Three-Dimensional Etching Profiles and Surface Speciations (via Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy) of Silicon Nanowires in NH4F-Buffered HF Solutions: A Double Passivation Model

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A systematic study of the etching behavior, in terms of three-dimensional profiles, of one-dimensional (1-D) silicon nanowires (SiNWs) in NH4F-buffered hydrofluoric acid (BHF) solutions of varying concentrations and pH values and the surface speciations of the resulting etched SiNW surfaces, as characterized by attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, is reported. It was found that SiNWs are stable only in relatively narrow pH ranges of the BHF solutions. The results are rationalized in terms of a "double passivation" model. When SiNWs are etched in BHF solutions with pH values of 1−3, the surfaces are passivated with hydrogen (inner layer) giving rise to surface moieties such as Si−H$_x$ species ($x = 1$−3); at high HF concentrations, the H-terminated Si surfaces are covered with a hydrogen bonding network of HF and related molecules (oligomers, etc.), providing an outer-layer passivation. When SiNWs are etched in BHF solutions with pH values of 11−14 (by adding a strong base such as NaOH), the surfaces are oxygen-terminated with surface moieties such as Si−(O$^-$)$_x$ species ($x = 1$−3); at high NH4F concentrations, the negatively charged Si surfaces are stabilized by NH4$^+$ ions via ionic bonding, again providing outer-layer passivation. In BHF solutions with pH values of 3−11, the surface speciation, consisting of Si−(OH)$_x$(O$^-$)$_y$ ($x + y = 1$−3) species, is unstable and etched away rapidly. The surface speciations of SiNWs etched in various BHF solutions were explored via ATR-FTIR spectroscopy. It was found that, while etching SiNWs with HF-rich BHF solutions with pH < 4 gave rise to Si−H$_x$ surface species, no surface Si−H$_x$ species were observed with SiNWs etched in BHF solutions with pH ≥ 4 (HF/NH4F ≤ 1:1). In sharp contrast, etching of two-dimensional (2-D) Si wafers with either HF, NH4F, or BHF etchants produces Si−H$_x$ species on the surface. Finally, while HF is a much more efficient etchant than NH4F for 2-D Si surfaces, NH4F is found to be as efficient an etchant as HF for SiNWs (this work). We believe that these differences can be attributed to the nanometer size (corresponding to the roughness scale in 2-D wafers) of SiNWs on one hand and the lack of "passivation" by the hydrogen bonding network of HF and related molecules at pH ≥ 4 on the other. These two factors, among others, contribute to the rapid hydrolysis of the surface Si−H$_x$ species (and the etching of the SiNWs), particularly in BHF solutions with low HF/NH4F ratios and high pH values (pH ≥ 4).

Introduction

In the silicon industry, wet etching is a key step in producing ultraclean silicon surfaces that are contamination-free, topologically flat, and chemically stable for subsequent wafer processing.[1−17] One of the widely used techniques for removing silicon oxide from a silicon surface is etching with dilute hydrofluoric acid (HF), usually buffered with concentrated ammonium fluoride (NH4F) solution. These buffer solutions are commonly referred to as NH4F-buffered HF (BHF) etchants. It is now known that, upon HF, NH4F, or BHF treatment, the silicon surfaces are terminated with various hydride species such as SiH, SiH$_2$, and SiH$_3$.[8−20,43−57]

In recent years, one-dimensional (1-D) silicon nanowires (SiNWs) have attracted much attention, both in fundamental research and in potential device applications, because of their apparent compatibility with the two-dimensional (2-D) silicon wafers. Many synthetic methods, for example, vapor−liquid−solid (VLS) reaction and oxide-assisted growth,[21−27] have been developed to generate bulk quantities of SiNWs. Properties such as the photoluminescence, electron field emission, thermal and electronic conductivities, and surface chemical reactivity of SiNWs have been studied extensively.[28−39] Unfortunately, relative to the 2-D Si wafers, information regarding the surface states of 1-D SiNWs is relatively scarce.

Recently, we reported the etching behavior and the surface speciation of SiNWs in various pristine HF and NH4F etching solutions.[38,39] Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopic measurements showed that, while etching SiNWs with HF gives rise to Si−H$_x$ surface species, no Si−H$_x$ species can be observed when SiNWs are etched with NH4F. This latter finding is at odds with the

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TABLE 1: Molar Concentrations of Mixed HF−NH$_4$F Solutions Used To Etch the SiNWs

HF conc (%)	molar concentrations at the following NH$_4$F conc (%)							
	0	1	2	5	10	20	35	40
0		0.27	0.54	1.37	2.77	5.67	10.27	11.88
0.5	0.25	0.25:0.27	0.25:0.54	0.25:1.37	0.25:2.77	0.25:5.67	0.25:10.27	
1	0.5	0.5:0.27	0.5:0.54	0.5:1.37	0.5:2.77	0.5:5.67	0.5:10.27	
2.5	1.25	1.25:0.27	1.25:0.54	1.25:1.37	1.25:2.77	1.25:5.67	1.25:10.27	
4	2	2.0:0.27	2.0:0.54	2.0:1.37	2.0:2.77	2.0:5.67	2.0:10.27	
5	2.52	2.52:0.27	2.52:0.54	2.52:1.37	2.52:2.77	2.52:5.67	2.52:10.27	
10	5.14	5.14:0.27	5.14:0.54	5.14:1.37	5.14:2.77	5.14:5.67		
20	10.7	10.7:0.27	10.7:0.54	10.7:1.37	10.7:2.77	10.7:5.67		
35	19.56	19.56:0.27	19.56:0.54	19.56:1.37				
40	22.8							

corresponding results reported for the 2-D Si wafers where etching with NH$_4$F also produces Si−H$_x$ species on the surface.

To further delineate the different etching actions of HF vs NH$_4$F on silicon surfaces of 1-D SiNWs vs 2-D Si wafers and the resulting surface speciations, we decided to perform a systematic study of the etching behaviors of 1-D SiNWs in mixed HF−NH$_4$F solutions. Specifically, three-dimensional etching profiles of SiNWs, prepared via the oxide-assisted growth technique, in various NH$_4$F-buffered HF (BHF) solutions of different concentrations and pH values were determined. Furthermore, the surface speciations of the resulting etched SiNWs were characterized by ATR-FTIR spectroscopy. The results are reported herein. Surprisingly, while there are many similarities between 1-D and 2-D systems, there are also striking differences. These findings are rationalized in terms of an etching mechanism and a "double passivation" model involving hydrogen bonding of the surface Si−H moieties with HF molecules (at low pH of <4) or ionic bonding of the surface Si−O$^-$ species with NH$_4^+$ ions (at high pH of >10), depending upon the relative concentrations of HF vs NH$_4$F and the pH of the etching solution. It is hoped that detailed information regarding the etching behavior and surface speciation of SiNWs will facilitate the future development of SiNWs in mesoscopic electronic device applications and the transition of silicon-based microelectronics/photonics to nanoelectronics/photonics.

Experimental Section

SiNWs were prepared by the thermal evaporation of pure SiO powder (Aldrich, 325 mesh, 99.9%) at 1250 °C in an evacuated alumina tube.[25] The carrier gas consisted of 95% Ar and 5% H$_2$ with a flow rate of 50 sccm (standard cubic centimeters per minute), and the system was kept at a pressure of 400 mbar during the growth for 4 h. The products were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As-prepared SiNWs are free-standing wires of hundreds of nanometers in length. Each wire has a single crystalline silicon core of approximately 15−20 nm in diameter and is sheathed with an oxide layer of about 3−5 nm in thickness.

To investigate the etching behavior of SiNWs in different chemical solutions, as-prepared SiNWs (in the shape of a spongy golden-yellow ball of approximately 3 mm in diameter) were immersed into 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 mixed HF−NH$_4$F solutions of varying concentration ratios. The percent and molar concentrations are given in Table 1. The measured etching times are tabulated in Table 2 and plotted in Figures 1−3. Figures 1 and 2 are cross sections of the three-dimensional (3-D) plot shown in Figure 3. The etching times are taken as measures of the relative "stability" of the SiNWs in the respective solutions.

TABLE 2: Etching Times in Minutes of SiNWs in Various Mixed HF−NH$_4$F Solutions with Molar Concentrations Tabulated in Table 1

HF conc (%)	etching times at the following NH$_4$F conc (%)							
	0	1	2	5	10	20	35	40
0		380	310	260	198	145		115
0.5	620	460	400	320	250	180	130	
1	190	270	230	205	190	170	130	
2.5	112	180	140	118	110	100	100	
4	172	260	225	212	185	158	135	
5	228	290	258	236	220	210	195	
10	305	335	310	290	260	240		
20	485	390	355	330	295	272		
35		435	395	368				
40	780							
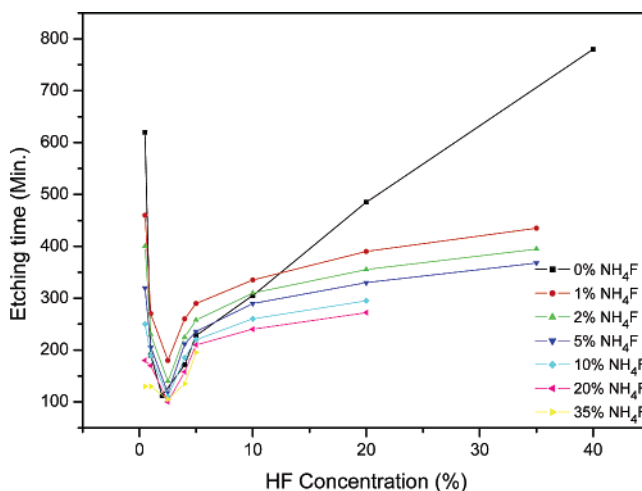
Figure 1. Etching time of SiNWs in mixed HF−NH$_4$F solutions as a function of HF concentration at various NH$_4$F concentrations (mass %).

It was found that the etching profile critically depends on the pH value of the solution. Hence, it was deemed necessary to measure the pH of the solutions used. The pH measurements were performed with a glass electrode pH meter. The results are tabulated in Table 3. A 3-D plot of the pH values is shown in Figure 4. To minimize corrosion of the glass electrode, the time of each pH measurement was kept to a minimum. Furthermore, the accuracy was checked by measuring the known pH values of standard solutions before and after each measurement.

To characterize the surface speciation of the etched SiNWs, ATR-FTIR spectra of SiNWs etched with select mixed HF−NH$_4$F solutions were recorded. For FTIR measurements, the as-prepared SiNWs samples were etched in a freshly prepared etching solution for 20 min. The solution mixtures used were of different molar ratios, namely, HF/NH$_4$F = 9:1, 7:3, 5:5,
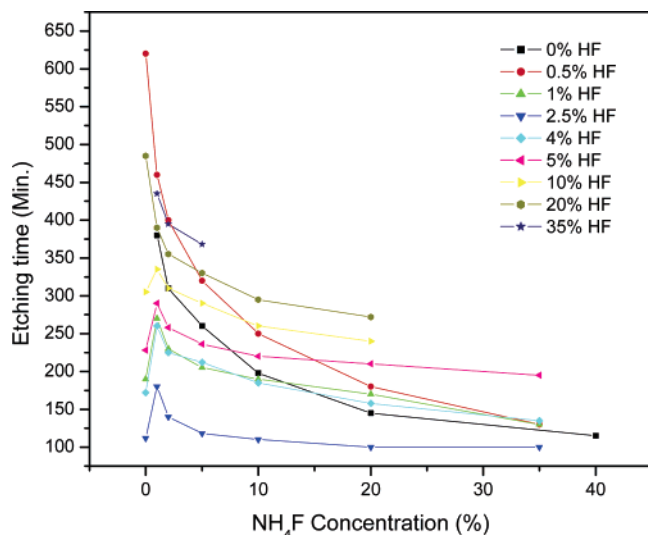
Figure 2. Etching time of SiNWs in mixed HF−NH$_4$F solutions as a function of NH$_4$F concentration at various HF concentrations (mass %).
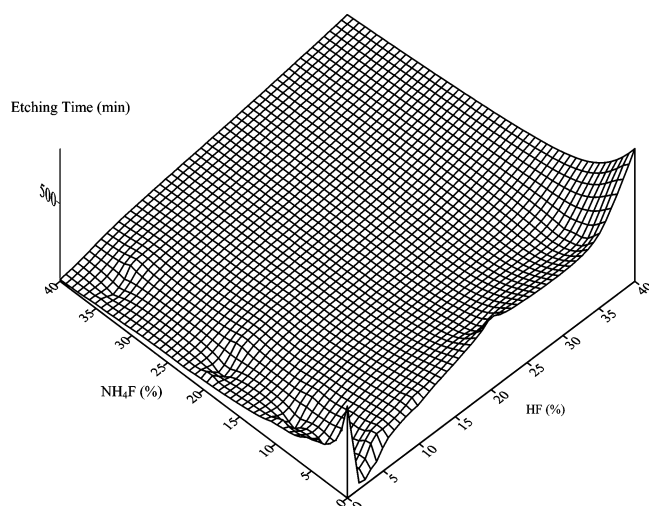

Figure 3. Contour map of the etching times as functions of HF and NH$_4$F concentrations (mass %).

TABLE 3: Measured pH Values of the Various Mixed HF−NH$_4$F Solutions with Molar Concentrations Tabulated in Table 1

HF conc (%)	pH values at the following NH$_4$F conc (%)							
	0	1	2	5	10	20	35	40
0		5.83	6.00	6.25	6.42	6.89		7.18
0.5	1.90	4.03	4.23	5.12	5.75	5.93	6.44	
1	1.74	3.92	4.09	5.03	5.59	5.97	6.22	
2.5	1.59	3.42	3.37	4.35	4.90	5.34	5.83	
4	1.42	3.07	3.16	3.98	4.52	4.88	5.57	
5	1.38	2.90	3.04	3.86	4.40	4.71	5.28	
10	1.22	2.13	2.21	2.79	3.20	3.47		
20	1.07	1.57	1.69	2.30	2.81	3.04		
35		1.24	1.37	1.81				
40	0.91							

and 3:7 prepared from 5% HF and 40% NH$_4$F solutions. The final molar concentrations of HF/NH$_4$F were 2.41:0.27 M, 2.28:0.97 M, 2.05:2.05 M, and 1.67:3.89 M, and the measured pH values were 2.82, 3.13, 4.21, and 5.60, respectively. To avoid unwanted reactions on the surfaces of the etched SiNWs, the rinsing step was skipped; the etched SiNWs were dried in a vacuum and stored under nitrogen until ATR-FTIR measurements. The ATR-FTIR measurements were performed in air
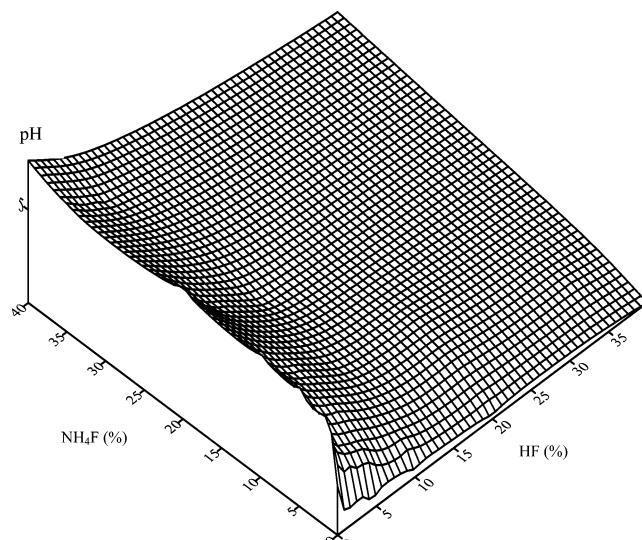

Figure 4. Contour map of the pH values as functions of HF and NH$_4$F concentrations (mass %).

using an i-series FTIR microscope equipped with a 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}. ATR-FTIR spectra in the range of 700−4000 cm^{-1} are depicted in Figure 5.

Teflon spatulas and containers were used throughout the experiments. Unless specified otherwise, all operations and/or measurements were conducted under ambient conditions. For each measurement, efforts were made to use the same amount of SiNWs in order to minimize the effect due to the sample size. Furthermore, SiNWs from the same preparative batch were used to avoid unwanted nanowire-size effects.

Results

Etching Profiles. Figure 1 shows the etching time of SiNWs as a function of HF concentration for a given NH$_4$F buffer. In this paper, the etching time is taken as a measure of the stability of the SiNWs. In this context, the stability (or the "dissolution time") is inversely proportional to the etching rate. Since it takes only 10−30 s to etch away the oxide sheathings of SiNWs, terms such as stability, dissolution time, and "etching rate" in this paper all refer to the etching of the crystalline silicon cores of the SiNWs.

As was found in our recent work (ref 39), 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 an ca. 2% (1 M) HF solution. By adding NH$_4$F to a HF solution (this work), the pH value increases and the V-shaped etching curve moves downward, especially at high HF concentrations, as depicted in Figure 1.

Figure 2 shows the etching time of SiNWs as a function of NH$_4$F concentration for a given HF concentration. It can be seen that, within each curve, the etching time generally decreases with increasing NH$_4$F concentration (and increasing pH, as per Table 3). The shapes of the curves are different from those of the V-shaped etching curves shown in Figure 1. By adding HF to the NH$_4$F solutions (this work), the NH$_4$F etching curves first move downward, reaching a minimum at 2.5% HF, and then inch upward at higher HF concentrations. The shapes of the curves also change somewhat in the course of increasing the HF concentration.

Figure 3 depicts a 3-D contour plot of the etching time as functions of HF and NH$_4$F concentrations. The 3-D contour plot
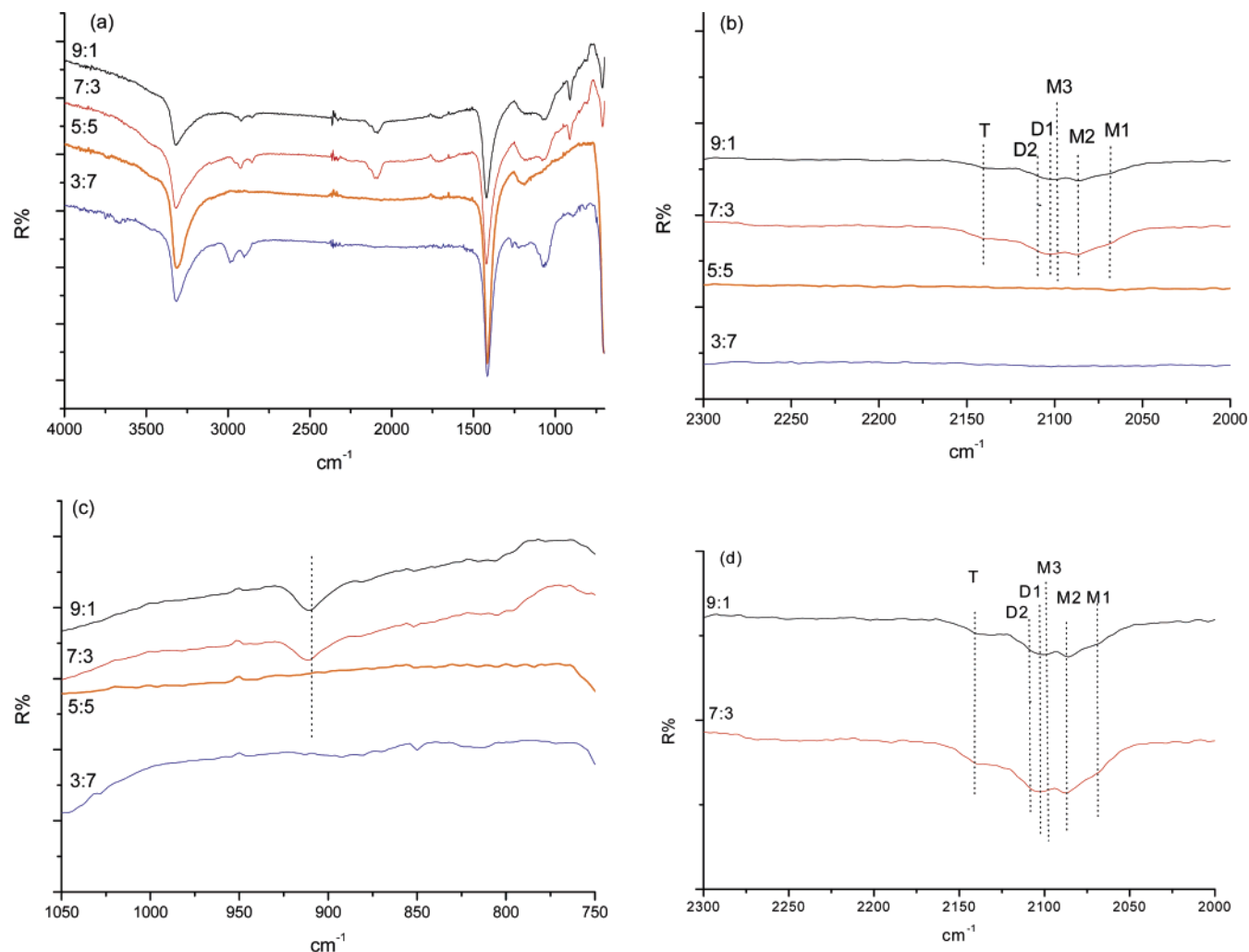
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Figure 5. ATR-FTIR spectra of SiNWs after etching in mixed HF−NH$_4$F solutions with HF/NH$_4$F molar ratios of 9:1, 7:3, 5:5, and 3:7 (a) in the range of 700−4000 cm^{-1}; (b) in the range of 2000−2300 cm^{-1}; (c) in the range of 750−1050 cm^{-1}; and (d) in the range of 2000−2300 cm^{-1} (expanded version).

for the pH values is given in Figure 4. (The small glitches in both contour plots are in part graphical and in part experimental fluctuations.) The corresponding data are tabulated in Tables 2 and 3, respectively. It can be seen that, in general, fast etching rates can be correlated with high pH values and high NH$_4$F concentrations (upper right of Tables 2 and 3). The maximum etching rate occurs at a solution mixture of fairly dilute (2.5%) HF and rather concentrated (35%) NH$_4$F concentrations with a pH value of 5.8. A detailed analysis of Figures 3 and 4 also revealed that long etching times (relatively high stabilities) are observed for low pH values (≤3) and high HF concentrations (lower left of Tables 2 and 3). The pH, in particular, is a critical parameter.

It can be seen from Table 3 that the natural pH of a mixed HF−NH$_4$F solution ranges from 0.91 (40% HF) to 7.18 (40% NH−F), in going from the lower left corner to the upper right corner of Table 3, respectively. In particular, the pH of pristine HF solutions ranges from 1.9 for a 0.5% solution to 0.91 for a 40% solution (first column of Table 3) and that of pristine NH$_4$F solutions ranges from 5.83 for a 1% solution to 7.18 for a 40% solution (first row of Table 3). To investigate the effect of pH on etching beyond this range, we studied the HF etching profile of SiNWs by adding a strong base to extend the pH to 14 in one of our previous works.[39] It was found that SiNWs are relatively stable only in base-modified HF solutions with pH

< 3. At pH > 3, SiNWs are etched away quickly, even in fairly dilute (5%) HF solutions. In a similar manner, we also studied the etching profile of SiNWs in a 40% NH$_4$F solution modified by adding a strong acid or a strong base to extend the pH to 2 or 14, respectively. It was found that SiNWs are relatively stable only in base-modified NH$_4$F solutions with pH ≥ 11. At pH < 11, SiNWs are etched away quickly. In ref 39, we also demonstrated that, while SiNWs are unstable in etchants with high NH$_4$F concentrations, they are relatively more stable in base-modified NH$_4$F solutions with high pH values (e.g., pH > 11) and high concentrations (e.g., 40%). As we shall see later, these seemingly contradictory trends stem from the differences in, and can be correlated with, the pH values of the etching solutions.

ATR-FTIR Characterization of Etched SiNW Surfaces. Our previous ATR-FTIR studies showed that HF-etched SiNW surfaces were terminated by hydrogen[38] (with Si−H$_x$ where x = 1, 2, 3 and absorptions in the region 2000−2200 cm^{-1} and at ∼900 cm^{-1}) whereas no Si−H$_x$ bands were observed for SiNWs etched in pristine NH$_4$F solutions.[39] In the present work, we focused our attention on the etching behavior of SiNWs in NH$_4$F-buffered HF (BHF) etchants. Representative solution mixtures of HF and NH$_4$F, with different HF/NH$_4$F molar ratios of 9:1, 7:3, 5:5, and 3:7, were used to etch the as-prepared SiNWs. The results are shown in Figure 5. It can be seen that

the Si−O bands[40] at ∼1060 and ∼810 cm^{-1} decrease dramatically with increasing HF/NH$_4$F ratios. New absorption bands attributable to Si−H$_x$ (at 2000−2200 and ∼900 cm^{-1}) were observed for BHF etchants with high HF concentrations (HF/NH$_4$F = 9:1 and 7:3). The Si−H$_x$ stretching region is expanded in Figure 5d. Here, we assign M, D, and T bands as being due to monohydrides, dihydrides, and trihydrides, respectively. Three types of monohydrides, labeled M1 (2070 cm^{-1}), M2 (2088 cm^{-1}), and M3 (2098 cm^{-1}); two types of dihydrides, labeled D1 (2102 cm^{-1}) and D2 (2108 cm^{-1}); and a broad peak of the trihydride, labeled T (2138 cm^{-1}), were observed.[38]

For the HF/NH$_4$F molar ratios of 1:1 or lower, no Si−H$_x$ bands were observed, as exemplified by the ratios of 5:5 and 3:7 (see Figure 5). These observations are consistent with our previous results[39] on the etching of SiNWs in pristine NH$_4$F solutions. Both are, however, at odds with the well-known fact that NH$_4$F etching of Si wafers produces H-passivated surfaces.[1−20,43−57]

We will provide a theoretical rationale for the different etching effects of HF vs NH$_4$F for SiNWs in a later section. It is sufficient to say here that the reason lies in the pH of the etchant. *The borderline seems to be a pH value of ca. 4.* Thus, the observation that BHF etchants with HF/NH$_4$F molar ratios of 9:1 and 7:3 give rise to H-terminated SiNW surfaces, whereas the corresponding ratios of 5:5 and 3:7 result in OH-terminated surfaces, can be correlated with the measured pH values of 2.82 and 3.13 and 4.21 and 5.60, respectively, for the four etchants employed in our FTIR study. In fact, we may generalize this statement to include all the BHF etchants listed in Tables 1 and 3, as follows. Those with HF/NH$_4$F molar ratios greater than unity all have pH < 4 and will give rise to H-terminated SiNW surfaces (cf. lower left corner of Tables 1 and 3). For those with HF/NH$_4$F molar ratios of unity or less, which have pH ≥ 4, OH-terminated SiNW surfaces are to be expected (cf. upper right corner of Tables 1 and 3).

Discussion

The most widely used technique for removing silicon oxide from a silicon surface is solution etching.[59−61] There are two broad classes of wet etchants: "isotropic" and "anisotropic". Isotropic etchants include, but are not limited to, HF, HF buffered with NH$_4$F (BHF), and HNA (HF/HNO$_3$/HAc, where HAc stands for acetic acid). Commonly used anisotropic etchants are KOH, NaOH, CsOH, EDP (ethylenediamine pyrocatechol), N$_2$H$_4$·H$_2$O, etc. In this work, we chose to focus our attention on the etching behavior and the resulting surface speciation of SiNWs in mixed HF−NH$_4$F solutions (isotropic etchants). The results are rationalized with an etching mechanism in conjunction with a double passivation model.

Generally speaking, the solution chemistry of a mixed HF−NH$_4$F solution can be represented by the following reactions:

$$HF \leftrightarrow H^+ + F^- \tag{1}$$

$$HF + F^- \leftrightarrow HF_2^- \tag{2}$$

$$2HF \leftrightarrow (HF)_2 \tag{3}$$

$$NH_4OH \leftrightarrow NH_4^+ + OH^- \tag{4}$$

The first is the ionization process. The equilibrium constant of 3.53×10^{-4} (pK_a = 3.45)[41a] implies that only a few percent of the HF dissociates in water. The second is the complexation between the HF molecule and the F$^-$ ion to form the hydrogen

difluoride ion HF$_2^-$. It has an equilibrium constant K_F of 3.96.[41b] The third is the dimerization of HF with an equilibrium constant K_D of 2.7.[41b,c] The fourth reaction is the equilibrium of the weak base ammonia, which has a pK_b of 4.752. In reality, the aqueous solution chemistry of a mixed HF−NH$_4$F solution is much more complicated than that represented by these four equilibria. For example, neutral and/or oligomeric (HF)$_n$ (n = 1, 2, 3, ...) molecules may form chains or rings and anionic (HF)$_n$F$^-$ (n = 1, 2, 3, ...) may form branches; both stem from the extraordinarily strong hydrogen bonding capability of fluorine (as a result of its high electronegativity). Notwithstanding these facts, any attempts to rationalize the etching behavior of SiNWs by NH$_4$F-buffered HF solutions must take into account eqs 1−4 at the very least.

As in our previous work,[39] we may interpret the peculiar V-shape etching profile of SiNWs in HF solutions (Figure 2 of ref 39) as follows. It is known that the "active" species responsible for the etching are HF, HF$_2^-$, etc. In fact, the difluoride HF$_2^-$ is believed to be four times more active than HF as an etchant. On the other hand, the fluoride ion and the oligomers (HF)$_n$ are deemed inactive.[58] Thus, at very low concentrations (e.g., 0.5%), the etching rate is slow because the HF concentration is low. As the HF concentration increases, the etching rate increases. The highest etching rate was observed for a 2% (1 M) HF solution. The etched SiNW surfaces are H-terminated. Beyond this critical concentration and especially in concentrated HF solutions, the equilibria are shifted in favor of the formation of oligomers. The resulting oligomers (HF)$_n$ form an extensive hydrogen bonding network on the surfaces of the SiNWs. In other words, the H-terminated SiNW surfaces are effectively covered with HF and oligomeric (HF)$_n$ species linked together by strong hydrogen bonding, thereby providing "outer-layer" passivation. We may call this double-layer passivation or simply "double passivation". Since only "free" HF and HF$_2^-$ are active etchants, the etching process is increasingly impeded as the hydrogen bonding network coverage increases, leading to increasing etching times at high HF concentrations.

The same mechanism applies to the etching profiles of SiNWs in HF solutions buffered with NH$_4$F, as depicted in Figure 1. By adding NH$_4$F to the HF solutions, the V-shaped HF etching curves move downward because of the increase in the pH and the HF$_2^-$ concentration (see Table 3). The maximum etching rate occurs with a mixed solution of fairly dilute (2.5%) HF and rather concentrated (35%) NH$_4$F concentrations with a pH value of 5.8. A detailed examination of Figures 3 and 4 also revealed that relatively high stabilities (long etching times) are observed for low pH values (<3) and high HF concentrations (lower left of Tables 2 and 3). Coupled with our ATR-FTIR observations (cf. Figure 5), we conclude that SiNWs etched with HF are terminated with Si−H$_x$ species which are relatively stable in BHF solutions with pH ≤ 3 due to the double-layer passivation by the strong hydrogen bonding network of (HF)$_n$ (n = 1, 2, 3, ...), especially at high HF concentrations.

We now turn to the etching profiles of SiNWs in NH$_4$F solutions with HF added. As depicted in Figure 2, upon adding increasing amounts of HF, the NH$_4$F etching curves first moved downward, reaching a minimum at 2.5% HF, and then shifted upward at higher HF concentrations. This can be understood as follows. By adding HF to an NH$_4$F solution, the concentration of the HF$_2^-$ increases rapidly. Since HF$_2^-$ is believed to be four times more effective than HF as an etchant,[58] the etching curves move downward (i.e., faster etching), reaching the minimum at 2.5% HF. The upward shift of the etching curves upon further addition of HF, on the other hand, can be

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rationalized in terms of the impedance of the etching process as a result of the increased HF coverage of the SiNW surfaces (double-layer passivation), as described above. Finally, in the course of these shifts, the shape of the curves changed from a monotonically decreasing trend to an inverted V-shape and, finally, back to monotonic again (see the contour "landscape" of Figure 4).

Our ATR-FTIR measurements showed no Si$-$H$_x$ absorptions in the spectra of SiNWs etched in mixed HF$-$NH$_4$F solutions with pH $\geq$ 4 (cf. Table 3 and Figure 5). The same result was observed with pristine NH$_4$F solutions as etchants.[39] This particular etching behavior differs from that of a Si wafer when NH$_4$F is used as an etchant. With NH$_4$F, or indeed with any of the BHF etchants, a Si wafer almost always produces H-passivated surfaces.[8−20,43−57]

The reason for the difference may be that, at pH $\geq$ 4, Si$-$H$_x$ species are not stable and are easily hydrolyzed to give Si$-$OH moieties (cf. Scheme 1). Even if the surface Si$-$H$_x$ (x =
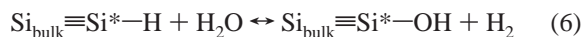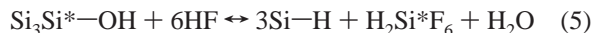
SCHEME 1: Schematic Representations of Different Surface Species on SiNW Surfaces in Various HF$-$NH$_4$F Solutions with Different pH Values
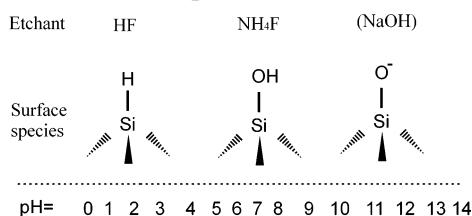
1$-$3) species were to survive for a while (minutes) after the etching process, the Si$-$Si back-bonds (the under layer) will be attacked by water molecules to form O$_3$SiH, O$_2$SiH$_2$, and OSiH$_3$ moieties within minutes, as indicated by our previous ATR-FTIR study of the stability of HF-etched SiNWs in neutral water.[38] The O$_3$SiH, O$_2$SiH$_2$, and OSiH$_3$ moieties thus formed on the surfaces of SiNWs will readily be etched away by further reactions with the etchant, leaving the surfaces OH-terminated.

Etching Behavior of Silicon Surfaces. The stabilities of various Si surfaces in different etching solutions have been well studied.[1−20,43−57] It was found that surface morphology, among other properties, plays an important role in the etching process. Thus, rough surfaces with open adstructures such as adatoms, kinks, steps, and corners are prone to attacks and easily removed, whereas more compact structures such as atomically smooth planes or straight steps are more resistant to attacks and have a lower etching rate (higher activation energy).

It was also observed that the higher the pH of the solution, the easier it is to remove the surface species from the Si surface. The generally accepted mechanism is that HF etching of the oxygenated or hydroxylated silicon surface leaves behind a new H-terminated Si surface, as represented by eq 5. The newly formed SiH$_x$ surface moieties can be hydrolyzed in nearly neutral media to form hydroxylated surfaces or in strongly basic media (pH $>$ 10) to form negatively charged oxide surfaces, as shown in eqs 6 and 7, respectively. In general, the former (eq 5) is a fast reaction, while the latter two reactions (eqs 6 and 7) are the slow, rate determining steps. However, as in the case of the solution chemistry of silanes, the hydrolysis reactions may be catalyzed by traces of hydroxide ion or accelerated in strongly acidic or basic media. We shall use eqs 5$-$7 to denote, schematically, the solid/aqueous interface reactions on the silicon surfaces in acidic, neutral, and basic etching solutions containing HF and NH$_4$F, respectively.

$$Si_3Si^*-OH + 6HF \leftrightarrow 3Si-H + H_2Si^*F_6 + H_2O \quad (5)$$

$$Si_{bulk}\equiv Si^*-H + H_2O \leftrightarrow Si_{bulk}\equiv Si^*-OH + H_2 \quad (6)$$

$$Si_{bulk}\equiv Si^*-H + OH^- \leftrightarrow Si_{bulk}\equiv Si^*-O^- + H_2 \quad (7)$$

In these equations, Si* represents the surface Si atom and Si$_{bulk}$, the underlayer silicon atoms. Also, while we show only monosubstituted surface moieties in eqs 5$-$7, the same applies to di- and trisubstituted species. We shall make use of these reactions in the following discussions.

Double Passivation Model. We now wish to propose a double-layer passivation (or simply double passivation) model, which can be used to rationalize the etching behavior of SiNWs in HF, NH$_4$F, or mixed HF$-$NH$_4$F (BHF) solutions. It involves two passivation layers on the silicon surface: a strong, co-valently bonded inner layer and a weakly bonded outer layer. The weak outer layer interactions could range from relatively strong hydrogen bonding or ionic bonding to dipole$-$dipole to very weak van der Waals interactions. Referring to Scheme 1, SiNWs are relatively stable in BHF solutions with pH $<$ ca. 3. Here, the silicon surfaces are terminated with hydrogens (the inner surface layer) and further covered with (i.e., passivated by) an outer layer of neutral and/or oligomeric (HF)$_n$ chains or rings, or anionic, branched (HF)$_n$F$^-$ species (where n = 1, 2, 3, ...) held together by strong hydrogen bonding, especially at high concentrations. The interactions between the inner H-terminated silicon surface layer and the chemisorbed outer layer may also range from hydrogen or ionic bonding to weak van der Waals interactions. This model is in accord with our ATR-FTIR results that surface Si$-$H$_x$ (x = 1, 2, 3) bands were observed only in HF$-$NH$_4$F solutions with pH $<$ ca. 3 (HF/NH$_4$F ratios of 9:1 and 7:3, see Figure 5b).

At pH $\geq$ 4, hydrolysis, direct attack by water molecules or the OH$^-$ ions, or air oxidation of the surface Si$-$H$_x$ gives rise to Si$-$(OH)$_x$(O$^-$)$_y$ moieties (where $(x + y) < 3$) on the surfaces of SiNWs. The hydrolysis reactions may be catalyzed by traces of base or the presence of an acid. This renders the SiNWs unstable in BHF solutions with pH $\geq$ 4. In fact, as depicted in Figure 5b, HF/NH$_4$F molar ratios of 1:1 or less with pH $\geq$ 4 completely wipe out the Si$-$H$_x$ bands. This latter observation is consistent with our previous ATR-FTIR results that no SiH$_x$ bands were observed with NH$_4$F as an etchant.[39]

Finally, for etchants with pH $>$ 11 (by adding a strong base), the surface layer is predominantly Si$-$(O$^-$)$_y$ where y = 1, 2, 3 and this inner, negatively charged silicon oxide surface is further passivated by an outer layer of NH$_4^+$ ions via ionic bonding, especially at high concentrations.

Etching Behavior and Surface Speciation: Comparison of 1-D and 2-D Si Systems. In this section, we shall provide a comparison of the etching behaviors of 1-D and 2-D silicon systems. As expected, many factors and effects come into play. Furthermore, while there are many similarities between 1-D and 2-D silicon systems, there are also striking differences.

Effects of Etchant Concentration and Composition: Buffered Oxide Etchants (BOEs). It is interesting to compare the etching rates for 1-D and 2-D Si systems, and the resulting silicon surface speciation, as functions of both the concentration and the composition of the etching solution. In the silicon industry, silicon wafers are normally etched with the so-called *buffered oxide etchants* (BOEs).[59] In general, HF is too fast an etchant for the oxide on a silicon wafer, making the undercut and line-width control rather difficult. It is therefore commonly used as a buffered solution (usually with NH$_4$F) in order to keep the

etching rate low and constant by moderating the pH and the concentration of the solution. Hence, the buffered HF solutions are also called "buffered oxide etchants". Conventional BOEs consist of mixtures of NH_4F (abbreviated as A) and HF (abbreviated as F) solutions. Depending on specific applications, the buffered oxide etchants (BOEs) range from predominantly NH_4F (e.g., AF 500:1, which contains 40% NH_4F and 0.1% HF) to fairly concentrated HF solutions (e.g., AF 3:1, which contains 30% NH_4F and 13% HF). It was found that the etching rate increases monotonically from 1.35 nm min^{-1} for AF 500:1 to 342 nm min^{-1} for AF 3:1, indicating that HF is a much more efficient etchant than NH_4F for 2-D Si surfaces. Atomically flat H-terminated Si(111) surfaces are normally prepared with an RCA clean,[59] followed by a final etch in a 40% NH_4F solution.[60,61]

These trends are *very different* from the etching behavior of 1-D SiNWs reported here. In particular, in the absence of air, NH_4F is as efficient an etchant as HF for SiNWs. In the presence of air or oxygen, NH_4F becomes even more efficient than HF, as a result of surface oxidation by oxygen. As reported in this paper, the surface speciations are also different for the two systems with regard to the NH_4F-buffered HF solutions.

Anisotropic vs Isotropic Etchants. In fact, the etching rate depends not only on the concentration and the composition of the etching solution but also on the morphological terrain of the silicon surface. Indeed, etchants can be classified as *anisotropic* or *isotropic*, depending upon whether the etching rate is site-specific or not. Previous morphological studies have shown that OH$^-$ is a highly *anisotropic* oxidant with the following trend of site-specific rates of attack (via reaction 6 or 7):

$$\text{kink} > \text{dihydride step} > \text{monohydride step} \gg \text{terrace} \quad (8)$$

On the other hand, HF is an *isotropic* oxidant with the following trend of site-specific rates of attack (via reaction 5):

$$\text{dihydride step} \approx \text{monohydride step} \geq \text{kink} \gg \text{terrace} \quad (9)$$

We shall see later that oxygen is also an *isotropic* oxidant (via reaction 10, vide infra). We shall make use of these rate differences in later discussions.

Effects of Dimensionality and Scale. The differences in the etching behavior and the resulting surface speciation between 1-D SiNWs and 2-D silicon wafers as reported here may be attributed to the nanometer size and the low dimensionality of the 1-D SiNWs with respect to the 2-D Si wafers. The following consideration, based on a "steric effect" of the etching process and the nanosizes of the SiNWs, may shed light on the differences. As in the case of Si wafers, the etching process is believed to begin with the attack of the atoms at defect and step sites. The surfaces of SiNWs grown by the thermal disproportionation of SiO are predominantly the Si(111) surfaces.[25] The etched SiNWs of roughly 15 nm in diameter are comparable in size to the steps and terraces of 2-D Si surfaces which make them prone to attacks by the etching agent. It is also known that, in the etching of Si(111) wafers, when an "atomically flat surface" is achieved, the etching process is greatly "impeded". For the SiNWs used in our studies (this work and refs 38 and 39), the nanosized wires are round with circular cross sections of roughly 15 nm in diameter, which means the absence of the so-called atomically flat surface. As a result, the etching agent can etch away the surfaces of SiNWs layer by layer until they are totally dissolved. As a result, the etching rate increases as the NH_4F concentration increases (cf. Table 2

and Figure 3). This rationale also explains why NH_4F is a slow etchant for 2-D Si wafers but an efficient one for 1-D SiNWs.

The pH Effect. The pH of an etching solution also plays a pivotal role in determining the etching behaviors as well as the surface speciation of both 1-D and 2-D silicon systems. There are numerous studies regarding the pH dependence of the etching of Si wafers in various etching solutions. The etching rate, as well as the resulting surface, can be modulated by controlling the pH of the solution. For example, Jakob and Chabal[2,3,17] 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. These observations have also been rationalized by Garcia et al.,[56] based on a "kinetic competition" model (vide infra). We believe that the pH dependence of the etching behavior and surface speciation of 2-D Si wafers in BHF solutions, as reported by these and other researchers, is consistent with the etching mechanism and the double passivation model proposed here for the 1-D SiNW systems.

Effect of Oxygen. Oxygen has been shown to affect the etching behavior as well as the surface speciation of both 1-D and 2-D silicon systems. For example, we have previously demonstrated that oxygen in air greatly accelerates the etching of SiNWs in NH_4F solutions but has little effect in HF solutions.[39] This effect is related to the etching behavior of 2-D silicon wafers in oxygen-containing vs oxygen-free etchants.[55,56] Detailed discussions on the effect of oxygen can be found in the literature.[39,55,56] For example, Garcia et al.[56] reported that Si(111) surfaces etched in buffered HF (BHF) solutions containing oxygen are much rougher than those etched in oxygen-free BHF (both of pH ~ 4.7). This effect was interpreted by these authors using 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 reaction 6 or 7) or by O_2 (see reaction 10 below), followed by rapid etching of the oxidized species (reaction 5). The oxygen-induced oxidation may be represented schematically as follows:

$$\text{Si}_{bulk}\equiv\text{Si*}-\text{H} + {}^1/_2\text{O}_2 \leftrightarrow \text{Si}_{bulk}=(\text{SiO})\text{Si*}-\text{H} \quad (10)$$
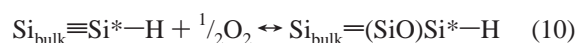
Here, (SiO) represents the attack of the silicon back-bonds by the dissolved O_2 and the formation of the underlayer oxides, resulting in surface moieties such as O_3SiH, O_2SiH_2, and $OSiH_3$, described earlier.

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 on kinks and steps by OH$^-$ are much faster than that on 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).[3,17,59-61]

Effect of Crystal Orientation. It is also well-known that the etching behavior of the silicon wafer is sensitive to the surface morphologies and crystal orientation. For example, the etching rate for silicon, as well as the resulting surface roughness, follows the general trend of Si(110) > Si(100) > Si(111).

Si Nanowires in NH$_4$F-Buffered HF Solutions

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Atomically flat silicon (111) surfaces can be obtained using NH$_4$F as an etchant. On the other hand, Si(110) and Si(100) generally give rise to rougher surfaces. It was suggested that Si(111) surfaces are more compact and that small defect adstructures on the Si(111) planes are preferentially removed, leaving behind the flat, ideally H-terminated Si (111) surfaces. Other anisotropic etchants (e.g., KOH) give rise to similar trends.

Evidence of Double Passivation in 2-D Si Systems. A recent report by Schmidt et al.[53] showed that, in fairly acidic (pH ∼ 0.5) solutions (e.g., HF/H$_2$SO$_4$), etching of Si(100) surfaces can also produce smooth surfaces. This particular observation may be related to the etching behavior of SiNWs in the acidic (pH < 1) HF solutions described in this paper. Here, the effect of oxygen on the etching curve was minimal (almost nonexistent) in low pH solutions. In other words, under acidic conditions, the passivation of the H-terminated silicon surfaces by the hydrogen bonded network of (HF)$_n$ (n = 1, 2, 3, ...) and/or related protic species protects the surfaces from subsequent attacks by oxygen (oxidation). We conclude that the double passivation model proposed here for 1-D SiNWs is also applicable for 2-D Si systems.

Oxidizing Power of the Etchant. Yet another factor to be considered is the oxidizing power of the etchant. In the example cited above, as pointed out by Schmidt et al.,[53] 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 wafer system, one must also consider the oxidizing power of the etchant (and its anisotropy, if any) 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 the case of conventional etching, in dilute HF solution could be achieved when the pH was lowered by adding HCl instead of H$_2$SO$_4$.[53] In contrast, for 1-D SiNWs, no significant differences were found in etching behavior when either HCl or H$_2$SO$_4$ was used to alter the pH of the solutions.[39]

Conclusion

We conclude that NH$_4$F is as efficient an etchant as HF for SiNWs and that SiNWs are stable only in relatively narrow pH ranges of NH$_4$F-buffered HF (BHF) solutions. To explain the relative "stabilities" of SiNWs in BHF solutions with low and high pH values, we propose a double passivation model. Thus, when SiNWs are etched in BHF solutions with pH values in the range of 1−3, the surface moieties are predominantly Si−H$_x$ species (x = 1−3) and, at relatively high HF concentrations, the H-terminated Si surfaces are covered with, and passivated by, a network of hydrogen bonded HF and oligomeric (HF)$_n$ molecules. When SiNWs are etched in BHF solutions with pH values of 11−14, the surface species are mainly Si−(O$^-$)$_x$ species (x = 1−3), and at high NH$_4$F concentrations, the negatively charged Si surfaces are stabilized, and passivated, by NH$_4^+$ ions via ionic bonding. In BHF solutions with pH values of 3−11, the surface speciation, consisting of mixtures of Si−(OH)$_x$(O$^-$)$_y$ ($x + y$ = 1−3) species, is unstable and the surface is etched away rapidly.

The similarities and differences of the etching behaviors, and the resulting surface speciations, between 1-D SiNWs and 2-D Si wafers, using the same etchants and under similiar conditions, are also explored. For example, while etching SiNWs with HF-rich BHF solutions with pH < 4 gives rise to Si−H$_x$ surface species, no Si−H$_x$ species were observed when SiNWs were etched in BHF solutions with pH ≥ 4 (for HF/NH$_4$F ≤ 1:1). In

contrast, etching of Si wafers with either HF, NH$_4$F, or BHF etchants produces Si−H$_x$ species on the surface. Furthermore, while HF is a much more efficient etchant than NH$_4$F for 2-D Si surfaces, NH$_4$F is as efficient an etchant as HF for SiNWs. In the presence of air or oxygen, NH$_4$F becomes more efficient than HF, owing to the added etching process by way of underlayer attack by oxygen. We believe that both the nanoscale size (comparable to the roughness scale in 2-D wafers) of SiNWs and the lack of "protection" by the network of hydrogen bonded HF and related molecules at pH > 4 contribute to the rapid hydrolysis of the surface Si−H$_x$ species, particularly in BHF solutions with HF/NH$_4$F molar ratios of unity or less and pH values of 4 or greater.

We believe the etching mechanism and the double passivation model proposed here are fully consistent with the etching behaviors and surface speciations of 1-D SiNWs and 2-D Si wafers in HF, NH$_4$F, or mixed HF−NH$_4$F (BHF) solutions. The dissimilarities between 1-D and 2-D silicon surfaces can be understood in terms of the differences in the scale and dimensionality of the two systems. A detailed comparison of the etching behaviors and the surface speciations of 1-D and 2-D silicon systems is also provided.

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