Etching Behavior of Silicon Nanowires with HF and NH₄F and Surface Characterization by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy: Similarities and Differences between One-Dimensional and Two-Dimensional Silicon Surfaces

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A systematic study of the etching behavior of one-dimensional (1-D) Si nanowires (SiNWs) in various HF and NH₄F etching solutions is reported. The concentration and pH dependences of the etching time (which is inverse to the "stability") of the SiNWs in these solutions were investigated. A V-shaped bimodal etching curve was observed for HF solutions with concentrations of 0.5–40%. Specifically, SiNWs exhibit high stability in both low (0.5%) and high (40%) concentrations of HF solution, with the lowest stability (i.e., fastest etching rate) occurring at 2% (1 M) HF solution. With NH₄F, the time needed to totally etch away the SiNWs sample decreases with increasing concentration (from 1–40%). The opposite is true when the pH of the NH₄F solution was maintained at 14. These surprising results were rationalized in terms of "passivation" of the SiNW surfaces by HF or related molecules via hydrogen bonding for Si–H-terminated surfaces in HF solutions (with low pH values) and by NH₄⁺ ions via ionic bonding for Si–O⁻-terminated surfaces in NH₄F solutions (with high pH values), respectively. Furthermore, it was found that SiNWs are stable only in relatively narrow pH ranges in these solutions. When SiNWs are etched with HF, the stability range is pH = 1–2 where the surface moieties are Si–H$_x$ species (x = 1–3). When SiNWs are etched with NH₄F, the stability range is pH = 12–14 where the surface moieties are mainly Si–(O⁻)$_x$ species (x = 1–3). These rationales were confirmed by attenuated total reflection Fourier transform infrared spectroscopy measurements, which showed that, while etching SiNWs with HF gave rise to Si–H$_x$ surface species, no Si–H$_x$ species were observed when SiNWs were etched with NH₄F. The latter finding is at odds with the corresponding results reported for the two-dimensional (2-D) Si wafers where etching with either HF or NH₄F produces Si–H$_x$ species on the surface. This difference suggests either that the etching mechanisms for NH₄F versus HF are different for SiNWs or, more likely, that the Si–H$_x$ surface species produced in NH₄F solutions are so unstable that they are hydrolyzed readily at pH > 4. The similarities and differences of the etching behaviors and the resulting surface speciations between the 1-D SiNWs and the 2-D Si wafers suggest that the nanoscale structures as well as the low dimensionality of SiNWs may have contributed to the rapid hydrolysis of the surface Si–H$_x$ species in NH₄F solutions, especially at high pH values.

Introduction

One-dimensional (1-D) nanomaterials such as nanotubes and nanowires are of great importance and are expected to play a vital role as both interconnects and functional components in future electronic and photonic devices. Owing to the importance of silicon in nanoelectronics and nanophotonics, silicon nanowires (SiNWs) have attracted much attention, both in fundamental research and in device applications. Many successful synthetic methods, using vapor–liquid–solid (VLS) reaction and oxide-assisted growth,[1–3] have been developed, giving rise to bulk quantities of SiNWs. Properties such as morphology,

structure, optical and electronic properties, and electronic transport properties have also been studied extensively.[4–9] To date, SiNWs have enabled the assembly and fabrication of field-effect transistor (FETs),[10–11] integrated logic circuits,[12] and biosensors.[13,14] With the advancement of applications of SiNWs, especially in nanoelectronics and sensing, information regarding the surface properties of SiNWs is urgently required. In comparison to a two-dimensional (2-D) Si wafer, the most important material in present microelectronics industry, whose surface properties have been well-established,[15–48] little has been known about the surface properties of SiNWs such as surface speciation, surface stability, and surface chemical reactivities until recently.[49–56] Obviously, such information is crucial to the application of SiNWs in nanoelectronics.

In the semiconductor industry, particularly silicon wafer processing, ultra clean silicon surfaces can be achieved by wet chemical cleaning.[15–21] Indeed, wet etching is a key step in producing silicon surfaces that are contamination-free, topologically flat, and chemically stable for subsequent processing in silicon technology. One of the commonly used techniques for

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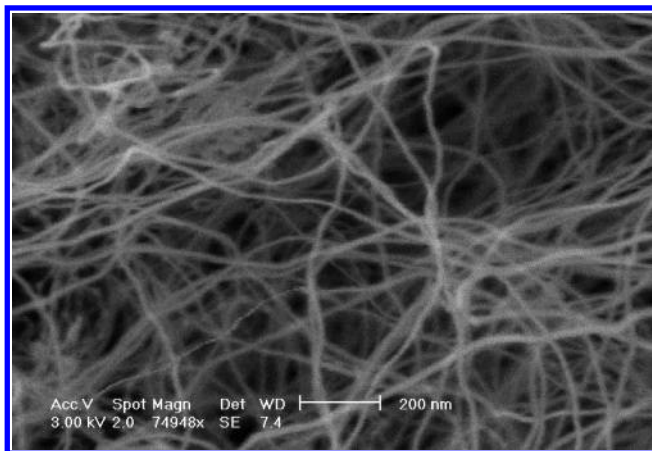⊥ Department of Chemistry, University of Illinois at Chicago.

Figure 1. SEM image of as-grown SiNWs.

removing silicon oxide from a silicon surface is etching with dilute hydrofluoric acid, usually buffered with concentrated ammonium fluoride solution. It is known that, upon HF or NH_4F treatment, the silicon surfaces are hydrogen-passivated. During the past decade, there have been numerous studies on the hydrogen-terminated Si surfaces of bulk silicon materials.[25−51] It is now well-established that etching with HF or its buffered solutions leaves behind Si surfaces terminated with various hydride species such as SiH, SiH_2, and SiH_3. These surface species have been characterized by high-resolution electron energy loss spectroscopy (HREELS),[21,22,40] Fourier transform infrared spectroscopy (FTIR),[23−32,46] scanning tunneling microscopy (STM),[33−35] low energy electron diffraction (LEED),[37,38] X-ray photoelectron spectroscopy (XPS),[41] etc.

In a recent publication,[56] we investigated the surface properties of HF-etched silicon nanowires by FTIR. In view of the fact that little is known about the etching behavior of 1-D silicon nanowires (SiNWs) as a function of the etchant as well as the concentration and pH of the etching solution, we have conducted a systematic study of the etching behavior of 1-D SiNWs in various etching solutions and conditions. The results are compared with those of 2-D Si wafers (where a vast literature is available). Surprisingly, while there are many similarities between the two systems, there are also striking differences. This information, we believe, is important in the further development of integrated silicon-based nanodevices using both SiNWs and Si wafers.

Experimental Section

SiNWs were prepared by thermal evaporation of pure SiO powder (Aldrich, 325 mesh, 99.9%) at 1250 °C in an evacuated alumina tube as described in the literature.[3] The carrier gas consisted of 95% Ar and 5% H_2 with a flow rate of 50 sccm (standard cubic cm per min) and the entire system was kept at a pressure of 400 mbar during the growth process. The products were examined by scanning electron microscopy (SEM). Figure 1 shows a typical SEM image of the SiNWs used in the present study. It can be seen that the as-grown SiNWs are long, free-standing wires. Transmission electron microscopy (TEM) results (not shown) showed that each wire has a single crystalline silicon core of approximately 15 nm in diameter, which is sheathed with an oxide layer whose thickness is about 3−5 nm.

To investigate the etching behavior of SiNWs in different chemical solutions, as-grown SiNWs from the same preparative batch (in the shape of a spongy golden-yellow ball of approximately 3 mm in diameter) were immersed in the solutions, and the time required for the SiNWs to completely "dissolve"

(i.e., disappear) in each solution was measured with a stop watch. The etching solutions used in the present study were HF or NH_4F solutions of varying concentrations and/or pHs. The measured time was taken as a measure of the "stability" of the SiNWs. In all cases, the oxide layers of SiNWs were etched away within several minutes,[51,56] followed by the etching of the crystalline silicon core. Hence, the term stability refers to the stability of the crystalline silicon core. To avoid unwanted size effects, SiNWs from the same preparative batch were used.

All of the experiments were performed in a controlled manner. The controllable variables included the composition of the etchant, the concentration and the pH of the solution, etching time, the rinsing time, etc., as specified in the captions of Figures 2−10. Specifically, in Figure 2, HF solutions of different concentrations were used. The mass concentrations used were 0.5, 1, 2, 4, 5, 10, 20, and 40% (the equivalent molar concentrations were 0.25, 0.5, 1.0, 2.0, 2.54, 5.17, 10.7, and 22.8 M, respectively). In Figure 3, NH_4F solutions of 1, 2, 5, 10, 20, and 40% (equivalent to molar concentrations of 0.272, 0.55, 1.37, 2.77, 5.67, and 11.88 M, respectively) were used. In Figure 4, NH_4F solutions with the same concentrations as in Figure 3 were employed except that the pH values of the solutions were maintained at 14 by adding appropriate amounts of 10% NaOH (2.6 M). In Figure 5, the pH of a 5% HF (2.55 M) solution was modified by adding appropriate amounts of a 10% NaOH (2.6 M) solution to yield pH values ranging from 2 to 14. Similarly, in Figure 6, the pH of a 40% NH_4F (11.88 M) solution was modified by adding appropriate amounts of a strong acid (for pH of 2 to 7) such as 96% H_2SO_4 (18 M) or 37% HCl (11.3 M) or a strong base (for pH of 7 to 14) such as 10% NaOH (2.6 M).

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy measurements were performed using an i-Series FTIR microscope equipped with an HgCdTe detector cooled with liquid nitrogen. The micro-ATR objective is a germanium crystal with a probe size of 100 μm in diameter. The resolution of the spectra was 2 cm^{-1}. For FTIR measurements, the as-prepared SiNWs samples were first etched in a particular freshly prepared etching solution for a predetermined time period, rinsed in deionized water for a specific time period, and then dried gently in a N_2 stream. All samples were further dried in a vacuum chamber overnight and kept under nitrogen until ATR-FTIR measurements. Extreme care was taken to protect the integrity of the samples after etching and/or rinsing. ATR-FTIR spectra in the range of 700−4000 cm^{-1} were obtained.

In Figure 7a, SiNWs were immersed in 1, 5, and 10% NH_4F (0.272, 1.37, and 2.77 M, respectively) for 100 min and then rinsed in deionized water for 1 min. The samples were then dried in a slow N_2 stream, put into a vacuum chamber overnight, and stored under N_2 before the ATR-FTIR measurements. In Figure 7b, the immersion times in 20 and 40% NH_4F (5.67 and 11.88 M) solutions were 5 min. The subsequent workup procedure was the same as above. In Figure 8, the SiNWs were etched in 5% NH_4F (1.37 M) for 10, 50, and 100 min, respectively, followed by a 1 min rinse with deionized water. In Figure 9, the SiNWs were immersed in 5% NH_4F (1.37 M) for 100 min and then rinsed for 0, 1, and 5 min, respectively. In Figure 10, the SiNWs were etched in a 40% NH_4F (11.88 M) solution for 5 min and then rinsed for 0, 1, and 5 min, respectively.

Unless specified otherwise, all operations and/or measurements were conducted under ambient conditions (atmospheric pressure and room temperature). The effect of oxygen in air, if any, was investigated by remeasuring the etching curves (solid
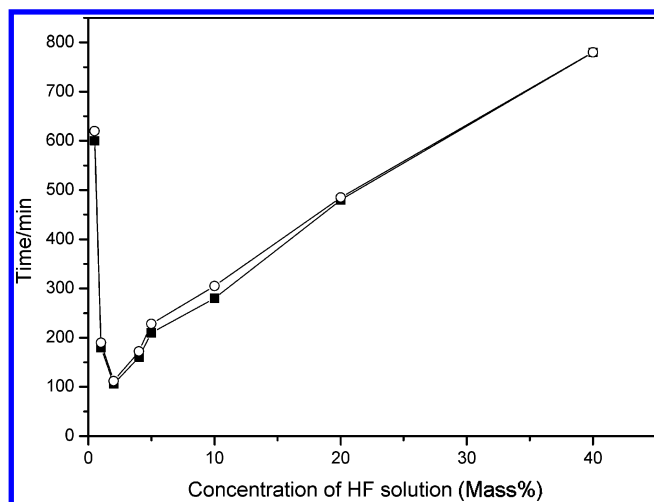
Etching Behavior of Si Nanowires with HF and NH₄F

J. Phys. Chem. B, Vol. 109, No. 21, 2005 **10873**

Figure 2. Concentration dependence of the stability of as-grown SiNWs in HF solutions (0.5−40%) with pH ≈ 1−2. (solid squares, in ambient air; open circles, under bubbling nitrogen).

Figure 3. Concentration dependence of the stability of as-grown SiNWs in NH₄F solutions with concentrations of 1−40%. (solid squares, in ambient air; open circles, under bubbling nitrogen).

Figure 4. Concentration dependence of the stability of as-grown SiNWs in NH₄F solutions with concentrations of 5−40%. The pH of the solution was kept at 14.

squares) shown in Figures 2 and 3 while bubbling nitrogen through the solutions during the etching experiments (open circles).

All etching curves as well as the ATR-FTIR spectra were measured at least twice. For each etching curve, efforts were made to use the same amount of SiNWs to minimize the effect due to the sample size. Furthermore, SiNWs from the same preparative batch were used so as to avoid unwanted nanowire size effects. Nevertheless, the results were not significantly affected by small variations in sample size or nanowire diameter (both within 10%).

Results

Etching Behavior: Etchant, Concentration, and pH Dependences. Figure 2 shows the etching behavior of SiNWs in HF solutions of varying concentrations. Solid squares are data acquired in air; open circles are data acquired under nitrogen. It can be seen that the two curves are virtually identical, indicating that oxygen in air had very little effect on the etching with HF as etchant. Here, the ordinate represents the time required for the SiNWs to dissolve (i.e., disappear) completely in a particular etching solution. The "dissolution time" can be taken as a measure of the stability of the SiNWs. Thus, the longer the etching time, the more stable the SiNWs will be in the particular etching solution, regardless of the surface composition and/or the reactions. Conversely, a shorter time is taken to imply a faster etching rate. In this context, the stability (or the dissolution time) is inversely proportional to the etching rate. Since it takes only minutes to etch away the oxide sheathings of SiNWs, terms such as stability, dissolution time, and etching rate discussed in this paper refer to the crystalline silicon cores of the SiNWs.

As can be seen from the Figure 2, the SiNWs exhibit high stability in both low (0.5%) and high (40%) concentrations of HF solution. The lowest stability (i.e., fastest etching rate) was observed for a 2% (1 M) HF solution in which, after about 100 min of immersion, the nanowires totally disappeared. We note that the pHs of the HF solutions range from 2 for a 0.5% solution to 1 for a 40% solution. This peculiar etching behavior, in particular, the V-shaped bimodal curve depicted in Figure 2, will be rationalized in the Discussion section.

Figure 3 shows the etching results of SiNWs in NH₄F solutions of different concentrations. Solid squares are data acquired in air; open circles are data acquired under nitrogen.
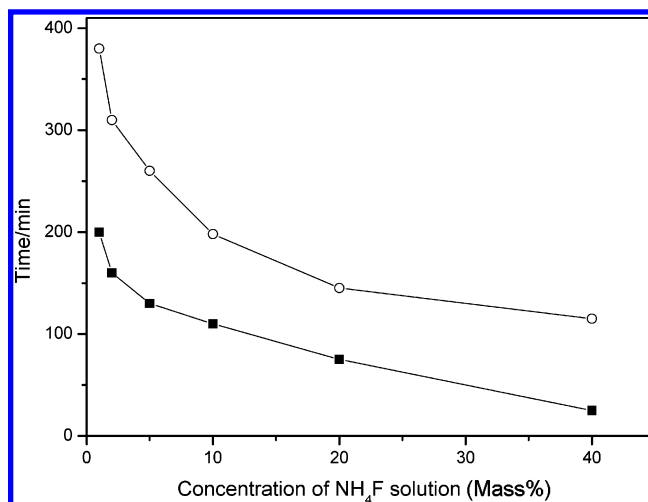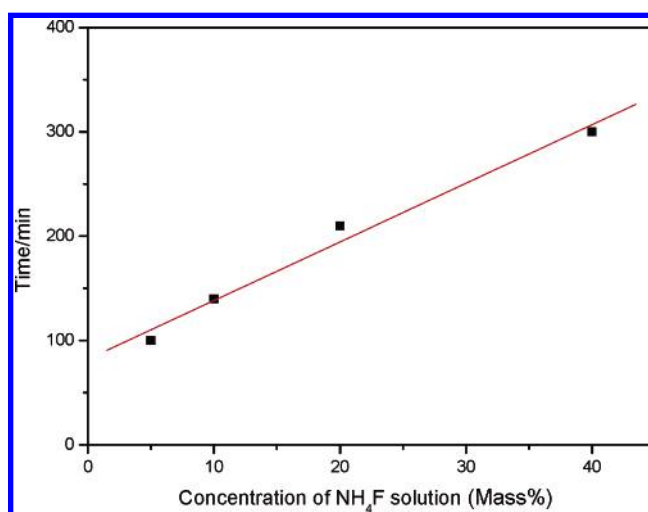
It can be seen that the two curves have similar shapes but shifted upward by roughly a factor of 2 in the etching time, indicating that oxygen in air causes an increase in the etching rate by about a factor of 2 with NH₄F as the etchant (vide infra). In both cases, the time needed to totally etch away the SiNWs sample decreases with increasing NH₄F concentration. This monotonic behavior is very different from the V-shaped bimodal etching curve observed for HF shown in Figure 2. Nonetheless, this dependence, though not linear, is understandable because as the NH₄F concentration increases, so will the concentration of HF in solution (note that HF is a weak acid). It is interesting to note that, with the exception of very low HF concentrations (<1%), the trends depicted in Figure 2 and Figure 3 for HF and NH₄F, respectively, are *opposite* to one another, suggesting that either the etching mechanism and/or the resulting surface states are different for these two etchants.

The concentration dependence of the stability of SiNWs in modified NH₄F solutions, with the pH maintained at 14 by adding a strong base such as NaOH, was also studied, and the results are shown in Figure 4. As can be seen from the figure, when the pH of the etching solution is maintained at 14, the time required to totally etch away the SiNWs increases linearly with increasing NH₄F concentration. This trend is opposite to the results obtained from pristine NH₄F solutions shown in
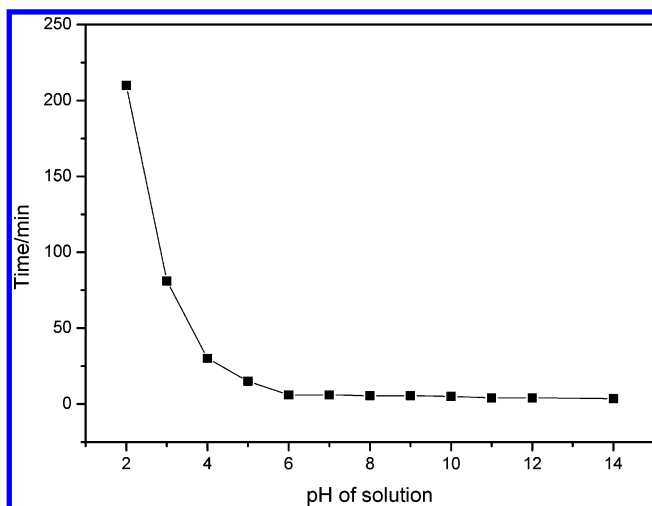
Figure 5. pH dependence of the stability of as-grown SiNWs in modified HF (5%) solutions.
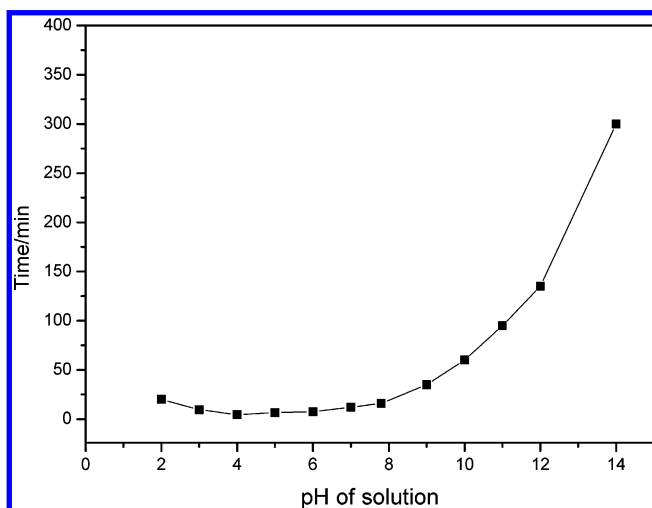

Figure 6. pH dependence of the stability of as-grown SiNWs in modified NH$_4$F (40%) solutions.

Figure 3. The contrast between Figure 3 and Figure 4 is rather striking.

The dramatic difference in the etching behavior in NH$_4$F solutions as a result of a change in pH prompted us to study the pH dependence of the stability of SiNWs in modified HF and NH$_4$F solutions. Thus, base-modified 5% HF solution was employed to study the stabilities of SiNWs at different pH values. (Throughout this paper, unless stated otherwise, the terms "base-modified" or "acid-modified" should be taken to mean that the pH of the etching solution had been modified by adding a strong base such as NaOH or a strong acid such as HCl, respectively.) The results are shown in Figure 5. It can be seen that SiNWs exhibit relatively poor stability in base-modified HF solutions, especially at pH > 4.

The pH dependence of the stability of SiNWs in modified 40% NH$_4$F solutions was also investigated, and the results are shown in Figure 6. Here, the pH of the solution was modified by adding a strong acid such as HCl or H$_2$SO$_4$ (for low pH values < 7.8) or a strong base such as NaOH (for high pH values >7.8). It can be seen that SiNWs show relatively low stabilities (fast etching) in the pH range of 2−10 but exhibit high stabilities (slow etching) at pHs greater than 10.

The contrast between Figure 5 and Figure 6 is also striking. While SiNWs are stable in HF solutions with low pH values (<4), they seem to be stable in NH$_4$F solutions with high pH

values (>10). Even more amazing is the observation that, while SiNWs exhibit "high stabilities" in base-modified NH$_4$F solutions of high pH values (say, pH of 14, see Figure 6) and high concentrations (say, 40%, see Figure 4), they show "low stabilities" in unmodified concentrated (40%) NH$_4$F solutions, as shown in Figure 3. As we shall see later, this disparity stems from the difference in the pH values (note that the natural pH of a 40% NH$_4$F solution is 7.8).

To understand these interesting contrasting etching curves, we attempted to characterize the surface species on the SiNWs, using ATR-FTIR spectroscopy, after controlled etching with the various solutions for specified time periods. In this work, we focused our attention on NH$_4$F as the etchant since the corresponding ATR-FTIR spectra of HF-etched SiNWs had been reported by us recently.[56] The results are discussed in the next section.

FTIR Characterization of Etched SiNW Surfaces. The major findings of our recent ATR-FTIR study[56] of HF-etched SiNWs relevant to the discussion here will be summarized below. In the spectrum of as-prepared SiNWs (Figure 1a of ref 56), only Si−O vibrations at ∼1050 and ∼800 cm^{-1} were observed. After the SiNWs were etched with a dilute (5%) aqueous HF solution, new absorption bands attributable to Si−H$_x$ (2000−2200 and ∼900 cm^{-1}) were observed in the spectrum (Figure 2 of ref 56), while the Si−O absorption bands virtually disappeared (Figure 1b of ref 56). Three broad overlapping bands, labeled M, D, and T bands, in the range of 2000−2200 cm^{-1} were assigned to the monohydride (SiH), the dihydride (SiH$_2$), and the trihydride (SiH$_3$), respectively. The band at ∼900 cm^{-1} was assigned to the scissor mode of the dihydride or the umbrella mode of the trihydride. Detailed assignments of these peaks can be found in the literature.[23−27,56] These results suggest that HF-etched SiNW surfaces were terminated by hydrogen upon removal of the oxide layer by HF etching. Previous HRTEM studies indicated that the surfaces of SiNWs synthesized by the oxide-assisted method[4] have predominantly (111) surfaces, along with small percentages of (100) and (110) surfaces. As noted in the literature,[20−22] both Si(111) and Si(100) surfaces of a Si wafer treated by HF solution have three kinds of silicon hydride species, the monohydride (SiH), the dihydride (SiH$_2$), and the trihydride (SiH$_3$). The coexistence of these three types of hydride species is due to the microscopic roughness of the HF-treated Si surfaces. Owing to the nanoscale of the SiNWs, the three kinds of silicon hydrides and their adstructures are to be expected.

The stabilities/reactivities of HF-etched SiNWs in air and in water were also studied in ref 56. It was found that hydrogen-passivated surfaces of SiNWs showed better stability in air (under ambient conditions) but worse stability in water,[56] in comparison with HF-etched silicon wafers. After a 15-min rinsing in deionized water, absorption peaks due to surface oxide species, such as O$_3$SiH (at ∼2250 cm^{-1}) and O$_2$SiH$_2$ or O$_2$SiH (at ∼2200 cm^{-1}), began to appear (cf. Figure 6 of ref 56). Absorption bands at 2000−2200 and at ∼900 cm^{-1} due to silicon hydride species also started to degrade, especially the SiH$_3$ and SiH$_2$ species.

In sharp contrast to the Si wafers, we found in the present work that SiNWs etched with NH$_4$F gave rise to no Si−H$_x$ bands (in the region 2000−2200 cm^{-1}) in the IR spectra. Figure 7 shows the ATR-FTIR spectra of SiNWs etched in NH$_4$F of different concentrations. The SiNWs were etched for 100 min in 1, 5, and 10% NH$_4$F solutions (Figure 7a), while in 20 and 40% solutions the etching time was 5 min (Figure 7b). All of the samples were then rinsed in deionized water for 1 min. In
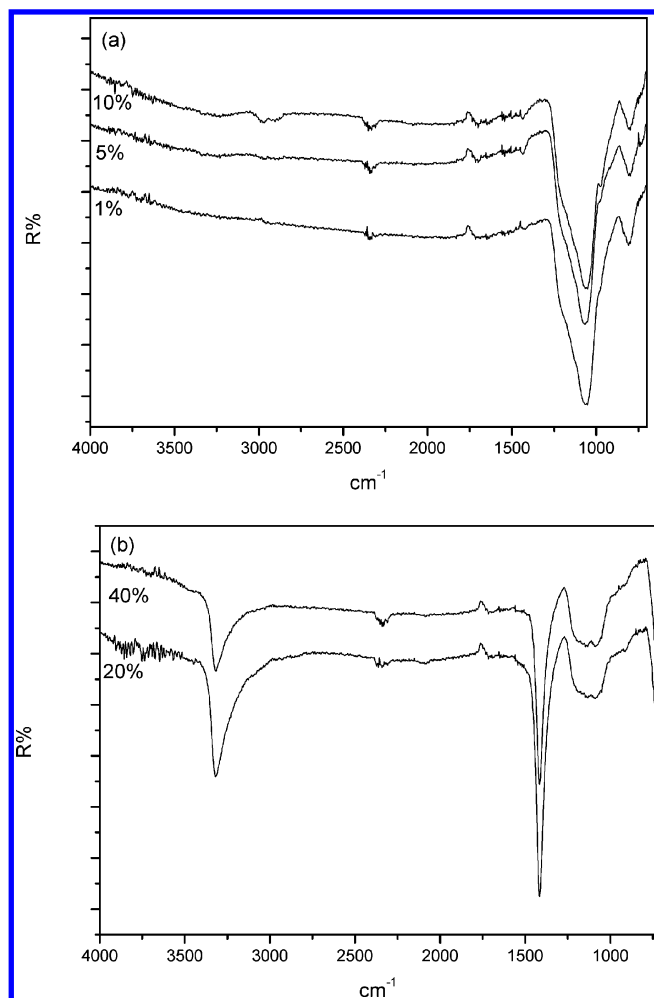
Etching Behavior of Si Nanowires with HF and NH₄F

J. Phys. Chem. B, Vol. 109, No. 21, 2005 **10875**

Figure 7. ATR-FTIR spectrum of NH₄F-etched SiNWs (a) in 1, 5, and 10% NH₄F solutions for 100 min and (b) in 20 and 40% NH₄F solutions for 5 min. All of the samples are then rinsed in deionized water for 1 min.
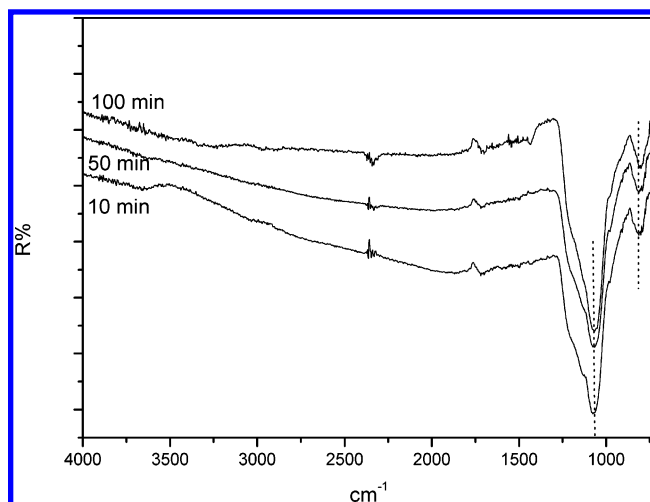

Figure 8. ATR-FTIR spectrum of SiNW etched in 5% NH₄F for different periods of time (followed by rinsing in deionized water for 1 min).

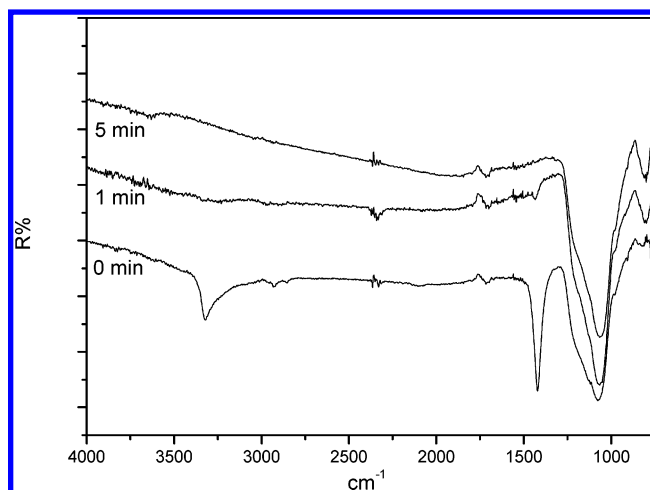**Figure 9.** ATR-FTIR spectrum of SiNW etched in 5% NH₄F for 100 min and rinsed in deionized water for different periods of time.

low-concentration solutions (1, 5, and 10%), only Si$-$O vibrations at 1064 and 810 cm^{-1} were observed. As stated previously,[56] the strong absorption near 1064 cm^{-1} is due to the asymmetric stretching of oxygen in the Si$-$O$-$Si moiety. Not only is this band very intense, it also has an asymmetric shape with a shoulder at 1240 cm.$^{-1}$ These two bands at 1064 and 1240 cm^{-1} are due to the transverse optical (TO) and longitudinal optical (LO) phonon bands, respectively.[57] The 810 cm^{-1} peak is due to the Si$-$O$-$Si bending mode.[58] In high-concentration solutions (20 and 40%), the absorption peaks at 1064 and 810 cm^{-1} decreased dramatically. A broad band was observed at 3320 cm^{-1}, which can be attributed to hydrogen bonding involving the NH₄$^+$ group.[58] A sharp peak observed at 1416 cm^{-1} was also observed, which may be attributed to NH₄F molecules attached to the surface of SiNWs. Apparently, rinsing with water for 1 min immediately after etching cannot completely remove the residual NH₄F on the surface for the high-concentration solutions.

To explore the different surface structures of SiNWs versus Si wafers, two extreme concentrations of NH₄F solutions, 5 and 40%, were used to etch as-prepared SiNWs, and their FTIR spectra were taken. As shown in Figure 8, after etching in 5% NH₄F for 10, 50, and 100 min and rinsing briefly in deionized water for 1 min, only Si$-$O bands at ~1060 and ~810 cm^{-1} were observed. No silicon hydride species, Si$-$H$_x$ (x = 1,2,3), were observed in all of the spectra. Figure 9 shows the effect

of water rinsing. After etching in 5% NH₄F for 100 min, followed by rinsing with deionized water for 1 and 5 min, the peaks at ~3320 and ~1420 cm^{-1}, attributable to the ammonium ions on the surfaces of the etched SiNWs, completely disappeared. This observation suggested that the residual NH₄F molecules adsorbed on the SiNW surfaces can be washed away by rinsing. Similar results were also obtained from SiNWs etched with a 40% NH₄F solution, as shown in Figure 10. The only difference here is that a longer time (5 min) was needed to remove the peaks at ~3320 and ~1420 cm^{-1} due to NH₄F for the high-concentration solution (40%).

These results suggest that the surfaces of HF-etched SiNWs are hydrogen-passivated but not the NH₄F-etched SiNWs. The latter finding is at odds with the well-known fact that the NH₄F etching of Si wafers, like HF etching, produces hydrogen-passivated surfaces. As we shall see later, this striking difference in the surface speciation as well as the differences in the etching behavior described earlier can be attributed to the high reactivity of SiNWs, due to their nanosizes, in terms of the hydrolysis of the surface hydrides in aqueous media, especially at high pH values.

Discussion

The dependence of the stability of hydrogen-terminated Si wafer surfaces on different etching solutions with different pH
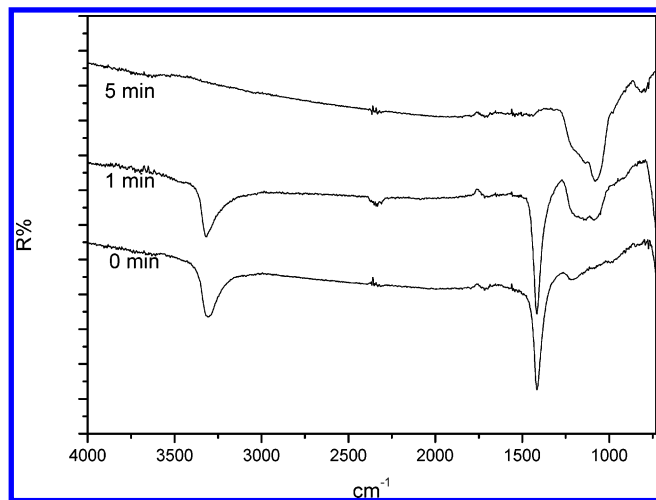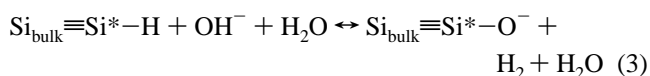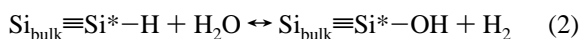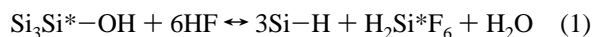
Figure 10. ATR-FTIR spectrum of SiNW etched in 40% NH_4F for 5 min and rinsed in deionized for different periods of time.

values had been reported in the literature.[24,26−27] Solutions such as dilute (2%) HF solution, concentrated (40%) NH_4F, and buffered HF solutions with different pH values had been used by many groups to etch Si surfaces of different morphologies. It was found that the etching rate increases as the scale of roughness decreases. Thus, more open adstructures such as adatoms, kinks, steps, and corners are prone to attacks and easily removed whereas more compact structures such as the atomically smooth (111) plane or a straight step (without atomic kinks) are more resistant to attacks and have a lower etching rate.

It was also observed that the higher the pH of the solution, the easier it is to remove the surface species from the Si wafer. The generally accepted rationale is that the H_2O molecule or the OH^- ion in the solution can attack the hydride species on the hydrogen-terminated Si surface. Possible solid/aqueous reactions in acidic, neutral, and basic etching solutions can be schematically represented by, respectively

$$Si_3Si^*-OH + 6HF \leftrightarrow 3Si-H + H_2Si^*F_6 + H_2O \quad (1)$$

$$Si_{bulk} \equiv Si^*-H + H_2O \leftrightarrow Si_{bulk} \equiv Si^*-OH + H_2 \quad (2)$$

$$Si_{bulk} \equiv Si^*-H + OH^- + H_2O \leftrightarrow Si_{bulk} \equiv Si^*-O^- +$$
$$H_2 + H_2O \quad (3)$$

where Si* represents the surface Si atom and Si_{bulk} represents the underlayer silicon atoms. Here, we show only monosubstituted surface moieties. The same apply to di- and trisubstituted species. In eq 1, HF etching of the hydroxylated silicon surface leaves behind a new hydrogen-terminated surface. This is a fast reaction. The newly formed SiH_x surface moieties are slowly hydrolyzed in neutral (eq 2) or basic (eq 3) media to form hydroxylated or negatively charged oxide surfaces, respectively. These are the rate-determining steps. We shall make use of these reactions in later discussions.

Etching Behavior. Conventionally, the ionization of HF in water can be represented by a two-step process

$$H_2O + HF \leftrightarrow H_3O^+ + F^- \quad (4)$$

and

$$HF + F^- \leftrightarrow HF_2^- \quad (5)$$
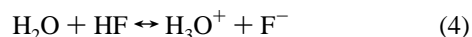
The first step, with an equilibrium constant of 3.53×10^{-4} (pK_a = 3.45) at 25 °C,[59] implies only a few percent of HF dissociates in water. The secondary association has an equilibrium constant of 3.96.

On the basis of these reactions, the peculiar etching behavior for HF (Figure 2, solid squares) can be rationalized as follows. From our previous FTIR spectroscopic study, it is known that the surfaces of HF-etched SiNWs are passivated by $Si-H_x$ species (see ref 56 for details). In very low concentrations (e.g., 0.5%), the etching rate is slow because the HF concentration is low, i.e., there are simply not enough HF molecules to attack the SiNWs. As the HF concentration increases, the etching rate increases, and the time required to dissolve the SiNWs decreases. The highest etching rate (i.e., the shortest time in Figure 2) was observed for a 2% (1 M) HF solution, which may have the highest concentration of the "active" molecules (such as HF or HF_2^-) responsible for the etching. Beyond this critical concentration, especially in concentrated HF solutions (e.g., 20% and 40%), the solution contains significant proportions of higher oligomeric (dimers, trimers, hexamers, etc.) species such as $(HF)_x$ and $(HF)_x \cdot F^-$, thereby depleting (relatively) the concentration of the active molecule(s). Another scenario, though not necessarily mutually exclusive, is that the hydrogen-passivated SiNW surfaces are effectively covered with HF (as well as with related species such as higher oligomers, HF_2^-, F^-, etc.) in higher-concentration solutions, thereby impeding the etching process. This latter effect is made possible by the extensive networks of strong hydrogen bonding between the $Si-H_x$ species on the passivated surface and the chemisorbed HF (and related) molecules. As a result, the etching process is tempered as the coverage increases, and the etching rate becomes increasingly slow as the concentration of the HF solution increases. Since the natural pH of the HF solutions ranges from 1 to 2, we conclude that SiNWs etched with HF are covered with $Si-H_x$ species and are stable in this pH range. These results are similar to those of the 2-D Si wafers in which the maximum etching rate for HF was observed at a pH of 2.5 and the resulting surfaces are hydrogen-terminated. These latter surfaces are stable in solutions with pH < 3.[26]

Figure 3 shows the etching results (solid squares) of SiNWs in NH_4F solutions of different concentrations (0.5, 1, 2, 5, 10, 20, and 40%). The natural pH of these solutions is about 7.8. Since no $Si-H_x$ stretching frequencies were observed in the FTIR spectra of SiNWs etched with NH_4F (vide supra), we conclude that there are two possibilities. The first is that the NH_4F etching mechanism is different from that of HF etching for SiNWs. The second, more likely, scenario is that the $Si-H_x$ formed initially were so unstable that they were etched away immediately by further reactions with NH_4F or the OH^- ions. Either way, the etching behavior of SiNWs differs greatly from that of a Si(111) wafer when NH_4F is used as the etchant. With NH_4F, a Si wafer produces almost perfect "atomically flat surfaces" passivated with $Si-H_x$ species and with little defects.[24] We shall discuss this difference in the etching behaviors between 1-D and 2-D silicon systems later.

It should be emphasized that the different etching behaviors of SiNWs in NH_4F versus in HF may also be due to the different species present in the solutions. Since NH_4F is the salt of a weak base, NH_4OH, and a weak acid, HF, the solution chemistry is governed by (at least) two equilibria, as follows

$$NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+$$

$$F^- + H_2O \leftrightarrow HF + OH^-$$
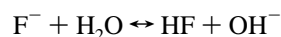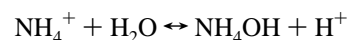
SCHEME 1: pH Dependence of Surface Species of SiNW in HF and NH₄F Etchants
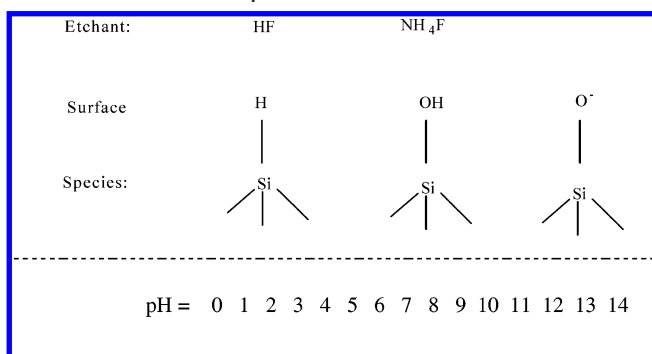
The $pK_b = 4.75$ of NH₄OH (or NH₃/H₂O) is somewhat larger than the $pK_a = 3.45$ of HF, resulting in the pH of the solution of 7.8, a slightly alkaline solution. We believe, however, that the observation that SiNWs are easily etched by NH₄F may be related to the natural pH of NH₄F solutions. At such a pH, Si−H$_x$ species are not stable and are easily hydrolyzed to give Si−OH moieties (Scheme 1) as shown in eq 2. Even if the surface Si−H$_x$ ($x = 1−3$) species were to survive for a while immediately after the etching process, the Si−Si back-bonds would have subsequently been attacked by water molecules to form O₃Si−H, O₂Si−H₂, and OSi−H₃ moieties within minutes, as indicated by our previous ATR-FTIR study[56] of the stability of HF-etched SiNWs in neutral water. The O₃SiH, O₂SiH₂, and OSiH₃ moieties thus formed on the surfaces of SiNWs are rapidly etched away by further reactions with the etchant, leaving the surfaces OH-terminated. We therefore conclude that SiNWs are relatively unstable in NH₄F solutions, especially at high concentrations.

Further support of these rationales comes from a comparison of etching behavior of SiNWs in NH₄F in air versus under nitrogen (solid squares and open circles, respectively, in Figure 3). As mentioned earlier, oxygen in air increases the etching rate by about a factor of 2. This phenomenon is not difficult to understand since at the natural pH of 7.8 silicon hydride species formed on the surfaces of SiNWs are unstable and are easily oxidized by the dissolved oxygen. The resulting silicon oxide layers are subsequently hydrolyzed and etched away. The etching rate decreases significantly when air is excluded. This behavior is in sharp contrast with the "passivation" of the silicon hydride surfaces of SiNWs by HF (or related) molecules in HF solutions (which greatly hinders air oxidation) such that the corresponding curves in Figure 2 are virtually identical. The dramatic effect of oxygen on the etching behavior of silicon nanowires can be compared to the similar effect first observed for a Si wafer by Wade and Chidsey[47] and further studied by other groups (for example, Garcia, Bao, and Hines.[48]) We shall discuss this effect in more detail later.

The concentration dependence of the stability of SiNWs in base-modified NH₄F solutions, with the pH maintained at 14, produced a totally different etching behavior shown in Figure 4. Here, the time required to totally etch away the SiNWs increases with increasing NH₄F concentration, which is in sharp contrast to the results obtained in pristine NH₄F solutions shown in Figure 3**.** In other words, SiNWs etched with NH₄F become increasingly more stable as the concentration of the etchant increases while maintaining the pH at 14. Given the FTIR results discussed previously, this peculiar etching behavior can be rationalized as follows. As discussed earlier, in alkaline (OH⁻-rich) solutions, the surface Si−H$_x$ ($x = 1−3$) moieties are readily converted to Si−(OH)$_x$ ($x = 1−3$) moieties. This can occur via

either the hydrolysis reaction catalyzed by the hydroxide ions (eq 2) or by direct attack of the Si−H$_x$ ($x = 1−3$) bonds by the OH⁻ ions (eq 3). At high enough pH (e.g., 14), the surface Si−(OH)$_x$ moieties are subsequently deprotonated to form Si−(O⁻)$_x$, as depicted in Scheme 1. (Note that Si−(OH)$_x$ is a weak acid; deprotonation occurs readily at pH > pK_a.) Subsequently, the negatively charged surface states are stabilized by NH₄⁺ cations. This effectively passivates the silicon surface, thereby impeding the etching process. Hence, the stability of the SiNWs increases with increasing NH₄F concentrations.

Base-modified 5% HF solution was also employed to assess the stability of SiNWs as a function of pH. The result is shown in Figure 5. SiNWs exhibit relatively poor stability in base-modified HF solutions, especially at pH > 4. This is consistent with the etching curves shown in Figure 2 where SiNWs are quite stable in the natural pH values ranging from 1 to 2 (for HF concentrations of 0.5 to 40%). At pH > 4, reactions with water (hydrolysis) or direct attack by the hydroxide ions convert the surface Si−H$_x$ bonds to surface Si−(OH)$_x$ moieties where $x = 1−3$. The surface Si−(OH)$_x$ moieties thus formed significantly weaken the Si−Si back-bonds and are etched away easily. The final product in solution is Si(OH)₄ or its dissociation product such as $[SiO_4H_2]^{2-}$ in alkaline solutions. It is thus concluded that SiNWs etched with HF, with the surfaces passivated by Si−H$_x$ ($x = 1−3$) moieties, are unstable at pH > 4.

The pH dependence of the stability of SiNWs in acid- or base-modified 40% NH₄F solutions was also investigated, and the results are shown in Figure 6. It can be seen that SiNWs exhibit relatively low stabilities in the pH range from 2 to 10 but exhibit high stability at pH values greater than 10. For pH > 10, the stability increases linearly with the pH. This etching behavior is very different from, indeed opposite to, the HF etching curve depicted in Figure 5. The striking difference can be understood in the following manner. At low or neutral pH, the lack of "protection" by HF or HF-related molecules renders the etched silicon surfaces vulnerable to attacks by the water molecules (hydrolysis reaction, which may also be catalyzed by hydroxide ions, as per eqs 2 and 3). At relatively high pH values, direct attacks by the OH⁻ ions convert the surface hydrides into surface hydroxides as described above. In both cases, the subsequent weakening of the Si−Si back-bonds facilitates further etching, contributing to the instability. At high enough pH values (pH > 10), however, the surface Si−(OH)$_x$ moieties are readily deprotonated to form Si−(O⁻)$_x$. And, as stated previously, the negatively charged Si surfaces are subsequently "covered" with or passivated by the NH₄⁺ ions (with a high concentration of 40%), thereby impeding the etching process. Obviously, the higher the pH (for pH > 10), more facile will be the deprotonation reaction and the subsequent passivation of the surfaces by the ammonium ion (which is in abundance in a 40% solution). As a result, the stability of the SiNWs increases, albeit unexpectedly, with pH for pH > 10.

Similarities and Differences in Etching Behavior between 1-D and 2-D Si. In this section, we shall discuss the similarities and differences of the etching behaviors and the resulting surface speciations between the 1-D SiNWs and the 2-D Si wafers. As we have already seen, while there are many similarities between 1-D and 2-D silicon systems, there are also striking differences.

First and foremost, our ATR-FTIR measurements showed that, while etching SiNWs with HF gave rise to Si−H$_x$ surface species, no Si−H$_x$ species were observed when SiNWs were etched with NH₄F. The former is in line with the 2-D results. The latter, however, is at odds with the corresponding results

reported for the 2-D Si wafers where etching with NH_4F produces $Si-H_x$ species on the surface. Indeed, etching Si wafers with HF, NH_4F, or HF buffered with NH_4F (BHF) all give rise to hydrogen-terminated silicon surfaces.

Second, it was found in this work that SiNWs are stable only in relatively narrow pH ranges in these solutions. When SiNWs are etched with HF, the stability range is pH = 1−2 where the surface moieties are $Si-H_x$ species ($x = 1-3$). When SiNWs are etched with NH_4F, the stability range is pH = 12−14 where the surface moieties are mainly $Si-(O^-)_x$ species ($x = 1-3$). These results are rationalized, for the first time, in terms of passivation of the SiNW surfaces by HF or related molecules via hydrogen bonding for Si−H-terminated surfaces in HF solutions and by NH_4^+ ions via ionic bonding with the $Si-O^-$-terminated surfaces in NH_4F solutions, respectively.

Third, the different effects of oxygen on the etching behavior of 1-D SiNWs in acidic (HF) versus basic (NH_4F) solutions, as exemplified by Figures 2 and 3, respectively, may be related to the dramatic changes in surface morphologies of 2-D silicon wafers upon etching in oxygen-containing versus oxygen-free etchants. For example, Garcia et al.,[48] reported that Si(111) surfaces etched in buffered HF solution (BHF) containing oxygen are much rougher than those etched in oxygen-free BHF (both of pH ≈ 4.7). This effect was interpreted by these authors via a model involving kinetic competition between oxygen-induced and etchant-induced oxidation reactions. These authors proposed a two-step mechanism involving the first, rate-determining oxidation reaction induced either by OH^- (similar to eq 2 or 3) or by O_2 (see eq 6 below), followed by rapid etching of the oxidized species (eq 1). The oxygen-induced oxidation may be represented schematically as follows

$$Si_{bulk}\equiv Si^*-H + {}^1/_2O_2 \leftrightarrow Si_{bulk}=(SiO)Si^*-H \qquad (6)$$
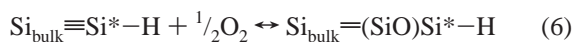
Here, (SiO) represents the attack of the silicon back-bonds by the dissolved O_2 and the formation of the underlayer oxides, resulting in surface moieties such as O_3SiH, O_2SiH_2, and $OSiH_3$ as described earlier. Furthermore, previous morphological studies have shown that OH^- is a highly *anisotropic* oxidant with the following site-specific rate of attack (for eq 2 or 3)

$$kink > dihydride\ step > monohydride\ step \gg terrace \qquad (7)$$

However, O_2 is an *isotropic* oxidant with the following site-specific rate of attack (eq 6)

$$dihydride\ step \approx monohydride\ step \geq kink \gg terrace \qquad (8)$$

According to these authors, the etched surface morphology reflects the kinetic competition between these two oxidants. In low pH solutions (i.e., low OH^- concentration), the etch morphology is rough since O_2 oxidation dominates and the etching is isotropic. In high pH solutions, the etching is dominated by OH^- (which has a high concentration), and the etch morphology is primarily determined by the anisotropy of the etchant (OH^-). Since the rates of attacks of kinks and steps by OH^- are much faster than that of the terraces, they are preferentially etched away. Thus, defect-free, almost perfect atomically flat surfaces of Si(111), passivated with $Si-H_x$ species, can be obtained by etching with NH_4F (which has a pH of 7.8).[27,60−63]

We should add that there are many other studies regarding the pH dependence of the etching of Si wafers in various etching solutions. For example, Jakob and Chabal[26] first reported that a Si(111) surface etched in low pH (<5) HF-containing solutions exhibited a rough morphology, whereas those etched in high

pH (∼6.6) HF-containing solutions gave rise to atomically smooth surfaces.[60] Most of these observations, in general, can be understood by taking into account the effects of pH and oxygen. For silicon wafers, a third important factor is the crystal orientation of the surface. Under similar conditions, for example, etching of Si(100) surfaces generally produces rougher surfaces. It is generally believed that the close-packing structure of the terminal hydrides on the Si(111) surfaces contributes to the smoothness of the surface by hindering the attacks by the etchants. However, a recent report by Schmidt et al.[45] showed that, in fairly acidic (pH ≈ 0.5) solutions such as HF/H_2SO_4, etching of Si(100) surfaces can also produce smooth surfaces. This latter observation may also be related to the etching behavior of SiNWs in acidic (pH < 1) HF solutions discussed in this paper (Figure 2). Here, the effect of oxygen on the etching curve was minimal (almost nonexistant). Apparently the passivation of the silicon surfaces by HF under acidic conditions protects the surfaces from attack by oxygen (oxidation) for both 1-D and 2-D Si systems.

A fourth factor is the oxidizing power and the anisotropy, if any, of the etchant. We already discussed the effect of the anisotropy of the OH^- ion. In the example cited above, as pointed out by Schmidt et al.,[45] one cannot rule out the possibility of the anisotropic etching effect of the sulfate ion (as an oxidant), which preferentially etches away the kinks and steps, thereby giving rise to smooth Si(100) wafer surfaces. In other words, in the 2-D Si system, one must also consider the oxidizing power (and its anisotropy, if any) of the etchant, in addition to the pH value of the solution. This is particularly true in view of the observation that no improvement in surface quality of Si(100), relative to conventional etching, in dilute HF solution can be achieved when the pH was lowered by adding HCl instead of H_2SO_4.[45] In contrast, for the 1-D SiNWs studied here, we find no significant differences in the etching behavior when using either HCl or H_2SO_4 to alter the pH of the solutions (Figure 6).

It is interesting to note that SiNWs used in this study were grown from SiO; they have mainly Si(111) surfaces, yet their etching behaviors differ from those of the 2-D systems in many instances. For example, while NH_4F is a very *slow* etchant for Si(111) surfaces in the 2-D system, it is an *efficient* etchant for the 1-D SiNWs, which also have predominantly Si(111) faces. We believe that this difference is attributable to the nanoscale dimensions of the 1-D SiNWs, which are comparable those of the kinks and steps of the 2-D silicon systems.

Conclusion

This paper reports a systematic study of the etching behavior and the surface speciation of SiNWs in various HF and NH_4F etching solutions. Specifically, the concentration and pH dependences of the etching time or the stability of SiNWs in these solutions were investigated. We conclude that both HF and NH_4F are efficient etchants for SiNWs and that SiNWs are stable only in relatively narrow pH ranges in these solutions. When SiNWs are etched with HF, the stability range is pH = 1−2 where the surface moieties are $Si-H_x$ species ($x = 1-3$), and at high HF concentrations, the hydrogen-terminated Si surfaces are covered with (passivated by) HF or HF-related molecules through hydrogen bonding. When SiNWs are etched with NH_4F, the stability range is pH = 12−14 where the surface moieties are mainly $Si-(O^-)_x$ species ($x = 1-3$), and at high NH_4F concentrations, the negatively charged Si surfaces are stabilized (passivated) by NH_4^+ ions via ionic bonding. These features can be represented schematically in Scheme 1, using mono-

substituted surface silicon as examples, respectively. The same principles apply to di- and trisubstituted surface speciations. It is interesting to note that, while etching SiNWs with HF gives rise to Si$-$H$_x$ surface species, no Si$-$H$_x$ species were observed when SiNWs were etched with NH$_4$F, as revealed by FTIR spectroscopy. In contrast, with Si wafers, etching with either HF or NH$_4$F produces Si$-$H$_x$ species on the surface. This difference suggests either that the etching mechanisms for NH$_4$F versus HF are different for SiNWs or, more likely, that the Si$-$H$_x$ surface species produced in NH$_4$F solutions are so unstable that they are hydrolyzed readily at pH > 4.

The similarities and differences of the etching behaviors and the resulting surface speciations between SiNWs and Si wafers, using the same etchants and under similar conditions are also discussed. It is obvious that, for both 1-D and 2-D Si systems, variables such as the concentration and the pH value of the etching solutions and the oxidizing power (and its anisotropy, if any) of the etchant, along with experimental parameters such as the etching time and the dissolved oxygen, all play important roles in determining the etching behavior, the resulting surface speciation, and the quality (smoothness, definition) of the surfaces. It is believed that the nanoscale structures as well as the low dimensionality (1-D) of SiNWs may have contributed to the rapid hydrolysis of the surface Si$-$H$_x$ species, especially at high pH values. In this context, 1-D SiNWs may also be considered as ensembles (or models) of kinks, steps, and narrow terraces of rough 2-D surfaces.

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