Electrochemical Etching of Silicon in Nonaqueous Electrolytes
Containing Hydrogen Fluoride or Fluoroborate

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The electrochemical behavior and surface chemistry of anodic silicon etching in nonaqueous electrolytes was studied. Etching of single-crystal p-type and n-type (100) silicon was carried out in acetonitrile and propylene carbonate with hydrofluoric acid (HF) or tetrafluoroborate (BF4⁻) providing fluoride to complex the oxidized silicon. Electrolytes containing HF resulted in tetravalent dissolution, and photocurrent quadrupling was observed. Electrolytes containing BF4⁻ also resulted in tetravalent dissolution; however, calculated quantum efficiencies were lower depending upon the electrolyte. Current-voltage behavior indicates the presence of surface states which affect both the onset potential for oxidation and the current multiplication. In situ multiple internal reflection Fourier transform infrared analysis confirms that silicon surfaces etched in electrolytes containing HF remain hydride-terminated throughout etching; however, silicon etched in BF4⁻ based electrolytes loses the initial hydride termination at the onset of etching.

Aqueous solutions containing hydrofluoric acid (HF) are frequently used for dissolving silicon dioxide in the cleaning and etching of silicon. The oxide dissolution mechanism has been studied in order to better understand and control the process.1-3 Silicon can be electropolished or formed into porous silicon through anodization in aqueous solutions, depending upon the selected parameters such as applied potential, pH, and dopant type or concentration. The role of water at low potentials, however, is unclear. Work by Allongue et al.4 suggests that at low potentials, water reacts with the oxidized silicon to form Si-OH intermediates which are then substituted with F⁻. This two-step mechanism helps explain electropolishing since the Si-OH surface species may condense at high potentials forming SiO2 which is subsequently dissolved chemically by HF. The in situ Fourier transform infrared spectroscopy (FTIR) results of Fonseca et al.5 support this view and provide experimental evidence that Si-O bonds are present at potentials both below and above the critical current peak (where the transition from porous silicon formation to electropolishing occurs).

Previous work6,7 demonstrated that silicon can be etched in acetonitrile (MeCN) containing anhydrous HF. The results demonstrate the ability to etch silicon without the complications caused by reaction with water and show that the direct oxidation of silicon to the soluble SiHF2⁺ species is possible. The structure and texture of the silicon surface etched with HF in MeCN with small amounts of water was found to be similar to anhydrous electrolytes.8 The oxidation in anhydrous electrolytes, however, offers a unique opportunity to examine fluoride complexing agents other than HF. The role of HF may thus be better understood since oxide or hydroxide intermediates, which usually require HF to dissolve, are not present here.

In this work, the behavior of silicon oxidation with HF and an alternative fluoride complexing agent, viz. BF4⁻, is presented. Quantum efficiencies, equivalents per mole, and current-voltage behavior have been determined for MeCN and propylene carbonate (PC) solutions containing HF or tetrafluoroborate (BF4⁻). The relationship between current-voltage behavior and chemistry at silicon-electrolyte interface has been investigated using in situ multiple internal reflection (MIR) FTIR.

Experimental

Silicon samples were cut from (100) prime grade, single-sided polished n-type and p-type silicon wafers (MEMC, Dallas, TX). The n-type silicon was doped with phosphorus to resistivities from 1 to 10 Ω cm, and the p-type silicon was doped with boron to resistivities from 1 to 10 Ω cm. Ohmic contact was made to the back side of the sample with GaIn alloy. All wafers were cleaned with acetone, methanol, and trichloroethylene and then dipped in an aqueous solution of dilute buffered oxide etch prior to etching to remove any native oxide.

Electrochemical experiments were performed in a three-electrode Teflon reactor with a sapphire optical window. A stainless counter electrode was used in the MeCN-based electrolytes and a graphite rod was used as the counter electrode with PC-based electrolytes. Silver wire was used as a pseudo-reference; potentials were adjusted to saturated calomel electrode (SCE) by measuring the difference between the silver reference and SCE following the etch.

Anhydrous MeCN, H2O < 50 ppm (Aldrich Chemical, Milwau-kee, WI) was purified by vacuum distillation and a reflux sequence over five chemical reagents as described previously.9 Anhydrous PC, H2O < 50 ppm (Aldrich Chemical), was dried by vacuum distillation followed by drying with alumina desiccant (grade F-1, Sigma Chemical, St. Louis, MO). The residual water content in the electrolytes was less than 10 ppm, as measured by Karl Fischer titration. Tetra- butylammonium tetrafluoroborate (TBABF4), lithium fluoroborate (LiBF4), and anhydrous hydrofluoric acid (HF) were used as fluoride sources in the nonaqueous etching of silicon. Semiconductor grade anhydrous HF was obtained from Matheson Gas (San Jose, CA). Tetraethylammonium perchlorate (TBAClO4) and lithium perchlorate (LiClO4) salts were used as supporting electrolytes for the HF/MeCN- and HF/propylene carbonate (PC) electrolytes, respectively. The TBABF4, LiBF4, TBAClO4, and LiClO4 were obtained from Aldrich Chemical and were dried under vacuum for 3 days at approximately 100°C.

All materials were handled in a Vacuum Atmosphere (Hawthorne, CA) inert atmosphere dry box maintained at less than 0.05 ppm water and 2 ppm oxygen. The electrochemical measurements were made using an EG&G PAR 273 (Princeton, NJ) potentiostat. A 0.65 mW HeNe laser with nominal beam diameter of 0.47 mm was used in the photoetching studies with neutral density filters (Oriel Corporation, Stratford, CT).

In situ MIR FTIR data was acquired using a Nicolet Magna IR 560 FTIR spectrometer (Madison, WI) coupled with the potentiostat. Figure 1 shows a sealed Teflon reactor which was fabricated to operate within the FTIR. MIR waveguides were fabricated using 3 mm thick, double-polished, single-crystal silicon wafers (Nova Electronic Materials, Richardson, TX). The wafers were (100) orientation, p-type with resistivities of 1 to 10 Ω cm. Waveguides with smooth, reflective windows were made from wafers by mechanical polishing using alumina slurries. The mirrored surfaces were created on the polished windows by sputter depositing 4000 Å of aluminum. The dimensions of the finished waveguides were 80.5 × 10 × 3 mm with a 45° angle of incidence, which resulted in approximately 13 bounce...
The photocurrent reaches an intensity-limited plateau and no maximized area for reflection to achieve high IR signal strength. The photogenerated holes are collected. In these experiments, holes critical current peak is observed. The initial forward scan during interface. As the silicon is biased positive of generated holes drift under the applied field to the silicon-electrolyte interface. The shape of the current-voltage curves follow that of an n-type semiconductor-electrolyte junction. At potentials negative of the flatband potential \( E_{\text{FB}} \), the silicon is in accumulation mode where photogenerated holes are filled by recombination with electrons in the bulk rather than initiating a surface reaction. At potentials more positive than \( E_{\text{FB}} \), a depletion layer is present and photogenerated holes drift under the applied field to the silicon-electrolyte interface. As the silicon is biased positive of \( E_{\text{FB}} \), the depletion layer thickness within the silicon increases until a steady-state fraction of the photogenerated holes are collected. In these experiments, holes which reach the electrolyte interface undergo a faradaic reaction resulting in the oxidation and dissolution of the silicon. Since the dissolution is not the rate-limiting process, a photocurrent plateau directly proportional to incident light intensity is observed.

Figure 2A shows the initial forward scan during laser illumination in 2 M HF/0.25 M TBAClO\(_4\)/MeCN. The onset of the photocurrent, which often correlates with \( E_{\text{FB}} \), is observed at 0.1 V vs. SCE. The photocurrent reaches an intensity-limited plateau and no critical current peak is observed. The initial forward scan during laser illumination in 0.5 M TBABF\(_4\) in MeCN is shown in Fig. 2B, where no HF was added to the electrolyte. Unlike the behavior of silicon in aqueous electrolytes containing TBABF\(_4\), the sustained phototoetching of silicon is observed. The potential for the onset of the photocurrent in Fig. 2B is nearly the same as in Fig. 2A; however, the current density is very small until potentials positive of 0.7 V vs. SCE. The shift in the photocurrent to more positive potentials for the less acidic electrolyte is not expected for an ideal semiconductor-electrolyte interface. Also, the saturation current for the TBABF\(_4\)/MeCN electrolyte is less than the saturation current in HF/MeCN despite using the same illumination source. The dark current scans for both HF/MeCN and TBABF\(_4\)/MeCN electrolytes (Fig. 2A and B) overlapped and are displayed in Fig. 2C.

The magnitude of the photocurrent was compared to the illumination intensity for the curves in Fig. 2. After accounting for interfacial light reflections, the magnitude of the saturation current (~770 \( \mu \)A) is 3.9 times the photon flux. This current multiplication, where one photogenerated hole in the valence band is followed by three electrons into the conduction band, has been discussed in an earlier work. The magnitude of the saturation current when TBABF\(_4\) is used without HF (~510 \( \mu \)A) corresponds to a current multiplication factor of 2.6. The decrease in current multiplication that is observed when HF is replaced with BF\(_4\) suggests several possible effects including: increased recombination of photogenerated holes, an alternate dissolution mechanism, or a decrease in coulombic efficiency toward silicon oxidation.

Cross-sectional profiles of two pits etched in silicon using 0.5 M TBABF\(_4\)/MeCN are shown in Fig. 3. The pit shown in Fig. 3A was etched using the 0.65 mW HeNe laser (Gaussian profile) with a 32% neutral density filter for 10 min. The diameter of the pit was approximately 500 \( \mu \)m the measured depth was 7.5 \( \mu \)m. A second pit was etched for 10 min with no light filters and is shown in Fig. 3B. Tripling the incident light intensity did not increase the maximum depth of the pit but did increase the diameter to approximately 700 \( \mu \)m (about 50% greater than the incident laser profile). The greatest illumination intensity from the laser beam occurs at the cen-

![Figure 1. Schematic diagram of the silicon waveguide within the MIR FTIR reactor used in the in situ analysis.](image1)

![Figure 2. Voltammograms of n-type silicon in MeCN: A, illuminated scan, 2 M HF/0.25 M TBAClO\(_4\)/MeCN. The onset of the photocurrent, which often correlates with \( E_{\text{FB}} \), is observed at 0.1 V vs. SCE. The photocurrent reaches an intensity-limited plateau and no critical current peak is observed. The initial forward scan during laser illumination in 0.5 M TBABF\(_4\) in MeCN is shown in Fig. 2B, where no HF was added to the electrolyte. Unlike the behavior of silicon in aqueous electrolytes containing TBABF\(_4\), the sustained phototoetching of silicon is observed. The potential for the onset of the photocurrent in Fig. 2B is nearly the same as in Fig. 2A; however, the current density is very small until potentials positive of 0.7 V vs. SCE. The shift in the photocurrent to more positive potentials for the less acidic electrolyte is not expected for an ideal semiconductor-electrolyte interface. Also, the saturation current for the TBABF\(_4\)/MeCN electrolyte is less than the saturation current in HF/MeCN despite using the same illumination source. The dark current scans for both HF/MeCN and TBABF\(_4\)/MeCN electrolytes (Fig. 2A and B) overlapped and are displayed in Fig. 2C.](image2)

![Figure 3. Cross-sectional profiles of pits etched with 0.65 mW HeNe laser for 10 min. (A) Using 32% neutral density filter; (b) full laser intensity.](image3)
ter of the pit. The spreading profile indicates that the etch rate near the center of the pit is dissolution limited due to the higher local current densities. Excess holes near the center of the pit can diffuse laterally and initiate an oxidation reaction recombine.

The equivalents per mole of silicon etched were found by integrating the charge passed during etching, and estimating the quantity of silicon etched. For the 2 M HF/0.25 M TBACIO4/MeCN, 4.3 equivalents per mole were calculated, showing that the silicon was dissolved in the tetravalent form. The equivalents per mole in 0.5 M TBABF4/MeCN were found to be dependent on etch time. Etch times between 5 and 10 min resulted in a range from four to six equivalents per mole. Values greater than four are most likely due to electrochemical side reactions at the silicon electrode which were verified visually and by the in situ MIR FTIR analysis. It was also observed that during longer etch times in the TBABF4/MeCN electrolyte, the dark current increased and discoloration of the solvent occurred. This was most likely related to electrochemical solvent decomposition at the counter electrode. Since protons were not available for reduction, TBA+ or MeCN were reduced at the counter electrode resulting in solution discoloration and fouling. For these reasons, an alternative organic solvent and cathodic reaction were investigated.

PC has a wide potential window9 (high electrochemical stability) and is used in nonaqueous battery applications. The intercalation of lithium ions into graphite was selected as a nondestructive counter electrode reaction for silicon etching in this study. The current-voltage behavior for (100) n-type silicon in PC are given in Fig. 4. The results are similar to those in MeCN. Figure 4A shows the initial forward scan during laser illumination with 2 M HF/0.2 M LiClO4/PC, and Fig. 4B shows the initial forward scan during laser illumination for 0.2 M LiBF4 in PC. The dark current scans for both HF/MeCN and LiBF4/MeCN electrolytes overlapped and are displayed in Fig. 4C. The photocurrent onset potential in HF/PC occurred near 0.1 V, and the current plateau was observed at potentials positive of 0.9 V vs. SCE. The magnitude of the photocurrent represents a current multiplication of 4.1. The onset of significant photocurrent for the LiBF4/PC electrolyte occurred at potentials positive of 0.65 V vs. SCE and photocurrent saturation was observed at potentials positive of 1.3 V vs. SCE. Current multiplication was lower for the LiBF4/PC electrolyte at 1.2 electrons per incident photon. These results are similar to those in MeCN, there was a positive shift in photocurrent potential and the current multiplication was lower when HF was replaced with BF3. The saturation current observed for LiBF4/PC was somewhat lower than TBABF4/MeCN. This was most likely due to an increased oxidation of PC, (as compared the MeCN) a process which does not result in current multiplication.

The equivalents per mole of silicon etched were also determined for samples etched using PC-based electrolytes. The results for HF/PC electrolyte were similar to the HF/MeCN electrolyte at 4.6 equivalents per mole silicon, indicating tetravalent dissolution with the possibility of a minor side reaction. As the oxidation time was increased for etching in the LiBF4/MeCN electrolyte, the equivalents per mole ranged from four to as high as twenty. Although the calculated equivalents per mole were high with the LiBF4/PC electrolyte (indicating lower coulombic efficiency), electrolyte decomposition and electrode fouling was not observed in the PC-based electrolyte. Another source for disparities in the calculations for the number of equivalents per mole are errors in the estimation of the total volume etched including the porous surface.

The shift in the onset potential for the photo-oxidation of the n-type silicon reflects the stability of the fluoride complex, and is not like that of an ideal semiconductor-solution Schottky barrier. The current-voltage behavior of p-type silicon further demonstrates this nonideal effect. Figure 5 shows the cyclic voltammograms for p-type silicon in the 2 M HF/0.25 M TBACIO4/MeCN electrolyte (Fig. 5A) and p-type silicon in the 0.5 M TBABF4/MeCN electrolyte (Fig. 5B). In the HF/MeCN electrolyte, the onset of the oxidation of p-type silicon occurs at 0.25 V vs. SCE, which is slightly positive of the onset potential observed for illuminated n-type silicon. The oxidation of p-type silicon in the TBABF4/MeCN electrolyte occurs very near the same potential for photo-oxidation of n-type silicon. An ideal semiconductor-electrolyte junction would exhibit a more positive onset potential for p-type than for illuminated n-type silicon. The expected difference between the onset potential for photo-oxidation of n-type and p-type semiconductor is equal to the difference in the Fermi levels. The results presented here indicate that the silicon surface is dominated by surface states or charged species which affect the potential drop across the interface. The evidence of surface states is reflected by the change in the potential of the bandedges.

**In situ MIR FTIR analysis.**—MIR FTIR analysis was used to evaluate the surface chemistry during oxidation in the nonaqueous electrolyte. This technique has been used to investigate the silicon-electrolyte interface and is sensitive to interfacial species since the evanescent wave is held tightly to the waveguide surface (within 1 μm). Figures 6 through 9 show the in situ FTIR difference spectra taken during oxidation of the p-type silicon waveguide in the nonaqueous electrolytes. Difference spectra were obtained by subtracting spectra taken immediately prior to anodization from the in situ spectra during oxidation; all spectra were divided by the background spectra and normalized per reflection given as ΔH/I. The anodic current density was maintained by potentiostatic control at 10 μA/cm2 while 256 scans were averaged at 4 cm−1 resolution. Difference spectra are shown for three successive 10 min anodization intervals in each of Fig. 6 to 9.
During anodization of p-type silicon in the 2 M HF/0.2 M LiClO₄/MeCN electrolyte, the formation of surface Si–H bonds (broad peak at 2100 cm⁻¹) is observed in the FTIR spectra shown in Fig. 6. The broad shape of the Si–H vibrational spectra suggests contributions of all three silicon surface species (SiH, SiH₂, SiH₃); however, since the band maximum is observed during anodization at 2104 cm⁻¹, the SiH₂ group signal is considered to be the major contributor. Although the surface was hydride terminated at the start of the experiment, the Si–H signal increased with anodization time; this result is similar to aqueous electrochemical etching at low current densities.¹¹,¹² This may be attributed to two factors: (i) the increased surface area resulting in a greater number of Si–H bonds and (ii) an increase in SiH₃ species near the surface as suggested by Peter et al.¹¹

A reorganization of the double layer during anodization was also observed. A similar effect was described previously in the electrochemical studies by Rao et al.¹³ In this case, the positive dc potential causes the migration of anions to the surface, displacing MeCN and trace H₂O near the surface. This displacement causes the broad O–H peak (3100-3500 cm⁻¹), C–H peaks (3165, 3005, and 2995 cm⁻¹), and C=N vibrational intensities (2254 and 2295 cm⁻¹) to decrease during anodization. The decreasing peaks at 2274 and 2305 cm⁻¹, which are not usually associated with MeCN, may be due to a shift in C=N vibrational frequency associated with fluorinated MeCN (which was presumably generated in small amounts when anhydrous HF chemically reacted with MeCN prior to etching). The chemical fluorination was verified by the slight pink color change observed following addition of anhydrous HF to MeCN.

Figure 7 shows the difference spectra for the anodization of the p-type silicon waveguide in the 0.5 M TBABF₄/MeCN electrolyte. Prior to anodization, the waveguides were cleaned in aqueous buffered oxide etching solution producing a hydride-terminated surface. Upon initial anodization in the TBABF₄/MeCN, the surface hydride is removed (as shown by the decrease in absorbance at 2100 cm⁻¹) and does not reappear during the etch. This confirms that the silicon surface and electrolyte double layer are significantly different during etching than in the case of HF/MeCN electrolyte. An increase in the absorbance peak at 2360 cm⁻¹ is observed with oxidation time. This peak corresponds to that for boron trifluoride (BF₃), which is expected to be generated as a product of the following surface reaction:

\[ \text{Si} + 6\text{BF}_4^- + n\text{H}^+ \rightarrow \text{SiF}_6^{2-} + 6\text{BF}_3 + (4 - n)e^- \]

A rearrangement of the double layer is also observed in the TBABF₄/MeCN electrolyte. The positive potential applied to the silicon waveguide causes BF₄⁻ ions to migrate toward the interface, displacing MeCN and trace H₂O near the surface. In this case, however, the shifted doublet observed in the HF/MeCN electrolyte at 2274 and 2305 cm⁻¹ tends to increase during oxidation. The increase is attributed to the electrochemical fluorination of MeCN during anodization. When anhydrous HF reacted chemically with MeCN prior to etching, the fluorinated MeCN was displaced along with the unaltered MeCN, as seen in Fig. 6. In the TBABF₄/MeCN electrolyte, the fluoride salt did not react with the solvent until a positive potential was applied. The electrochemical formation of fluorinated MeCN observed in Fig. 7 is in agreement the lower coulombic efficiency observed when BF₄⁻ is used in place HF.

In situ FTIR spectra for the 2 M HF/0.2 M TBAClO₄/PC electrolyte are shown in Fig. 8. The broad Si–H peak tended to increase with oxidation time similar to the spectra in the HF/MeCN electrolyte. The highest intensity for the peak appeared near 2106 cm⁻¹ (similar to Fig. 6) suggesting that SiH₂ is the major contributor. A reorganization of the double layer in this case is presumably caused by the migration of ClO₄⁻ ions to the surface. The anions displace the PC and H₂O causing the decrease in O–H stretching (3100-3500 cm⁻¹) and decreases in all C–H vibrational peaks (2850, 2883, 2923, 2941, and 2990 cm⁻¹). The decreasing doublet near 2341 and 2364 cm⁻¹ may be due to solvent oxidation or the formation of fluorinated PC.

Figure 9 shows the in situ FTIR spectra for the 0.2 M LiBF₄/MeCN electrolyte. The increased noise and lower absorbance seen here may be due to the higher potential required to maintain the constant current density used in the experiment. The initial Si–H surface (2100 cm⁻¹) is removed during the initial oxidation of the silicon, similar to the results in the TBABF₄/MeCN electrolyte. Decreases due to surface reorganization are less evident in these spectra. In-
creases observed in the peak at 3000 cm\(^{-1}\) and smaller peaks near 2940 and 2880 cm\(^{-1}\) suggest shifts in the C–H peaks due to either the Stark effect or oxidation of the PC.

**Discussion**

Silicon oxidation in nonaqueous electrolytes provides an interesting contrast to the behavior of silicon in aqueous electrolytes. Since intermediate oxides are not involved in nonaqueous electrolytes, there is no critical current peak and the silicon may be complexed with fluoride from either BF\(_4^-\) or HF. While the semiconducting behavior of the silicon can be seen (i.e., photocurrent and Schottky barrier), the reaction pathway is complex and depends upon the fluoride source. The one- to fourfold photocurrent multiplication indicates that energetic intermediates are involved which inject charge into the silicon. The shift in oxidation onset potential (for BF\(_4^-\) vs. HF, and n-type vs. p-type) indicates that the potential distribution across the silicon-electrolyte interface depends on the nature of the silicon surface and/or silicon complex formed at the interface.

A positive shift in the photocurrent potential for n-type silicon is observed when HF is replaced with BF\(_4^-\) (Fig. 2 and 4). This suggests that the bandages are shifted to more positive potentials, indicating that the surface is populated by more positively charged species. As seen in the MIR FTIR data in Fig. 6 and Fig. 8, the surface of the silicon remains hydride terminated when HF is present. However, in the case of silicon etching in BF\(_4^-\) containing electrolytes, the hydride termination is removed during the initial oxidation of the silicon (Fig. 7 and 9). From the FTIR analysis, the surface termination of the silicon in BF\(_4^-\) containing electrolytes is not clear. The source of the increased density of positive charges at the surface may be from oxidized silicon species. Namely, oxidized silicon species at the surface which have not been complexed by the electrolyte. Also, negatively charged species (e.g., free-fluoride from HF) adsorbed at the surface tend to shift the bandages to more negative potentials. The concentration of free-fluoride with HF is expected to be much higher than BF\(_4^-\) as the equilibrium lies far to the left:

\[ BF_4^- \rightleftharpoons BF_3^+ + F^- \quad \text{where} \quad k = 10^{-39} \]

The small positive shift in onset potential observed for p-type with respect to n-type in HF/MeCN may also be related to surface states. The effect is more evident in the TBABF\(_4\)/MeCN electrolyte where the oxidation potentials for p- and n-type are very close.

Current doubling from electron injection in aqueous fluoride containing electrolytes is thought to coincide with the formation of either Si–OH or Si–F surface species. However, the in situ MIR FTIR analysis in this study does not indicate any increased surface OH species during anodization. There is also no observed shifting in the SiH vibrational bands which are associated with back-bonds with oxygen. This suggests that the trace water present in the electrolytes is not responsible for the electron injection observed here. The previously proposed mechanism for dissolution in MeCN containing HF attempts to explain the current quadrupling via electron injection into the conduction band forming SiF\(_2^+\) surface species. Although the formation of surface Si–F bonds was not observed with the IR analysis (due to the strong phonon absorption in silicon below 1500 cm\(^{-1}\)), existence of these bonds may not be ruled out. When HF is replaced with BF\(_4^-\) a similar oxidation mechanism is expected (resulting in SiF\(_2^-\) surface species) although the current multiplication is decreased. This apparent decrease in current multiplication can be related to the alteration of the hydride-terminated surface and the increased oxidation of the electrolyte. From the FTIR spectra for the nonacidic electrolytes, the initial hydride is removed and remains absent as silicon continues to etch. Due to the loss of the hydride-terminated surface, the extremely low surface recombination velocity usually associated with SiH surfaces\(^{28}\) may be significantly increased by several orders of magnitude. Photogenerated electron-hole pairs may recombine via a Shockley-Read-Hall (nonradiative) mechanism at recombination sites with energy levels lying between the conduction and valance bandedges. The nature of surface states presumed here are difficult to isolate; however, the surface states may be due to oxidized silicon, adsorbed species, or dangling bonds. Reddy et al.\(^{29}\) have recently shown that dangling bonds introduce deep states (Shockley traps) in the bandgap which efficiently act as recombination centers. The increased surface recombination velocity tends to decrease the apparent quantum efficiency, as the calculations presented here do not account for recombination. Increasing the surface recombination velocity also affects the positive shifting observed in the current-voltage behavior for the n-type silicon as detailed in the analytical model presented by Mancini.\(^{30}\)

It was also observed in the BF\(_4^-\)-containing electrolytes that a fraction of the photogenerated holes participated in the oxidation of the electrolyte rather than silicon, thus forcing the current multiplication to approach values closer to unity. The oxidation appears more pronounced at the higher potentials needed to reach the photocurrent saturation for the BF\(_4^-\)-containing electrolytes. In consideration of both the increased hole recombination resulting from the nonhydride terminated surface and the increased solvent oxidation, it is likely that the real quantum efficiencies for the silicon reaction in the electrolytes containing BF\(_4^-\) are significantly higher.

The tetravalent dissolution of silicon as observed here is due to the lack of oxidizing agents in solution, even though protons are available in both aqueous and nonaqueous electrolytes containing HF. Values greater than four electrons per silicon observed in the acidic electrolyte were due to minor side reactions. The number of equivalents per mole of silicon etched in the BF\(_4^-\)-containing electrolytes were typically greater than four due to increased electrolyte oxidation. However, values near four were observed at short oxidation times and tetravalent dissolution is believed to be present.

The major contrast in the oxidation-dissolution pathway between the HF and BF\(_4^-\) electrolytes concerns the breaking of the silicon back bonds and the hydride termination which is observed during etching with HF and which is absent when etching with BF\(_4^-\). In HF solutions it is thought that the formation of Si–F surface bonds polarize the silicon back bonds; thus increasing their chemical reactivity and allowing the sitting of HF. In the case of the nonacidic BF\(_4^-\)-containing electrolytes, the silicon dissolves in the absence of any available HF or H\(_2\)O. This indicates that the breaking of the back bonds in the nonacidic case may occur via either an electrochemical process or an alternate chemical process which does not result in hydride termination.

**Conclusions**

The results presented here demonstrate that silicon may be anodically etched in nonaqueous solutions of HF or BF\(_4^-\). In the BF\(_4^-\)-containing electrolytes the hydride termination is absent during etching and an increased density of surface states are believed to be present. This surface leads to positive shifting in the onset potential for oxidation due to charged species at the interface and decrease current multiplication due to the presence of recombination sites.
The ability of oxidized silicon to strip fluoride from a relatively stable fluoroborate to form Si–F bonds is interesting from several points of view. Mechanistically, it shows that the affinity of oxidized silicon for fluoride is greater than that of BF₃ for fluoride. For silicon etching, fluoroborate can provide sufficient fluoride to complex the oxidized silicon without increasing the concentration of free-fluoride to hazardous levels. Thus, silicon can be oxidized and dissolved in the presence of BF₄⁻ without dissolving silicon dioxide, which is not possible in aqueous solutions.

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