperature after crystals were cleaned ultrasonically in acetone and ethanol then rinsed in distilled water. Etching was performed under Ar and the dead volume in the water and HF containers was always filled with Ar to reduce the effects of dissolved O₂ and CO₂. V₂O₅ (Fisher certified grade) was added to produce V(V). Fluoride was supplied from HF (JT Baker 48–51% analytical grade). After etching the samples were rinsed several times, first in 1:1 water/ethanol then ethanol (three times), and then dried in a stream of Ar.

Scanning electron microscopy was performed with an FEI Quanta 400 ESEM or an Hitachi S-4800 FE-SEM. Imaging with the ESEM was performed in a background of ~100 Pa of water using both backscatter and secondary electron detectors. The ESEM operated with integrated Oxford INCA energy dispersive X-ray spectroscopy (EDS). Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet Prote`ge´ 460. IR spectra were recorded in infrared spectroscopy (FTIR) was performed with a Nicolet Prote`ge´ 460. IR spectra were recorded with a diffuse reflectance attachment purged with dry N₂ at a resolution of 4 cm⁻¹ by averaging 512 scans. A planar hydrogen-terminated surface created by etching a polished Si(100) wafer in 50% HF for 5 min was used for a reference spectrum and the data acquisition procedure includes an instrumentally defined correction for H₂O and CO₂ absorption. A purge time of 15 min was sufficient to completely remove CO₂ absorption. H₂O does not absorb in the region of the Si–H stretch. A linear baseline correction was applied prior to integrating the spectra. The rate of oxidation of silicon is enhanced by the presence of both O₂ and water. We attempted to minimize the amount of oxidation that occurred between when the sample was etched and when the FTIR spectrum was acquired by minimizing the time between etching and data acquisition (often as little at 15 min) and by placing the samples in an Ar-filled desiccator.

3. Results
What has been little appreciated is that infrared spectroscopy cannot only identify surface species and measure coverage in the monolayer regime, but also that it measures the surface area of por-Si. When por-Si is made, the surface is completely H-terminated. The signal of the Si–H stretch transition at ~2100 cm⁻¹ (absorbance in transmission or the Kubelka–Monk function in diffuse reflectance) is linearly proportional to the concentration. All of the Si–H that contributes to this surface area is bound at the surface. If we were to measure the signal generated by 1 ML, we would obtain a calibration that would allow us to estimate the surface area from the integrated area under a peak in the IR spectrum. Currently we do not have this value for our experimental setup. Nonetheless, this FTIR method allows us to measure the relative surface area. It also gives us a tool to quantify the change in surface area as a function of time and, therefore, to measure the kinetics of film formation.

Infrared spectroscopy of H on Si has been studied in detail, particularly by Chabal [45–47]. Chabal and co-workers [48,49] and Niwano and co-workers [50,51] have also studied the initial oxidation of H-terminated silicon surfaces. From their work, we obtained assignments of the IR peaks shown in Table 1. These assignments were used as the basis for deconvolution of the IR spectrum into various components. The total integrated peak area is proportional to the surface area exposed in the porous film. As with any deconvolution of broad overlapping peaks, there will be some uncertainties in precise interpretation. Nonetheless, the peaks in the monohydride region (Si–H, 2072–2090 cm⁻¹) are well resolved from the dihydride region (SiH₂, 2107–2117 cm⁻¹) as well as the trihydride region (SiH₃, 2129–2139 cm⁻¹). The only exception is the defect mode of the dihydride on the Si(110) surface, which overlaps with the trihydride region. Therefore, we can determine what type of hydride is present. The deconvolution can also be used to give a general impression of the proportion of the exposed surface that corresponds to Si{100} versus Si{110} and Si{111} planes.

In addition, the FTIR spectrum can readily determine whether oxidation of the surface has set in. The last three entries in Table 1 show that the insertion of an oxygen atom in the backbonds of the Si atom bound to the adsorbed H atom significantly shifts the
stretch frequency of that adsorbed H atom due to an induction effect. Therefore, it is possible to distinguish SiH (an adsorbed H atom with no oxygen inserted into the backbond) from OSiH (an adsorbed H with one O atom inserted) from O₂SiH (an adsorbed H atom with two O atoms inserted) from O₃SiH (three inserted O atoms). To minimize the number of free parameters in the fit, the components are all assumed to be described by Gaussian profiles, the peak positions are held fixed, and the SiHₓ stretches are assumed to all have the same width parameter, which is distinct from the one width parameter used to describe the oxidized OₓSiHₓ stretches.

Figure 1 displays a typical DRIFTS spectrum of a por-Si film etched in aqueous HF + 0.121 M V₂O₅. Filled circles represent the data, the fit is the solid line and the deconvolved peaks are also shown. In aqueous solutions, using the peaks associated with just one Si plane could not fit the spectra. Using only those peaks associated with Si(100) and Si(110) represented the spectra well. Si(111)-related peaks made very little, if any, contribution. For short etch times, roughly ≤300 s, SiHₓ alone without OₓSiHₓ-related peaks fitted the spectra. OₓSiHₓ peaks were required for longer etch times (≥600 s). Even then, the relative contribution from oxide-related peaks was in the few percent range and was mainly composed of the peak associated with one oxygen backbonded to the surface silicon atom. The surfaces of solutions etched in aqueous HF + 0.121 M V₂O₅ were predominantly terminated with dihydride species (∼60%) with

Table 1. IR peak assignments for H-terminated Si surfaces.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2072</td>
<td>SiH(100)/(110) as</td>
</tr>
<tr>
<td>2083</td>
<td>SiH(100) ss</td>
</tr>
<tr>
<td>2089</td>
<td>SiH(110) ss</td>
</tr>
<tr>
<td>2077</td>
<td>SiH(111)</td>
</tr>
<tr>
<td>2107</td>
<td>SiHₓ(100) ss</td>
</tr>
<tr>
<td>2111</td>
<td>SiHₓ(111)</td>
</tr>
<tr>
<td>2117</td>
<td>SiHₓ(100) as</td>
</tr>
<tr>
<td>2129</td>
<td>SiHₓ(100) as</td>
</tr>
<tr>
<td>2139</td>
<td>SiHₓ(100) ss, SiHₓ(111), SiHₓ(110)</td>
</tr>
<tr>
<td>2149</td>
<td>OₓSiH</td>
</tr>
<tr>
<td>2200</td>
<td>OₓSiH, O₂SiH</td>
</tr>
<tr>
<td>2252</td>
<td>O₃SiH</td>
</tr>
</tbody>
</table>

as, asymmetric stretch; ss, symmetric stretch.

Figure 1. Deconvoluted DRIFTS spectrum of a porous silicon sample etched for 180 s in 50% HF(aq) + 0.121 mol L⁻¹ V₂O₅.
significantly less monohydride coverage (~30%) and trihydrides as a minority species (<10%). Similar FTIR spectra have been reported for anodically etched por-Si films [52–58]. While these broad spectra have been attributed to a combination of SiH, SiH₂, and SiH₃ adsorbed species [52,56], they have not previously been quantitatively deconvoluted and analysed in terms of the hydride species and the crystallographic planes as done so here and, therefore, a quantitative comparison is not possible.

When ethanol was added to the etchant, the DRIFTS spectrum changed dramatically, as shown in Figure 2. First, we notice that the etch rate was significantly slower when ethanol was added, as evinced by a slower rate at which colour changes were observed on the face of the crystal during etching and by the slower growth rate of the DRIFTS signal. The etch rate could be increased by increasing the V₂O₅ concentration. Second, the contribution of the Si–H peaks associated with the Si{100} planes increased and in some cases the spectra were fitted by the Si{100}-related peaks alone with no contribution from Si{110}- and Si{111}-related peaks. How well resolved the peak at 2089 cm⁻¹ was and how broad the ~2120 cm⁻¹ feature was, varied from spectrum to spectrum but the trend was nonetheless clear. Therefore, the addition of ethanol changed the pore morphology by changing what planes were exposed on the pore walls. Concurrently the proportion of signal due to monohydride species dropped somewhat and there was an increase in dihydride and trihydride coverages. Third, the appearance of several smaller new peaks in the 900–1200 cm⁻¹ region and around 1390 cm⁻¹ and 2900 cm⁻¹ indicate the presence of an additional adsorbed species, some of which is adsorbed oxygen. On the basis of the assignment of Eng et al. [59], who studied the adsorption of ethanol on Si(100) single crystal surfaces, the low-frequency region contains modes indicative of the CCO stretch and the CO stretch of an adsorbed ethoxy species (Si–OCH₂CH₃). A confirmatory CH₃ deformation in combination with a C–H wag is located at 1390 cm⁻¹ and the C–H stretches are located at 2880–2980 cm⁻¹ for CH₂ and CH₃ groups. The low wavenumber peaks are difficult to quantify relative to the Si–H features because of a sloping background and broad Si–O-related features [60,61]. The very low intensity of the C–H peaks, which may also contain a contribution from adventitious adsorption of impurities from the atmosphere, is only a few percent of the intensity of the Si–H peaks and lies near the detection limit.

Gupta et al. [52] investigated the FTIR spectrum of por-Si anodically etched in HF + ethanol solutions. They acquired spectra under ultrahigh vacuum and found no surface oxide-related signal nor did they find any ethanol- or ethoxy-related features. Consistent with our results their IR spectrum closely resembled that of a H-terminated Si(100) surface with little or no contribution from other planes.

The thickness of the film as a function of the etch time was monitored with cross-sectional SEM images. An average of 30–60 measurements was taken from each cross section. The standard deviation in these measurements was used to depict the error bars shown in Figure 3. The error bars are thus a convolution of uncertainties introduced by film thickness variations and uncertainties caused by lack of sharpness in the images of the interfaces. Very long etch times (the exact time depending on the V₂O₅ concentration) could experience interference from bubbles and cracking. Note that a film thickness of over 7 µm was achieved in the 0.121 mol l⁻¹ V₂O₅ solution with a 60 min etch.

A fit weighted by the inverse of the standard deviation of each point in the linear portion of the graph (t ≥ 90 s) represented the data well and yielded a thickness growth rate of 1.91 ± 0.05 nm s⁻¹. A non-zero intercept of 292 ± 15 nm was found. The early time region (0 ≤ t ≤ 120 s) was well fitted by a quadratic dependence on time. The nonlinear-to-linear transition occurred between the 60 s and 90 s
data points. This transition corresponded to a film thickness of 350–475 nm. In the absence of por-Si formation, Kooij et al. found a linear relationship between etch depth and time for Si etched in HF + HNO₃ solutions [28].

The integrated area under the DRIFTS spectrum is proportional to the surface area. In a model in which pores with constant diameters increase in length linearly with time (vide infra) the square root of the surface area (and therefore square root of the IR peak area) increases linearly with time. Figure 4 demonstrates that the square root of surface area increased linearly with time. This was true for all time scales, i.e. there was no transition from short etch times to long times. The data in Figure 4 could not be extended to longer times for this etchant type as cracking of the surface at longer times changed the etched crystal face from a mirror finish to a dull rough appearance. Cracking can lead to a change in the scattering coefficient of the surface at which point deviations in linearity between DRIFTS peak intensities and surface area are to be expected.

To investigate the reaction order with respect to the V₂O₅ concentration, we measured the integrated DRIFTS peak area as a function of the formal molar V₂O₅ concentration in an aqueous 50% HF solution for a fixed etch time of 120 s. This time was chosen because it was deemed long enough to give reproducible results, because it lies in the linear region of Figure 3, and because no cracking or significant bubble formation was observed. In Figure 5 we see that the square root of the IR peak area is linear in V₂O₅ concentration. Again this is consistent with a linear increase in the rate of film growth (rate of change of the thickness) as a function of V₂O₅ concentration. In other words, the etching reaction is first order in V₂O₅ concentration. Etching of Si in HF + CrO₃ solutions (without por-Si formation) was also found to be first order in oxidant concentration by van den Meerakker and van Vegchel [62]. Our data indicate that there may be a small threshold value of [V₂O₅] = 0.011 ± 0.009 mol l⁻¹ to obtain porous film formation.

The reaction order with respect to the fluoride species has not been determined yet. In the concentration range of 10–47 mol l⁻¹ (formal HF concentration), the rate exhibited a nonlinear increase. However, this cannot be interpreted in terms of a reaction order. Fluoride solutions are extremely complex [63]. Kolasinski [64] has developed a series of equations to describe the activities and concentrations of the most important solutions species (HF, H⁺, F⁻, HF₂⁻, and H₂F⁻). These equations were developed under the assumption that the activity coefficients can be calculated as a function of ionic strength alone, and are obtained from fits to experimental data.
In future work, we will measure the rate in the concentration range in which the fluoride species can be tracked quantitatively.

4. Discussion

Brumhead et al. [44] postulated that film formation begins when a few fast developing pores initiate and propagate from the surface into the bulk. During the nonlinear growth rate phase, the number of pores increases until the density reaches a saturation value that achieves carrier depletion in the nanoscale-width pore walls in accord with quantum confinement models [65,66]. As described by Nahidi and Kolasinski [39] specifically for stain etching, charge injection only occurs if the oxidant’s acceptor level is at or below the energy of the silicon valence band maximum (VBM). Quantum confinement in nanoscale silicon structures under 5 nm across lowers the energy of the VBM [21,67]. As the VBM drops below the energy of the oxidant’s acceptor level, hole injection and therefore etching cease. Quantum confinement causes silicon stain etching to be self-limiting in acidic fluoride solutions. At this point the walls of the pores are passivated with adsorbed hydrogen and charge injection can only occur at the pore bottom. Thereafter, growth of the film is linear as the pores propagate at a steady rate without nucleation of further pores. This scheme is presented in Figure 6.

Our observations for por-Si films produced by stain etching are consistent with this model, and for the system presented in Figure 3, this transition to uniform film growth occurred at a thickness of 350–475 nm. Figure 4 demonstrates that the square root of surface area increased linearly with time as would be expected for pores of a uniform diameter increasing linearly in length with time. This was true for all time scales. Therefore, it appears that while the pore density was changing at early times, the pore diameter was not. Pores nucleated at different times and their diameters did not change substantially after nucleation. The pore growth rate was initially quite high but it slowed down as the pore lengthened. In this first phase, the increase in pore density compensated for the deceleration in pore lengthening to keep the expansion in surface area constant. The pore density increased in the first 60–90 s of etching at which point it reached a saturation value and no longer changed. Around this time the individual pore growth rates became uniform and all pores continued to grow at roughly the same rate such that the film increased in thickness linearly in time.

The scheme presented in Figure 6 is oversimplified. We do not imply ordering of the pores, a lack of branching or that all pores are oriented vertically with respect to the original surface of the substrate. The pores were too small to image in SEM. Therefore, we know that they are <10 nm in diameter. Preliminary transmission electron microscopy investigations indicated that pores may be around 3 nm in diameter [42].

The dynamics of adsorption and desorption at the gas/solid interface have to a large extent been
elucidated by molecular beam scattering [68–70], state-resolved measurements of desorbates [71–74] and sticking coefficient measurements [75,76]. The first two are not available for studies of the liquid/solid interface. The third has received surprisingly little attention; however, it would be of growing interest should theoreticians begin to turn their sights to calculating such quantities. Jung and Campbell [77] showed that the initial sticking coefficient of CH₃(CH₂)₇SH on Au is near unity when adsorption occurs from the gas phase. However, when adsorption occurs from solution, the sticking coefficient drops by seven orders of magnitude. They attributed this to the necessary shedding of the solvation shell and displacement of physisorbed water molecules. This should not be taken as an indication that sticking coefficients at the liquid/solid interface must necessarily be small, as Kolasinski [36] has shown that the sticking coefficient of F⁻ onto a photoexcited Si surface is near unity.

In order to better understand the kinetics and dynamics of the reaction, we need to develop a quantitative measure of the efficacy of the oxidant—

the reactive sticking coefficient. The etch rate is determined by the rate of hole injection [34,78]. Ideally, for each hole that is injected, one Si atom is etched. In practice, many of the holes may be lost to recombination or other non-reactive relaxation. The etch rate per unit surface area \( R_A \) is obtained by the product of the collision frequency of the oxidant \( Z_w \), the number of holes transferred per collision \( n_t \) and the reactive sticking coefficient \( s_R \). The reactive sticking coefficient is the reactive charge transfer probability: the probability that an oxidant/surface collision leads to the injection of a hole that initiates the etching of one Si atom. Thus,

\[
R_A = n_t Z_w s_R. 
\]

(3)

The linear etch rate \( R_b \) (increase of thickness \( h \) per unit time in m s⁻¹) for a film of porosity \( \varepsilon \) is related to \( R_A \) by

\[
R_b = R_A \rho_A \varepsilon, 
\]

(4)

where \( \rho_A \) is the atomic density of Si. The collision frequency in m⁻²s⁻¹ is given by [79]

\[
Z_w = c \left( \frac{k_B T^{1/2}}{2\pi m} \right) = 630.1 M^{-1/2} c, 
\]

(5)

with \( T = 300 \) K, \( c \) is the concentration in m⁻³ of the oxidant and \( M \) its molar mass in g mol⁻¹. Thus, the reactive charge transfer probability is

\[
s_R = \frac{R_b \rho_A \varepsilon}{n_t Z_w} = 7.923 \times 10^{25} \frac{R_b \varepsilon M^{1/2}}{n_t c}. 
\]

(6)

Dudley and Kolasinski [42] have recently determined the porosity of a film stain etched with ferric ion to be \( \varepsilon \approx 0.8 \), which should be a good estimate within ±0.1 for our film, based on the observation of visible photoluminescence in both cases. The photoluminescence is believed to arise from quantum-confined structures. The oxidant injects holes according to the following half-reaction:

\[
\text{VO}_2^+ + H^+ + e^- \rightarrow \text{VO}_2^{2+} + \text{OH}^-, 
\]

\( E_0 = 1.0 \) V, \( n_t = 1 \).

(7)

Assuming that all of the \( \text{V}_2\text{O}_5 \) dissolves to produce \( \text{VO}_2^+ \), the oxidant concentration used in the etchants involved in the thickness versus time data series was \( 1.46 \times 10^{26} \) m⁻³. The etch rate extrapolated to \( t = 0 \) when no transport issues can limit the reaction rate was \( R_b = 8.0 \) nm s⁻¹. Thus, the reactive charge transfer probability was \( s_R = 3.2 \times 10^{-8} \). The reactive charge transfer probability was very low either because very few holes are injected per collision of \( \text{VO}_2^+ \) with the surface and/or because the vast majority of the injected holes were lost to non-reactive relaxation. The complexity of reaction (7) may play a role in this. Therefore, it will be interesting to measure \( s_R \) for three other oxidants,

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}, \quad E_0 = 0.77 \) V, \( n_t = 1 \),

(8)

\[
\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}, \quad E_0 = 1.4 \) V, \( n_t = 1 \),

(9)

\[
\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}, \quad E_0 = 1.49 \) V, \( n_t = 5 \),

(10)

since these may have much different charge transfer kinetics and they also inject holes into different regions of the valence band. It is interesting to note that the highest etch rates measured by Koker and Kolasinski [36,80] for laser-assisted por-Si formation—a photoelectrochemical analogue of stain etching—were also in the several nm s⁻¹ range. Under their conditions, the laser generated a steady-state coverage of holes of about \( 1 \times 10^{-7} \) ML, the sticking coefficient of F⁻ onto hole-excited surface atoms was unity (over 10 order of magnitude higher than the sticking coefficient onto ground state surface atoms), and the etch rate was limited by the sticking coefficients and fluxes of HF and \( \text{HF}_2 \) onto the surface. In the present case, as shown in Figure 5, the reaction rate was first order in vanadium concentration. Hence, the concentration of holes at the surface available for reaction responded to the vanadium concentration. The formal
HF concentration was too high to allow for quantitative calculation of the fluoride concentrations. Therefore, estimations of the reactive sticking coefficients of the fluoride species will have to await future work.

When ethanol was added to the etchant, several consequences result. The film formation rate dropped significantly. The quantity of bubbles was reduced; they became smaller, and were more easily dislodged from the surface. The reduction in bubbles was related primarily to the reduction in etch rate, whereas the change in the nature of the bubbles was related to the ethanol acting as a surfactant. The termination of the pore walls also changed from a combination of Si{100} + Si{110} in aqueous solutions to almost exclusively Si{100} in water/ethanol mixtures. It is well known that the addition of alcohol changes the anisotropy of KOH etching of silicon [81–84]. A change in (or introduction of) anisotropy caused by ethanol addition would explain the change in pore wall morphology during stain etching with and without ethanol in solution. Additional IR bands are consistent with a very small coverage of what may be an ethoxy group (Si–OCH2CH3) adsorbed as a minority species on the otherwise H-terminated surface. V2O5 may be activating ethanol adsorption onto the por-Si during por-Si formation because an adsorbed ethoxy is not observed when por-Si is produced by anodic etching in an etchant containing ethanol. The adsorbed ethoxy group may influence the reduction in film formation rate. However, it seems unlikely that it is related to the change in the etch anisotropy since por-Si produced anodically in HF/water/ethanol solutions also appears to be primarily terminated with H-covered Si{100} planes [52].

At the very high ionic strength of these solutions, it is difficult to make any estimates of the solution composition. At lower ionic strength for laser-assisted por-Si formation, Koker and Kolasinski [80] have shown that HF and HF2− are the solution species that control the rate of por-Si formation and that HF2− is roughly 15 times faster at etching. Addition of ethanol has not only a dilutive effect, but also it can change the HF:HF2− ratio. Luxenberg and Kim [85] have shown that addition of ethanol to HF(aq) changed the equilibrium constant of HF dissociation and HF2− formation somewhat but not drastically. The changes lead to more dissociation of HF but roughly the same amount of HF2− formation. Nonetheless, addition of 20% ethanol reduced the film formation rate by almost a factor of 20, whereas dilution of concentrated HF(aq) with a similar amount of water decreased the rate by only about a factor of 6. Thus the effect of ethanol was much more than would be expected on the basis of simple dilution and was an indication that adsorption of ethanol onto the H-terminated Si surface hindered the etch reaction.

V2O5 oxidizes ethanol to ethanol or acetic acid [86,87]. However, these transformations are generally run near 100°C for ~24 h to obtain high yields; therefore, the reactions should be slow at room temperature. Nonetheless, it is clear that ethanol reacts with V2O5 and the solution composition may change during etch times of many tens of minutes. V2O5 nanobelts and nanorolls are stable in acetic acid [88]. Consequently, acetic acid may be a more stable and better choice to use as a surfactant. We will investigate this in future work.

5. Conclusion

Stain etching of moderately p-type doped Si(100) can produce visibly photoluminescent porous silicon films at a rate of several nm s⁻¹. Film thicknesses of over 5µm were easily obtained. Film formation was consistent with the model of Brumhead et al. [44], in which pore nucleation is initially random, with pores propagating rapidly at first but slowing as their density increases to a saturation value. Eventually, pores elongate at a constant rate and the film thickness increases linearly in time. In addition, we found through analysis of FTIR spectra of the Si–H stretching region that nucleation formed pores of a certain diameter and this diameter was roughly maintained throughout etching. The pore walls were predominantly terminated with Si{100} and Si{110} planes rather than the lower energy Si{111} planes. When ethanol was added to the etchant, the etch rate dropped precipitously and the pore morphology changed, becoming terminated almost exclusively with Si{100} planes. The formation of bubbles was reduced in the presence of ethanol, mostly because of slower etching. Even in the absence of ethanol when the etch rate was not too high, bubble formation occurred only at the edges of the crystals and the resulting films had mirror finishes and uniform colouration caused by white light interference effects. Uniform colouration is indicative of uniform porosity and film thickness. The probability that the collision of a VO2+ ion with the surface led to charge transfer (hole injection) and etching of a Si atom was ~3 × 10⁻³⁸. It is unclear what determines this very small probability: the charge transfer step or the localization of the hole at the surface until a F⁻ ion collides with it, or some combination of both.

Ogata and co-workers [89–93] have studied anodically etched por-Si extensively with transmission FTIR
spectroscopy. They also found that the Si–H stretching region exhibited bands produced by a mixture of SiH, SiH2 and SiH3 species. They exerted considerable effort, including supporting \textit{ab initio} density functional calculations, which allowed them to assign low frequency peaks attributable to the SiH bend (616 or 628 cm\(^{-1}\) for [110] or [111] planes, respectively) and the SiH3 wag (667 cm\(^{-1}\)). Their analysis allowed them to conclude that both on \textit{n}-type and \textit{p}-type Si substrates etched anodically in 20 wt% HF H\(_2\)O/ethanol solutions, the pore walls are covered primarily with [111] microfacets. This result is in contrast to the results we found here for stain etched samples.

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