FTIR Spectroscopic Studies of the Stabilities and Reactivities of Hydrogen-Terminated Surfaces of Silicon Nanowires

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Attenuated total reflection Fourier transform infrared (FTIR) spectroscopy was used to characterize the surface species on oxide-free silicon nanowires (SiNWs) after etching with aqueous HF solution. The HF-etched SiNW surfaces were found to be hydrogen-terminated; in particular, three types of silicon hydride species, the monohydride (SiH), the dihydride (SiH_2), and the trihydride (SiH_3), had been observed. The thermal stability of the hydrogen-passivated surfaces of SiNWs was investigated by measuring the FTIR spectra after annealing at different elevated temperatures. It was found that hydrogen desorption of the trihydrides occurred at ∼550 K, and that of the dihydrides occurred at ∼650 K. At or above 750 K, all silicon hydride species began to desorb from the surfaces of the SiNWs. At around 850 K, the SiNW surfaces were free of silicon hydride species. The stabilities and reactivities of HF-etched SiNWs in air and water were also studied. The hydrogen-passivated surfaces of SiNWs showed good stability in air (under ambient conditions) but relatively poor stability in water. The stabilities and reactivities of the SiNWs are also compared with those of silicon wafers.

Introduction

One-dimensional nanomaterials such as nanotubes and nanowires are important in studies of the roles that dimensionality and size play in influencing their chemical and physical properties in the nanorealm. The studies of the optical, electrical, and mechanical properties of these nano-materials may pave the way for many applications in nanotechnology in general and nanoelectronics in particular.[1,2] Because silicon is of great technological importance in microelectronics, silicon nanowire (SiNW) has been a topic that has attracted great attention recently. Many successful synthetic strategies have now been developed to obtain bulk quantities of SiNWs using both gas-phase and condensed-phase techniques[3−7] with or without metal cata-

lysts. A number of properties such as the morphology, structure, photoluminescence, electron field emission, electronic property, thermal and electronic conductivities, and surface chemical reactivity of SiNWs have been studied.[8−18] Although many efforts have been made in the investigation

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of the properties of SiNWs, information regarding the surfaces (surface species and their properties) of oxide-free SiNWs is relatively scarce. Obviously, the chemical properties of SiNW surfaces are crucial to their application in mesoscopic electronic devices in terms of their stabilities and transport properties, among many others.

As noted in the literature,[7,11] the SiNWs prepared by a thermal evaporation technique are known to have a relatively thick oxide layer. Its presence has been associated with the preferred linear growth of the SiNWs. SiNWs prepared by this method are literally very long, free-standing wires with diameters of several nanometers to tens of nanometers. Each wire has a crystalline silicon core of approximately 15 nm in diameter and is coated with an oxide layer whose thickness is of $^{1}/_{4}-^{1}/_{3}$ of the nominal diameter. The mass ratio of oxygen to silicon in these nanowires, as determined by energy-dispersive spectrometry (EDS) analysis, is about 3:7 on the average. It should be noted that the Si oxide layer serves as a protective layer, rendering the as-prepared SiNWs relatively inert. The inertness of the as-prepared SiNWs is unfavorable for applications of SiNWs in nanotechnologies. Further fabrication and processing require the removal of the oxide layer. It is thus of importance to investigate the surface properties in general and the stabilities in particular of SiNWs after removal of the oxide layer.

The surface properties of bulk Si materials such as Si wafers have been well studied. The most widely used technique for removing silicon oxide from the silicon surface is etching with dilute hydrofluoric acid. HF acid etching is a key step in producing silicon surfaces that are contamination-free and chemically stable for subsequent processing in silicon technology. After HF 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.[19−35] It is well-known that

HF etching results in the removal of the surface oxide layer and leaves behind Si surfaces terminated by hydrogen atoms. The SiH, SiH_2, and SiH_3 species have been observed on the HF-treated surfaces of Si by high-resolution electron energy loss spectroscopy,[19,20] IR spectroscopy,[21−30] scanning tunneling microscopy,[31−33] low-energy electron diffraction,[34,35] etc.

In this work, we investigated the thermal stability of the hydrogen-passivated surfaces of HF-etched SiNWs and their stabilities and reactivities in air and water using Fourier transform infrared (FTIR) spectroscopy. Specifically, microattenuated total reflection (ATR)-FTIR spectroscopy was employed to monitor the SiNW surface structure after etching with an aqueous HF solution. The results are also compared with those of silicon wafers.

Experimental Section

The SiNWs used in this study were prepared by thermal evaporation. As described in the literature,[7] the as-prepared SiNWs had a crystalline silicon core measuring $10-15$ nm in diameter and sheathed with a $3-5$-nm-thick oxide layer. Unless otherwise specified, the as-prepared SiNWs were immersed in a 5% HF aqueous solution for 5 min. The HF-etched, oxide-free SiNWs were placed onto several GaAs wafers and dried in a N_2 stream. The ATR-FTIR spectra of typical as-prepared SiNWs before and after HF etching are shown in Figure 1a,b, respectively. Figure 2 is the expanded Si−H stretching region of Figure 1b.

Isotopic substitution experiments were performed by etching a particular as-prepared SiNW sample with a predominantly deuterated HF solution. The latter was prepared by adding a small amount (1 mL) of 48% aqueous HF solution to a large quantity (10 mL) of D_2O and allowing the deuterium to exchange with the hydrogen to obtain a solution of DF in D_2O. The solution thus prepared contained 8% H and 92% D. The ATR-FTIR spectrum of the sample was taken, and the result, in two different spectral regions, is shown in Figure 3.

In the annealing experiments, five HF-etched, oxide-free SiNWs were placed onto several GaAs wafers, dried in a N_2 stream, and transferred immediately to an ultrahigh vacuum (UHV) chamber (base pressure < 10^{-10} Torr) for annealing at 550, 650, 750, and 850 K for 15 min. The samples were then cooled to room temperature in the UHV chamber, and their ATR-FTIR spectra were taken. The results are shown in Figure 4.

For investigation of the stability of the HF-etched SiNWs in air, a particular HF-etched SiNW sample was first dried in a N_2 stream and then exposed to ambient air, and their ATR-FTIR spectra were recorded for different periods of time. The results are shown in Figure 5.

The stability of the HF-etched SiNWs in water was investigated by dividing a particular HF-etched SiNW into four parts. One part was immediately dried in a N_2 stream; the remaining three parts were immersed in deionized (DI) water for 30 s, 5 min, and 15

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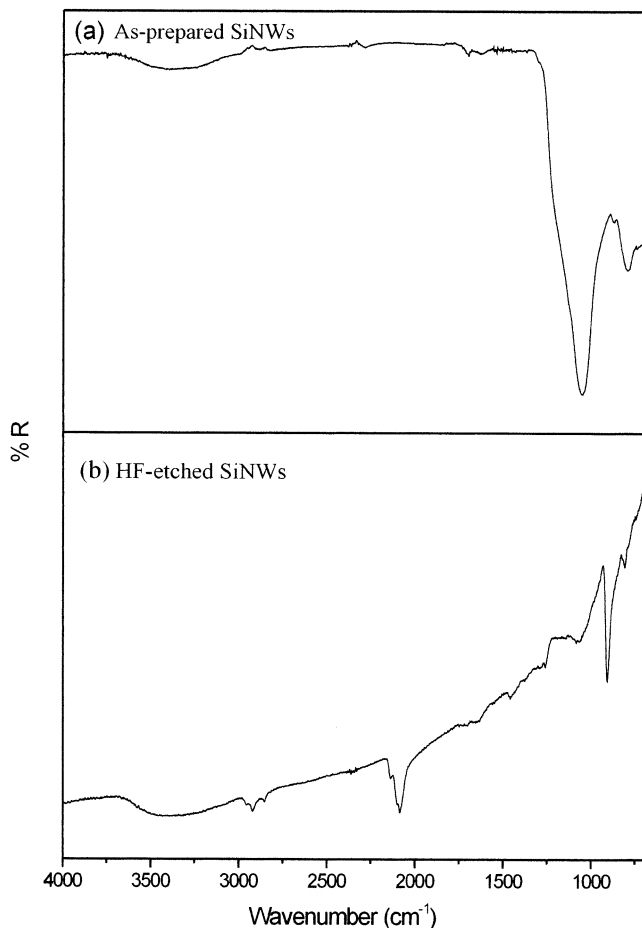(35) Hahn, P. O. *Mater. Res. Soc. Symp. Proc.* **1986**, *54*, 645.

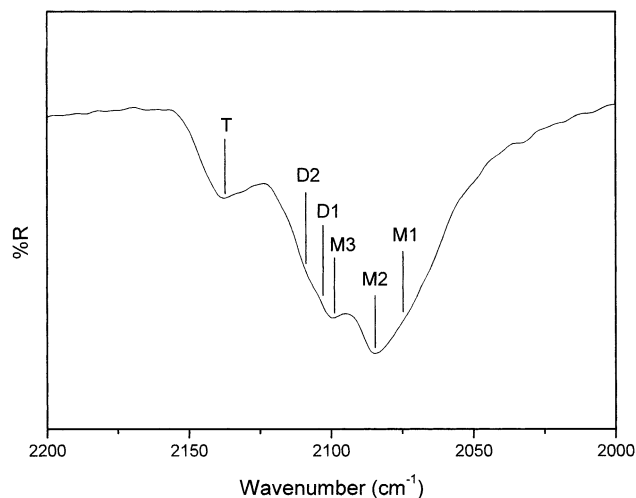**Figure 1.** ATR-FTIR spectra of (a) as-prepared SiNWs and (b) HF-etched SiNWs in the range of 700−4000 cm^{-1}.

Figure 2. ATR-FTIR spectrum of HF-etched SiNWs in the range of 2000−2200 cm^{-1}.

min and then removed from DI water and dried in a N$_2$ stream. All four samples were further dried in a vacuum overnight, and their ATR-FTIR spectra were taken. The results are shown in Figure 6.

All ATR-FTIR measurements were performed in air using a Perkin-Elmer Spectrum One FTIR spectrometer interfaced to 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}.

Results and Discussion

IR absorption methods have been widely used to study the chemical properties of silicon wafers.[21−26] In particular, FTIR spectroscopy, in the so-called ATR mode, has been shown to be extremely useful in the investigation of the surface chemistry of silicon wafers.[27−30] In this work, we studied the stabilities and reactivities of the hydrogen-passivated surfaces of HF-etched SiNWs, in particular the thermal stability and reactivities in air (under ambient conditions) and water, using ATR-FTIR spectroscopy. Specifically, micro-ATR-FTIR spectroscopy was employed to monitor the SiNW surface structure after etching with an aqueous HF solution because of the small quantities of the samples and difficulty in obtaining flat samples. It was found that, after a controlled HF treatment (i.e., as-prepared SiNWs were immersed in a 5% aqueous HF solution for 5 min), the morphology of the SiNWs remains essentially intact except for the removal of the surface oxide layer.[14,17,18] The diameter of the SiNWs decreased by $^1/_4$−$^1/_3$ of the original diameter after removal of the oxide layer by HF etching. EDS results showed that the etched SiNWs contained less than 2% oxygen. It was found that the dangling bonds created by etching were terminated by hydrogens, as in the case of bulk silicon[21−24] and porous silicon.[36,37]

Figure 1 shows the ATR-FTIR spectra in the range of 700−4000 cm^{-1} obtained from (a) as-prepared SiNWs and (b) HF-etched SiNWs. In the spectrum of as-prepared SiNWs (Figure 1a), only Si−O vibrations at ∼1050 and ∼800 cm^{-1} were observed. The strong absorption near 1050 cm^{-1} is due to a stretching vibration where the oxygen-atom motion is in the Si−O−Si plane and is parallel to the line of two adjacent silicon atoms. The absorption at about 800 cm^{-1} is due to bending vibration in which the oxygen atom moves in the plane of the Si−O−Si bonds along the direction of the bisector of the Si−O−Si angle.[38,39] Upon etching with a dilute (5%) aqueous HF solution, new absorption bands attributable to Si−H$_x$ (2000−2200 and ∼900 cm^{-1}) and CH$_x$ (2800−3000 cm^{-1}), where x = 1, 2, and 3, were observed in the spectrum, while the Si−O absorption bands virtually disappeared (Figure 1b). These results suggest that SiNW surfaces were terminated by hydrogen upon the removal of the Si oxide layer by HF etching. The CH$_x$ bands were due to contamination by organic species upon exposure to air.

Previous high-resolution transmission electron microscopy studies indicated that the surfaces of SiNWs synthesized by the oxide-assisted method[11] have predominantly (111) surfaces, along with a small percentage of (100) and (110) surfaces. As noted in the literature,[21−24] both the Si(111) and Si(100) surfaces of Si wafers treated by a HF solution have three kinds of silicon hydride species, the monohydride (SiH), dihydride (SiH$_2$), and trihydride (SiH$_3$). The coexistence of these three types of hydride species is due to the microscopic

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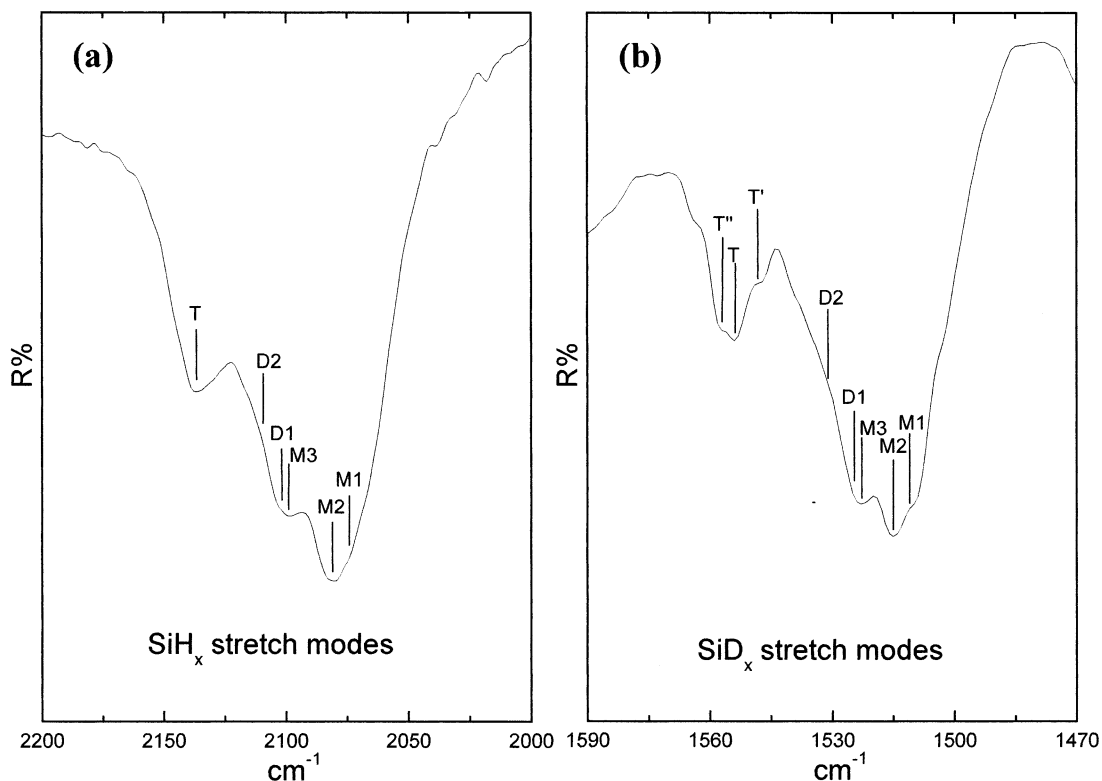(39) Galeener, F. L.; Sen, P. N. *Phys. Rev. B* **1978**, *17*, 1928.

Figure 3. ATR-FTIR spectra of a particular SiNW sample obtained by etching with an aqueous solution of HF/DF (ratio = 8:92) in two special regions corresponding to (a) SiH_x and (b) SiD_x stretching frequencies.
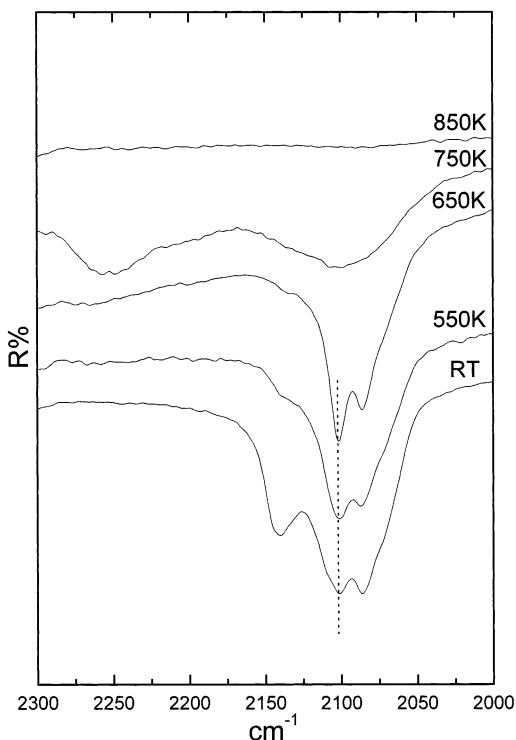

Figure 4. ATR-FTIR spectra in the Si−H stretching frequency region of the hydrogen-terminated SiNWs annealed at different temperatures.

roughness of the HF-treated Si surfaces. As a result of the nanoscale of the SiNW surface and the existence of many steps and defects as well as twins and stacking faults[16] in the SiNWs, the three kinds of silicon hydrides and their adstructures are expected. Figure 2 shows the vibrational spectra of HF-etched SiNWs in the frequency range of the

silicon−hydrogen stretching vibrations. The broadness and complexity of the absorption envelope suggest that the SiNW surfaces are not perfect or are ideally terminated by hydrogen atoms but are locally rather rough and may involve many different terraces and steps on the surfaces of the SiNWs. It is evident that the three broad bands are composed of several unresolved peaks attributable to the adstructures of different silicon hydride species.

To specify the adstructures, it is necessary to differentiate between the isolated versus interacting vibrational modes of silicon hydrides in the IR spectra. Figure 3 shows the SiH_x (Figure 3a) and SiD_x (Figure 3b) absorption bands of a particular SiNW sample obtained by etching with an aqueous solution of mixed HF/DF in the ratio of 8:92. When most of the H atoms (∼92%) are replaced by the heavier isotope, deuterium, the vibration modes are effectively decoupled, yielding only a single vibrational mode for each chemical structure. It can be seen that the shapes of the envelopes of the peaks are rather similar for SiH_x versus SiD_x absorptions. The SiD_x vibration bands (Figure 3b) seem to be more resolved than the corresponding SiH_x bands (Figure 3a). Furthermore, the ratio of the stretching frequencies is about 1.38, which agrees with the expected ratio of $\sqrt{2} = 1.41$ on the basis of the mass ratio of 2:1 for D versus H. A comparison of Figures 2 and 3a revealed no extensive coupling between the vibrational modes of the SiH_x moieties on the SiNW surfaces. Thus, the absorption peaks in Figures 2 and 3, labeled M1, M2, M3, D1, D2, and T, may be interpreted as due to different chemical adstructures. We should emphasize that these are the three main features of the SiH_x (or SiD_x) vibrational modes. There are, as is evident
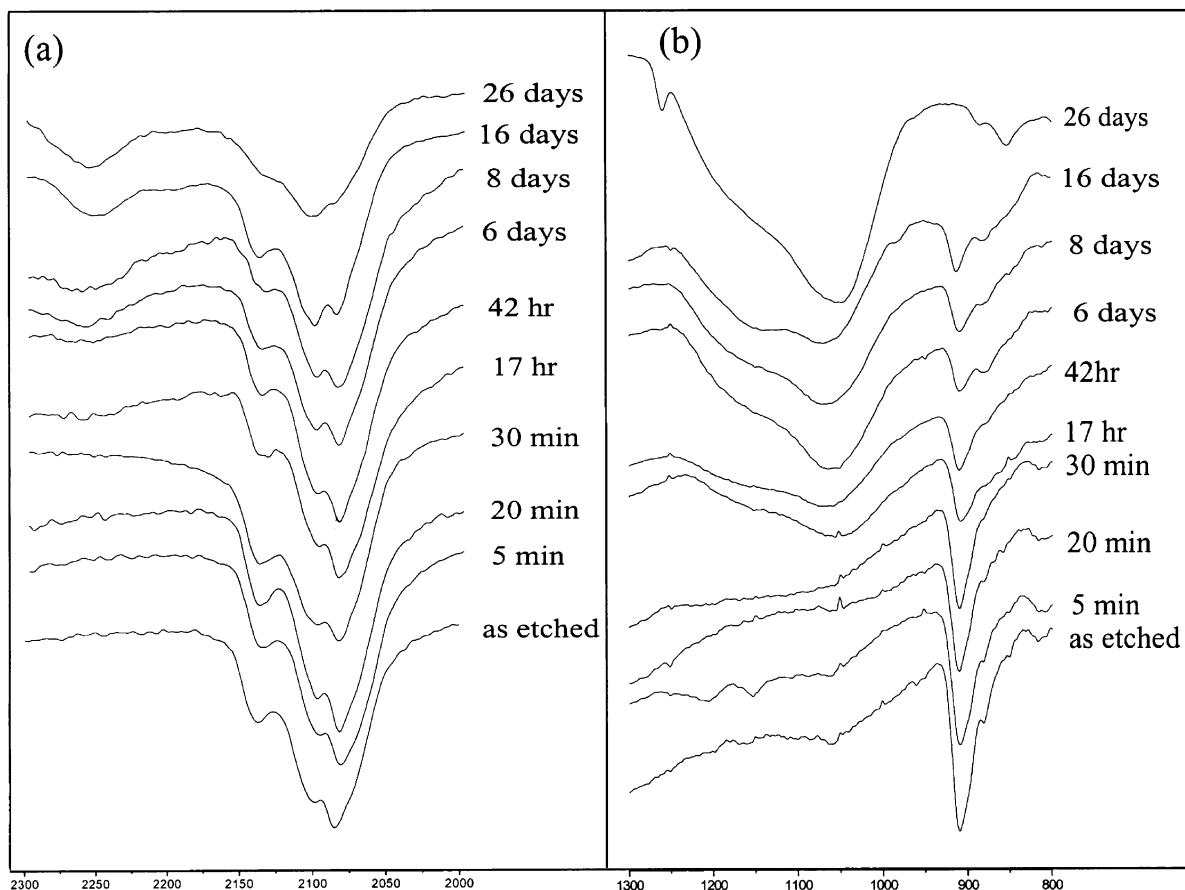
Figure 5. ATR-FTIR spectra of the hydrogen-terminated SiNWs recorded repeatedly after exposure to ambient air for different periods of time: (a) in the region of Si—H stretching vibrations and (b) in the region of 800—1300 cm^{-1}.
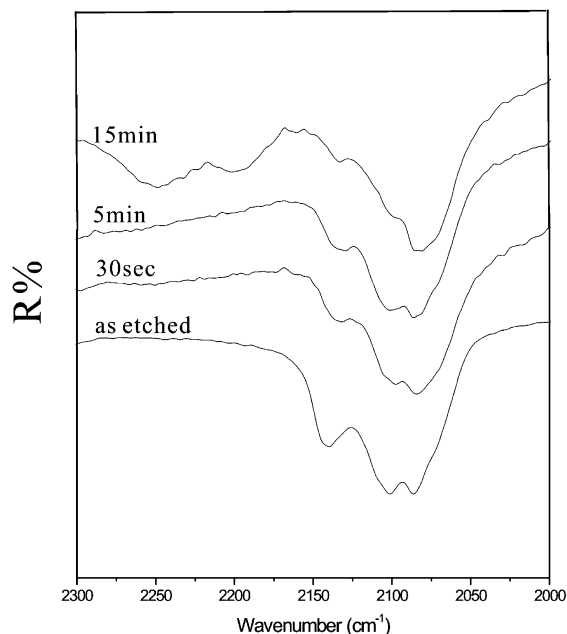

Figure 6. ATR-FTIR spectra of Si—H stretching vibrations of hydrogen-terminated SiNW surfaces after DI water rinsing for different time intervals.

from the figures, substantial overlaps between these three bands. Furthermore, more weak "shoulders" can be identified: for example, on the low-frequency side of the monohydride band and high-frequency sides of the dihydride and trihydride bands. The characterizations of these weak shoul-

ders must await further experimental evidence (which is beyond the scope of the present study). Finally, the assignments here are in a large part based on the battery of previous works on Si wafers.[21−24] In accordance with the FTIR results of the Si(111) and Si(100) wafers,[21−24] we assign M, D, and T bands as due to the monohydrides, dihydrides, and trihydrides, respectively. There are at least three different structural types, labeled M1, M2, and M3, of the monohydride species, as is evident from the spectra. The M2 mode, observed as the strongest feature at 2085 cm^{-1} for H and 1515 cm^{-1} for D, may be characterized as an ideal monohydride terminating on the (111) plane, designated here as Si_3Si-H (here Si_3 denotes three adjacent Si atoms on the surface; similar designations will be used for other adstructure representations in later discussions). The M1 mode, appearing as a weak shoulder at 2070 cm^{-1} for H and 1510 cm^{-1} for D, may be associated with an adatom structure Si—H-bonded to an adjacent SiH_2 (represented as $H_2Si-Si-H$) moiety. The M3 mode (observed at 2099 cm^{-1} for H and 1523 cm^{-1} for D) was observed only on the step defects of the Si(111) wafer.[23] It was believed to be due to a dimer structure (represented as HSi—SiH) formed by the coupling of two adjacent Si—H units via a Si—Si bond.

There are at least two types of dihydrides on the HF-etched SiNW surfaces, as can be seen from Figures 2 and 3a. The D1 mode, observed at 2102 cm^{-1} for H and 1525 cm^{-1} for D, is assigned to a relaxed dihydride (represented as Si_2-

SiH_2) on the Si(100) surface, and the D2 mode, observed at 2110 cm^{-1} for H and 1531 cm^{-1} for D, is due to a strained dihydride (represented as $H_xSi-SiH_2$). A broad band of the trihydride vibrational mode (T), observed at 2137 cm^{-1} for H, is probably due to the trihydride ($-SiH_3$) in different environments (we note, however, that a mode of the step dihydride had been identified at 2134 cm^{-1}).[24] At least three partially resolved peaks of SiD_3 were observed in the deuterated spectrum (Figure 3b), thereby confirming the presence of different types of trihydrides (labeled as T, T′, and T″). These modes can again be attributed to different adjacent adatom structures (e.g., $HSi-SiH_3$ or $H_2Si-SiH_3$). Finally, the band at ~900 cm^{-1} (Figure 1b) can be assigned to the scissor mode of the dihydride or umbrella mode of the trihydride, as suggested in the literature.[21]

The thermal stability of the silicon hydrides on the surfaces of HF-etched SiNWs was studied by measuring the FTIR spectra of samples annealed in the UHV chamber at different elevated temperatures. In each case, the same sample was annealed in the UHV chamber at the specified temperature and taken out of the chamber, stored under nitrogen, and transported to the FTIR spectrometer for measurements in air. Figure 4 shows a representative set of the ATR-FTIR spectra in the Si−H stretching vibration region of the hydrogen-terminated SiNWs surface-annealed at different temperatures. It is clear from Figure 4 that the absorption peak at 2137 cm^{-1} decreases dramatically upon annealing up to 550 K and practically disappears at temperatures above 650 K. In contrast, the absorption peak at 2100 cm^{-1} sharpens and increases in magnitude relative to the 2137-cm^{-1} peak as the annealing temperature increases from room temperature to about 650 K. This is taken to imply that, as the annealing temperature increases to around 550 K, the trihydride species (broad-band T at 2137 cm^{-1}) are first converted to dihydride species. Subsequently, at around 650 K, the dihydride species (peaks D1 and D2) are, in turn, transformed into monohydride species (peaks M1, M2, and M3). At or above 750 K, all peaks broaden dramatically, indicating the disintegration of all hydride species. Meanwhile, the peak at 2255 cm^{-1} begins to appear. Consistent with these observations, the peak at 900 cm^{-1} disappears completely at annealing temperatures above 650 K. It reinforces the notion that trihydrides and dihydrides are desorbed from the surface at about 650 K. This desorption temperature of the trihydride and dihydride species from the surfaces of SiNWs is similar to that at 670 K observed for porous silicon[40] and Si wafers.[41−43] It is interesting to note that, at annealing temperatures above 650 K, the monohydride peaks, especially the dimer configuration (M3), increase in intensity at the expense of the dihydrides (D1 and D2) and trihydrides (T, T′, and T″). This is probably due to surface reconstruction as H_2 desorbs from SiH_3 or SiH_2, and two adjacent silicon hydrides can combine to form mono-

hydride species, especially the dimer structure M3 (e.g., $SiH_2 + SiH_2 \rightarrow HSi-SiH + H_2\uparrow$). With further annealing at temperatures above 750 K, the monohydride peak eventually decreased in intensity and became very broad, while a new peak at 2255 cm^{-1} with a broad shoulder at 2210 cm^{-1} appears. This new peak may be attributed to the O_3SiH species (the shoulder being due to the O_2SiH species), resulting from the insertion of oxygen into a Si backbone (underlayers).[44−48] It may have come from the oxidation of the monohydride species by a trace amount of oxygen in the vacuum chamber or, more likely, by air oxidation of the coordinatively unsaturated silicon monohydride species on the SiNW surfaces as a result of hydrogen desorption. At annealing temperatures above 850 K, all Si hydride species eventually desorb from the SiNW surfaces, as evidenced by the disappearance of all the Si−H bands. Furthermore, no Si−O or Si−C peaks could be found in the spectrum, even after the sample was exposed to air for a long period of time (9 days). This suggests that the SiNW surfaces reconstruct once after the first hydrogen (disappearance of the trihydride and dihydride species) desorption at around 650 K and again after the second hydrogen (disappearance of monohydride species) and oxygen (disappearance of O_xSi-H peaks) desorptions at or above 850 K. The further reconstructed surfaces of SiNWs (after oxygen desorption) apparently have relatively good stability under ambient conditions.

Next, we studied the stabilities of the H-terminated SiNWs in air and water. To investigate the effect of the aging of H-terminated SiNW surfaces in air at room temperature, a HF-etched SiNW sample was exposed to air for different periods of time after HF etching, and their ATR-FTIR spectra were obtained. Figure 5a,b shows the results in two different IR spectral regions of the same sample. As can be seen from Figure 5, the surfaces of the as-etched SiNWs exhibited rather high stability in air. The spectra remained unchanged for nearly 2 days (42 h). Hence, the stability of the H-terminated surface of SiNWs is much better than that of the Si wafer.[44−46] Upon further exposure to air, absorption bands due to the oxidation species, O_3SiH at 2255 cm^{-1}, and that due to the Si−O vibration band at around 1100 cm^{-1} began to appear and increase in intensity with increasing exposure time. This observation suggests that the Si back-bonds are attacked by oxygen while the Si−H bonds remain more or less intact. Because a Si−H bond is considered to be much stronger than a Si−Si bond, it is reasonable to assume that Si−Si back-bonds are broken first to form Si−O−Si back-bonds.[47] Eventually, all of the SiH_x absorption bands degraded after 26 days (top curve, Figure 5a).

Although the H-terminated surfaces of SiNWs exhibit a relatively high stability in air, their stability in water is not

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as good. The ATR-FTIR spectra, in the Si–H stretching frequency region of the H-terminated SiNWs after rinsing with DI water for different periods of time, are shown in Figure 6. After 15 min of DI water rinsing, the absorption peaks due to the oxidation species, O_3SiH (at ~2250 cm^{-1}) and O_2SiH_2 or O_2SiH (at ~2200 cm^{-1}),[45] began to appear. Absorption bands due to silicon hydride species also started to degrade, especially the SiH_3 and SiH_2 species. These observations are in accord with the results of our previous studies of the reactivities of the HF-etched SiNWs in the aqueous solution of metal ions[15–18] and organic solvents,[49] wherein the surfaces of the HF-etched SiNWs were found to exhibit moderately high reactivities in the aqueous solutions of silver, gold, copper, etc., ions and some common organic solvents such as chloroform, dichloromethane, etc.[49]

The dramatic difference in the stabilities of the hydrogen-passivated SiNWs in air versus water is not clear at present. It is possible that it is associated with the hydroxide ion (albeit very low concentration in neutral solutions) in water[48] because it is known that hydroxide ions can attack the silicon surface. Qualitatively, the hydrogen-terminated surfaces of SiNWs appear to be less stable in water than that of the Si(111) wafer, as it takes the latter 30 min for the $O_3Si–H$ band at 2270 cm^{-1} to appear.[47] We should emphasize that such comparisons are qualitative at best because the stability probably depends on the orientations and defects of the

surfaces of both the SiNWs and the Si wafers, even under identical experimental conditions (e.g., temperature, humidity, etc.). Work is in progress to, hopefully, provide an explanation for or further insight into this observation.

In summary, FTIR spectroscopy studies of oxide-free SiNWs (after HF etching) showed that the SiNW surfaces were hydrogen-terminated; in particular, three silicon hydride species, the monohydride (SiH), dihydride (SiH_2), and trihydride (SiH_3), were observed. The thermal stability of the hydrogen-passivated surfaces of SiNWs was investigated by measuring the FTIR spectra after annealing in vacuum at different elevated temperatures. It was found that hydrogen desorption of the trihydride species occurs at ~550 K, and that of the dihydride species occurs at ~650 K. At or above 750 K, all silicon hydride species desorb from the surfaces of SiNWs, and at or above 850 K, the SiNW surfaces are free of hydride or oxygenated species. Finally, the H-terminated surfaces of SiNWs showed good stability in air (under ambient conditions) but relatively poor stability in water.

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IC020723E