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Wet-Chemical Treatment of Si_3N_4 Surfaces Studied Using Infrared Attenuated Total Reflection Spectroscopy

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Infrared attenuated total reflection spectroscopy has been used to observe the surface chemistry of Si_3N_4 films (grown on Si by low-pressure chemical vapor deposition) under steady-state conditions during exposure to dilute aqueous HF solutions. Surfaces etched in HF do not exhibit rapid growth of an SiO_2 layer when subsequently exposed to either humid room air at room temperature or to liquid H_2O. However, some evidence is found for the formation of an ultrathin oxide-like layer when the etched surface is rinsed in deionized H_2O. Removal of this layer in HF results in no detectable signal in the Si-H stretching region, unlike the case for Si subjected to a similar oxide-removal treatment. The presence of SiOH groups has been detected by observing their removal by reaction with aqueous acetic acid or HCl solutions, which suggests that SiH_x groups are rapidly hydrolyzed. An attempt was made to detect surface NH_x groups by protonation in aqueous acid to form NH_{x+1}^+, which should be more readily observable in the infrared spectrum. However, the surface coverage of NH_x, if any, is too small to be detected by this means.
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Silicon nitride (Si_3N_4) is important as a dielectric material[1] for use in electronic devices, including ion-sensitive field-effect transistors (ISFETs). For these applications, thin films are often grown by chemical vapor deposition (CVD) or by sputter deposition. In contrast to the situation for many other electronic materials, little is known of a fundamental nature about the mechanisms involved in the wet-chemical processing (*e.g.*, cleaning, etching, surface passivation, etc.) of Si_3N_4 films.

Previous studies[2-7] of the wet-chemical treatment of Si_3N_4 films have focused primarily on etching in aqueous hydrofluoric acid (HF). The etch rate at room temperature for Si_3N_4 grown by low-pressure chemical vapor deposition (LPCVD) is[2] $R(\text{Å/s}) = 0.16[\text{HF}] + 0.31[\text{HF}_2^-]$ (where [X] is the molar concentration of species X) and is considerably slower than for material grown by plasma-enhanced chemical vapor deposition (PECVD). Knotter and Denteneer[5] proposed a mechanism for the etch rate dependence on pH in which, for the approximate range of $1 < \text{pH} < 4.5$, the rate-limiting step is

$$(\text{-N-})_3\text{Si-NH}_3^+ + \text{F}^- \rightarrow (\text{-N-})_3\text{Si-F} + \text{NH}_3$$

while at somewhat higher pH it is

$$(\text{-N-})_3\text{Si-NH}_2 + \text{HF}_2^- \rightarrow (\text{-N-})_3\text{Si-F} + \text{NH}_3 + \text{F}^-$$

A subsequent nucleophilic attack by F^- at the $Si^{\delta+}$-$F^{\delta-}$ site is then relatively rapid. Bower *et al.*[8] studied the cleaning of PECVD films and found that a modified RCA clean, followed by dipping in 1% HF, is effective in promoting subsequent wafer bonding, possibly as a result of the surface being terminated in amine (NH_x) species.

Regrowth of the native oxide[9-12] (in air, in wet or dry O_2, or in liquid H_2O) on the HF-etched surface at room temperature is an important aspect of wet-chemical treatment and subsequent processing. Previous studies of LPCVD[9,10] or PECVD[11] Si_3N_4 have found that surface oxidation at or somewhat above room temperature occurs readily in room air and in H_2O vapor but more slowly in dry O_2. A high concentration of N-H bonds, which occurs in PECVD material, is found[11] to increase the reaction rate with H_2O. Hydrolysis[10,11] removes Si-H and NH_x groups, produces SiO_2 with surface SiOH groups, and releases NH_3. Ultrathin H-free Si_3N_4 films grown on Si(111) by reaction at high-temperature with NH_3 under ultrahigh vacuum (UHV) conditions,[12] are found to resist dry O_2 oxidation at temperatures up to ~500°C, to an extent depending on the preparation of the Si substrate prior to nitridation. An unresolved issue, which may depend on the details of Si_3N_4 growth and oxidation conditions, is whether the native oxide is better described as SiO_2 or as an oxynitride, possibly with a graded O/N ratio.

Results for the oxidation and/or hydrolysis of high-surface-area (HSA) Si_3N_4 powders,[13-15] obtained using primarily infrared (IR) spectroscopy, concur with those noted above for thin films. The reaction with H_2O vapor is more rapid than with dry O_2 and is accelerated by the presence of NH_x groups. After removal of adsorbed H_2O and other contaminants by evacuation at elevated temperature, $(\text{-N-})_3\text{SiOH}$ and $(\text{-Si-})_2\text{NH}$ are found[16,17] to be the dominant surface species. Other works,[18-26] reporting the interaction of HSA powders with liquid H_2O and/or aqueous acids, are also relevant. When immersed in H_2O at a pH of 7.0, HSA Si_3N_4 shifts the pH either higher or lower, depending[19] on the relative surface concentrations of basic [Si-(NH)-Si and Si-NH_2] or acidic [Si-OH] sites, and reversible hydrolysis of $(\text{-Si-})_3\text{N}$ sites can alter the concentrations of such species.[24] In nonetching acidic solutions, amine and hydroxyl sites can undergo reversible protonation[24,25] to form $\text{Si-}(\text{NH}_2^+)\text{-Si}$, Si-NH_3^+, and Si-OH_2^+.

In this work we are concerned with observing the surface chemistry of Si_3N_4 under steady-state conditions during exposure to aqueous HF. The experimental technique used here is IR attenuated total reflectance (ATR) spectroscopy which has been used previously (*e.g.*, Ref. 27-29 and works cited therein) for *in situ* studies of the wet-chemical processing of Si. The present work is, to our knowledge, the first attempt to extend such experiments to Si_3N_4.

Experimental

The samples were ~45 nm thick films of Si_3N_4 grown by LPCVD on both sides of a Si substrate. Details concerning the growth, surface cleaning under UHV conditions and characterization of these samples are given elsewhere.[30] No cleaning of the as-received sample was done prior to mounting it in the flow cell (see below). The Si substrate was an internal reflection element (IRE), cut in an arbitrary crystallographic orientation, which was obtained commercially (Harrick Corporation, Ossining, NY). The IRE was a $25 \times 15 \times 1$ mm^3 parallelepiped with a 60° internal reflection angle which gave a total of fourteen reflections at the two faces for light propagating parallel to the long edge. Of these, eleven reflections probed the fluid/sample interface (as opposed to the sealing surfaces of the cell). Following Queeney *et al.*,[27] the IRE geometry was chosen to reduce the intensity of the liquid H_2O absorption bands (see below) and to extend the transmission range so that SiO_2 modes could be studied.

The Si_3N_4-coated IRE was mounted in a Teflon flow cell[27-29] with both sides in contact with the reagent fluid. The Teflon, which

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was pressed tightly around the edges of the IRE to form a fluid-tight seal, contributed weak absorptions in ATR at 1152 and 1207 cm^{-1}, and the transmission cutoff of the Si IRE occurred at about 980 cm^{-1}. The cell was connected to a pumping system which permitted a continuous flow of fluid at room temperature and the changing of fluids without exposing the sample to air. The total cell volume was 5.3 mL, and the typical flow rate was ~20 mL min^{-1}. Teflon and polyethylene were the only materials, other than Si or Si_3N_4, in contact with the reagents. The HF solution was prepared by successive dilutions, with deionized (DI) H_2O, of a standard concentrated solution, which is 49% by weight in H_2O. With a density of 1.19 gm cm^{-3}, 34.3 mL of the concentrate contains 1 mole of HF.

Spectroscopic data were recorded with a Mattson Cygnus 100 Fourier-transform IR system and a narrow-band $HgCd_xTe_{1-x}$ detector at a resolution of 8 cm^{-1} with 2000 scans averaged in about 10 min. The entire optical path was purged with dry N_2. Triangle apodization with fourfold zero filling was used in processing the interferograms. A spectrum recorded with pure DI H_2O flowing through the cell was used as a reference and the quantity $\delta R/R$ obtained, where $\delta R(\ll R)$ is the fractional change in reflectance caused by addition of the reagent of interest (*i.e.*, $\delta R \equiv R_{\text{reagent}}\text{-}R_{\text{water}}$).

Results and Discussion

Preliminary considerations.—Before proceeding to the data, a numerical simulation of the ATR experiment is considered. This is useful in evaluating the sensitivity to species on the Si_3N_4 surface and in further analysis of the data. Calculations were done for a model system consisting of a Si substrate with a 45 nm thick Si_3N_4 overlayer covered by an adsorbate layer in contact with an H_2O ambient. As in the experiment, light is incident internally at an angle of 60° at the IRE/fluid interface. The calculations were performed using the matrix formalism (fully described in Ref. 31[a]) for the polarized reflectance of a multilayer system with ideal interfaces between homogeneous and isotropic materials. Complex optical constants (n,k) for liquid H_2O and for PECVD Si_3N_4 were obtained as functions of $h\nu$ from the literature (Ref. 32 and 33, respectively). For crystalline Si, the real index (n) in the region of low absorption $(h\nu > 1000\ cm^{-1})$ was obtained in the form of a Sellmeier function.[34] (Thus, the multiphonon absorptions above 1000 cm^{-1} were neglected.) For an SiO_2 adsorbate layer, the optical constants of silica glass[34] were used. Methanol was also used as a model adsorbate because the IR oscillator parameters for the liquid are available[35,b,36] and because it exhibits absorptions that are reasonably close in energy to those expected for SiH_x and NH_x on the Si_3N_4 surface (see below). The fact that an actual CH_3OH film would dissolve in H_2O is irrelevant since only the model optical constants are significant here.

Figure 1 shows R and $\delta R/R$ for both s and p polarization, where δR is the difference in reflectance (see above) with and without a 0.5 nm thick layer of randomly oriented (*i.e.*, liquid) CH_3OH as a model adsorbate. Downward-pointing features are due to the CH_3OH layer, while upward-pointing structure arises from H_2O. The latter features appear in $\delta R/R$ because the presence of the thin CH_3OH layer reduces accordingly the sampling depth into the H_2O ambient. Hence, when the CH_3OH is removed in the calculation of $\delta R/R$, the H_2O absorptions gain intensity and appear as positive features. The results illustrate the higher sensitivity in p polarization and also the difficulties imposed by the strong H_2O absorptions. For eleven internal reflections (see above), the estimated transmission for unpolarized light at the ~3400 cm^{-1} H_2O absorption maximum is 28% for a 60° angle of incidence. The situation is more favorable in the vicinity of the N-H bending modes, where the transmission at the 1634 cm^{-1} absorption peak is ~57%. Similar results for $\delta R/R$ at 45° (not shown) indicate an approximately fivefold higher sensitivity to adsorbates on the Si_3N_4 surface, the combined effect of a larger $\delta R/R$ per reflection and of a greater number of reflections for the same IRE length. However, the calculated R_p (Fig. 1b) shows that the sample would be effectively opaque in the regions surrounding the H_2O absorptions.

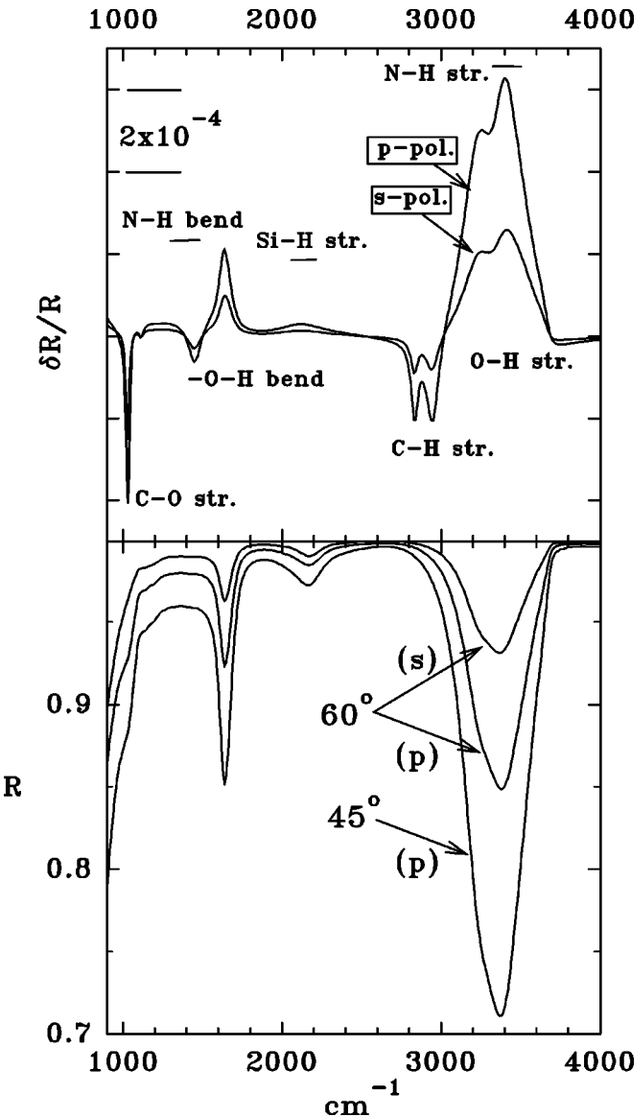

Figure 1. Results of model calculations for a Si IRE covered with a 45 nm thick Si_3N_4 layer having a 0.5 nm thick film of CH_3OH on the surface in an H_2O ambient. (a) Shows $\delta R/R$, the fractional change in reflectance caused by addition of the CH_3OH film, in p and s polarization at an internal reflection angle of 60°. All peaks are stronger in p than in s polarization. (b) Shows the reflectance at 60° for p and s polarization and at 45° for p polarization. The various vibrational modes are labeled (str. = stretching), including the approximate regions expected for H on the Si_3N_4 surface. The C-O, C-H and O-H modes are those of H_2O and/or CH_3OH. The magnitudes of R and $\delta R/R$ pertain to a single internal reflection.

Turning now to the etching reagents, dilute HF solutions (typically about 0.01-0.02 M, pH ≈ 2.7) were employed so that the etch rate would be sufficiently slow that the Si_3N_4 films would be useable for several experiments. There was no obvious dependence of

[a] There is a typographical error in this edition that affects calculations of multilayer transmission. Equation 4.170 should read $T = 1/S_{11}$.

[b] There is a typographical error that affects the application of the formalism in this paper. The factor of $4\pi/3$ in the numerator of Eq. 21b should be simply 4π.

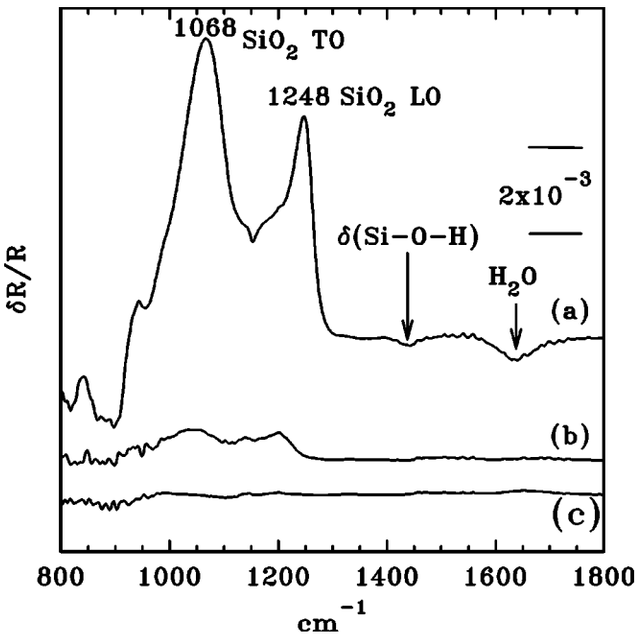

Figure 2. (a) Data in the region of SiO_2 absorption for a bare Si IRE in contact with 0.02 M HF. The reference spectrum was obtained in pure H_2O before exposure to HF; hence, positive-going features represent species removed by the HF. The native oxide was formed by exposure of an HF-treated surface to humid room air at room temperature (see text). (b) Shows data, as in (a), for the initial exposure of an as-received Si_3N_4 sample to the HF solution. (c) Shows a typical baseline obtained for two successive data sets with DI H_2O flowing in the cell. The traces have been displaced vertically for clarity. The sensitivity scale shows $\delta R/R$ per reflection. The IR beam was p polarized. Note that the IRE transmission is effectively zero below 980 cm^{-1}.

the data on the previous use of a sample (*i.e.*, on the number of prior experiments). Since, as noted above, the Si_3N_4 surface chemistry can depend on the nature of the film growth, a check of the etch rate was done by recording a normal-incidence IR transmission spectrum (in a dry N_2 ambient) for a Si_3N_4-coated Si sample before and after exposure to 0.087 M HF (pH $\approx$ 2.3). From the loss in the peak absorbance of the transverse optical (TO) phonon band, an etch rate of 0.14 nm min^{-1} was deduced which is in good agreement with previous results[2] (0.17 nm min^{-1}) for LPCVD Si_3N_4. Since it has been reported (see above) that HSA Si_3N_4 powders are attacked by water, it was considered useful to determine whether the same might be true for the LPCVD films used here. A Si_3N_4-coated Si wafer was etched in aqueous HF to remove the oxide and then immersed in static DI H_2O at room temperature. Based again on the absorbance of the TO mode, no significant loss of Si_3N_4 was seen after 43 h. This is consistent with the observation[2] that the LPCVD Si_3N_4 etch rate in aqueous HF goes to zero with the concentrations of HF and HF_2^-.

Infrared results.—Figure 2a shows results for a bare Si IRE (one for which the Si_3N_4 coating had been etched off) after exposure to humid room air[c] for four days to form a native oxide. The data provide a reference spectrum for an SiO_2 film obtained under the present conditions. The spectrum was recorded *in situ* with p polarized radiation after etching off the oxide in flowing 0.02 M HF. Upward-pointing (positive) features represent species removed by the HF, while downward-pointing (negative) structure is due to species that are added by the etching process. Removal of the oxide layer is evidenced by the peaks at 1068 and 1248 cm^{-1} which correspond,[27] respectively, to the TO and longitudinal optical (LO) Si-O stretching modes of SiO_2. The additional weak structure at $\sim$1154 cm^{-1} is due to a slight miscancellation of a Teflon absorption as noted above.

The weak feature at $\sim$1438 cm^{-1} is tentatively assigned to the bending mode of surface Si-O-H groups, hydrogen-bonded to H_2O, on the basis of the appearance of the C-O-H bending mode at 1452 cm^{-1} in liquid CH_3OH (cf. Fig. 1). However, it is noted that other studies[27,37] of wet-chemical growth or etching of oxides on Si have not reported this mode. The small peak at the 1634 cm^{-1} liquid-H_2O absorption, which also appears in the numerical simulations discussed above (cf. Fig. 1), arises from the fact that a slightly increased thickness of H_2O is sampled as the oxide layer is removed. Numerical simulation also indicates an oxide thickness of $\sim$1.5 nm based on the peak height of the TO band. The TO mode was used for the thickness estimate since the peak intensity, unlike that of the LO mode,[27] is insensitive to the exact optical constants of the ambient liquid. These simulations were done as described above using SiO_2, rather than CH_3OH, as the surface film.

In contrast to these results, data for an as-received Si_3N_4-coated IRE (Fig. 2b) gave little or no indication of the removal of an SiO_2 layer during the initial HF treatment. Figure 2b shows a spectrum recorded at the end of the Si_3N_4 native oxide removal. Continued exposure to HF resulted only in the monotonic growth of a feature (see below) due to the thinning of the Si_3N_4 film. Following removal of the oxide (if any) in HF, exposure to flowing DI H_2O for $\sim$30 min or to humid room air (overnight) did not result in the appearance of an SiO_2 spectrum (Fig. 2a) in data obtained during subsequent exposure to HF. This indicates that rapid hydrolytic oxidation does not occur under the present conditions for the LPCVD films studied here. Previously such rapid oxidation was observed somewhat above room temperature for PECVD films,[11] at room temperature for HSA powders,[13-15] and for LPCVD films undergoing chemomechanical polishing.[10] The present results appear to be consistent with those of Raider *et al.*[9] who etched LPCVD Si_3N_4 in HF and performed surface analysis, using X-ray photoemission spectroscopy, after exposure to room air. Rapid growth of 0.2-0.3 nm of oxide was seen, followed by only very slow growth beyond that point.

However, some evidence was found for the formation of an ultrathin oxide-like layer by hydrolysis of the HF-treated Si_3N_4 surface during postetch rinsing in H_2O. Figure 3a shows data, obtained with a nominally unpolarized IR beam, for prolonged exposure to HF. Unpolarized radiation was used in order to reduce the relative intensity[27] of the Si_3N_4 LO phonon absorption which peaks at about 1130 cm^{-1} (Ref. 30) and contributes to the tail extending to $\sim$1200 cm^{-1} in Fig. 3a. The peak at $\sim$1000 cm^{-1} results from the tail of the TO phonon absorption, which peaks at 804 cm^{-1} (Ref. 30), and the rapidly decreasing Si IRE transmission below 1000 cm^{-1}. Its appearance in $\delta R/R$ is due to the loss of Si_3N_4 absorption as etching progresses. The data in Fig. 3b resulted when the etched surface was rinsed in DI H_2O and then briefly treated again with HF. The spectrum shows the change, relative to the rinsed surface, caused by the brief ($\sim$10 min) HF treatment. The Si_3N_4 peak appears, due to the further etching of that material, together with a shoulder at about 1125 cm^{-1} which is ascribed to the removal of a layer formed when the etched surface was exposed to pure H_2O (or to dissolved O_2) during rinsing. Continued exposure to HF resulted in the further growth of the Si_3N_4 peak but not of the shoulder. The shoulder was difficult to observe, and Fig. 3b shows the clearest of several data sets.

In view of the very weak absorption (cf. Fig. 2), this layer might better be described as an ultrathin oxide-like layer rather than as SiO_2. The exact assignment of the $\sim$1125 cm^{-1} feature is uncertain. It is probably too high in energy to be ascribed to the Si-OH stretch

[c] The term humid room air means that the sample was rinsed with flowing DI H_2O to remove HF, after which the Teflon cell was drained and vented to room air. Water droplets retained in the lines to the pump are assumed to saturate the air in the cell.

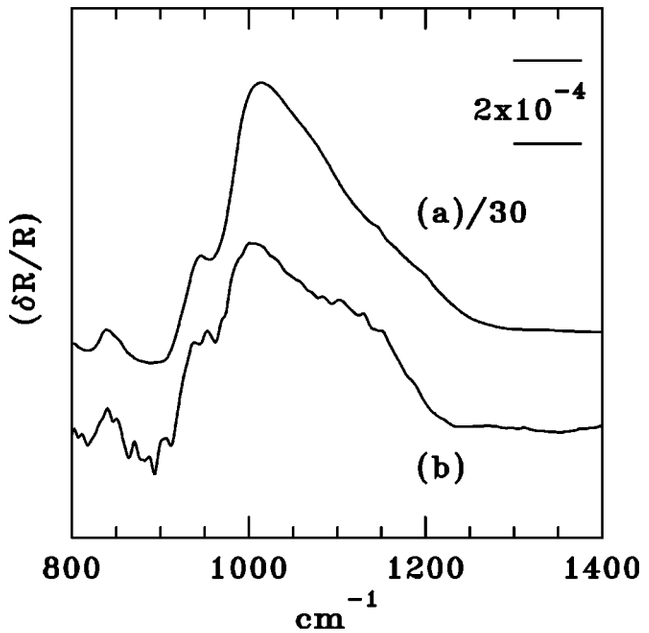

Figure 3. Data showing the hydrolysis of the HF-etched Si_3N_4 surface. (a) Shows the spectrum after prolonged HF etching, referenced to the as-received surface in DI H_2O. The peak at ~1000 cm^{-1} is related to the removal of Si_3N_4 (see text). (b) Shows data for this HF-etched surface after a ~30 min rinse in flowing DI H_2O. The spectrum was obtained after exposing the H_2O-rinsed surface again to HF (referenced to the rinsed surface) and shows the removal of more Si_3N_4 and of an oxygen species formed during the rinse. Trace (a) has been reduced in intensity by a factor of 30, relative to trace (b), and displaced vertically for clarity. The sensitivity scale shows $\delta R/R$ per reflection. The IR beam was nominally unpolarized.

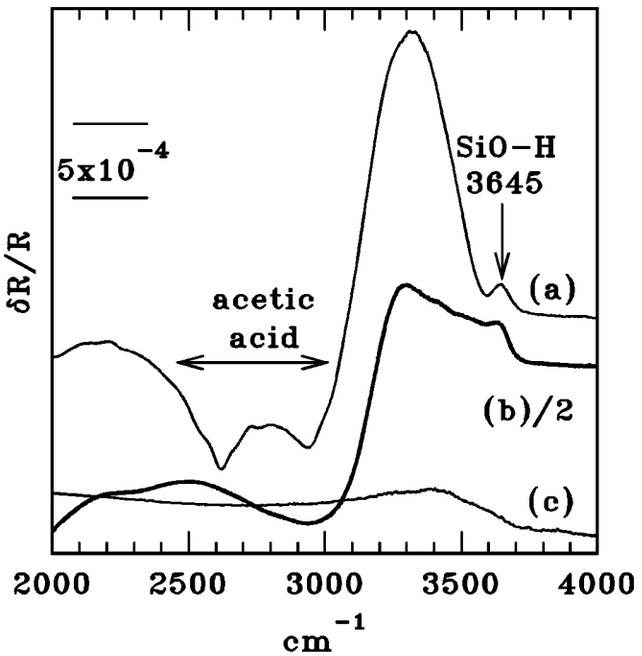

Figure 4. (a) Data obtained in p polarization showing the result of rinsing out the HF solution with a 5% (by volume) solution of glacial acetic acid in H_2O. The reference spectrum is that of the HF solution; hence, features pointing up (down) correspond to species removed (added) by the acetic acid. The structure in the 2500-3000 cm^{-1} range arises from acetic acid C-H stretching modes. The sensitivity scale shows $\delta R/R$ per reflection. (b) Similar to (a) but showing the effect of rinsing out the HF solution with 0.3 M HCl. The spectrum has been divided by a factor of two relative to (a). (c) Similar to (a) and (b) but showing the effect of rinsing out the HF with DI H_2O. The spectra have been displaced vertically for clarity.

which, for isolated OH groups on a Si surface, appears[38] at 840 cm^{-1}; although, the frequency may be higher for a Si site multiply-coordinated to N, instead of to Si, due to the partial positive charge on Si bonded to N. It is noted that various Si-O-Si stretching modes are seen[38] in the 990-1050 cm^{-1} range for Si(100) oxidized by H_2O vapor under UHV conditions. Hence, this mode might be due to an O bridging $(\text{-N-})_3\text{Si}$ sites.

Evidence for the existence of SiOH groups is seen in Fig. 4a. Here the HF etching solution was rinsed out with 5% (by volume) of glacial acetic acid in H_2O, rather than with pure H_2O. Formic acid [HOC(=O)H] vapor has been found[16] to react with SiOH groups on HSA Si_3N_4 powders to form the silyl ester [*e.g.*, $(\text{-N-})_3\text{Si-OC(=O)H}$]. The peak at 3645 cm^{-1} is assigned to the removal[d] of isolated OH groups (*i.e.*, those not H-bonded to H_2O). This mode is close in energy to that seen[29] on Si surfaces in contact with aqueous HF (3642 cm^{-1}); however, for HSA Si_3N_4 powders after high-temperature evacuation[17] the $(\text{-N-})_3\text{SiO-H}$ stretch appears at a somewhat higher energy, 3717 cm^{-1}. The corresponding Si-O-H bending mode (cf. Fig. 2) was obscured by the edge of the strong acetic acid absorption at 1392 cm^{-1}. The strong upward-pointing H_2O absorption band at ~3300 cm^{-1} appears because the acetic acid solution is more concentrated (*i.e.*, contains less H_2O) than the HF reference solution. There will also be a contribution in this region[29] from the removal of any SiOH groups that are H-bonded to H_2O. Figure 4b shows a similar feature when the HF is displaced by a 0.3 M aqueous HCl solution (see below). In this case, the removal of the isolated SiOH arises from the conversion[24,25] of SiOH to $SiOH_2^+$ in the strongly acidic HCl solution.

The reaction product is easily hydrolyzed since data obtained upon rinsing out the acetic acid or HCl solution with pure H_2O (not shown) indicate that the surface SiOH is reformed. However, when the HF is rinsed out with DI H_2O instead of an acid (Fig. 4c), no SiO-H peak is observed. It is also noted that no narrow IR absorption bands appear near this frequency for dilute aqueous HF solutions.[39,40] Furthermore, no additional structure was seen to indicate a similar interaction between acetic acid or HCl and surface NH_x species (see below).

It is useful to consider why SiOH appears in Fig. 4a,b but is not observed either during HF etching or after rinsing out the HF with pure H_2O (Fig. 4c). It has been proposed[41] that an acid attack on the SiOH group is the rate-limiting step in HF etching of SiO_2. If this process is slow for SiOH on the Si_3N_4 surface then the steady-state coverage of SiOH in dilute HF would not be much less than that in pure H_2O. The SiOH signature in $\delta R/R$ (dilute HF solution referenced to pure H_2O) would then be weak, recalling that the experiment detects only differences in surface composition. On the other hand, if a large fraction of the SiOH is removed, for example, by esterification in acetic acid solution, then this loss would be detected in $\delta R/R$.

Figure 5 shows data in the Si-H stretching region for a bare Si IRE (*i.e.*, one with no nitride layer) and for a Si_3N_4-coated IRE, all recorded using nominally unpolarized radiation. For Si_3N_4, native oxide refers to a surface exposed to DI H_2O after etching in HF, as described above. No evidence is seen for the formation of SiH_x groups on the Si_3N_4 surface following exposure to HF. The weak

[d] The actual reaction product cannot be identified from the present data due to interference from strong absorptions in the acetic acid solution. The appearance of the SiO-H mode in $\delta R/R$ means simply that the reaction has replaced the SiOH groups with another species not absorbing in the vicinity of 3645 cm^{-1}.

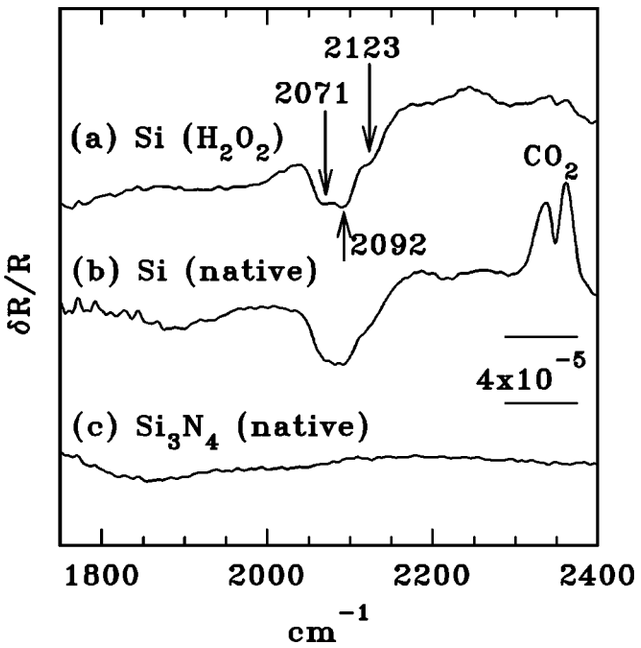

Figure 5. The Si-H stretching region for (a) a bare Si IRE after removal of an oxide layer formed in 15 wt % H_2O_2 in H_2O, (b) a bare Si IRE after removal of the native oxide formed by exposure to laboratory air at room temperature and (c) a Si_3N_4-coated Si IRE after removal of the native oxide (see text). In all cases, the oxide was removed by exposure to a flowing 0.087 M HF solution. The sensitivity scale shows $\delta R/R$ per reflection, and the spectra have been displaced vertically for clarity. Trace (b) shows a small residual signal from atmospheric CO_2 (and from H_2O vapor, below 1850 cm^{-1}) in the optical path. The IR beam was nominally unpolarized.

broad band at ~1850 cm^{-1} is a characteristic[39,40] of aqueous HF solutions.

For the bare IRE (Fig. 5b), removal of the native oxide in aqueous HF results in a clear Si-H signature[28,42] in the form of a broad band at ~2080 cm^{-1} with a shoulder at ~2115 cm^{-1}. This structure is somewhat better resolved after removal of an oxide grown by exposure[29] to 15 wt % H_2O_2 in H_2O, with peaks appearing at about 2071 and 2092 cm^{-1} and the shoulder at ~2123 cm^{-1}. Since the present Si surface is not crystallographically well-defined, no attempt is made to assign these features to specific SiH_x species.[28,42]

For Si_3N_4, the Si-H stretching modes would fall in the 2100-2300 cm^{-1} range,[43,44] depending on the local environment of the Si atom (*i.e.*, on back-bonding to N *vs.* O). In the bulk of the film, an Si-H stretching mode, due to a small amount of H remaining from LPCVD growth, was seen[30] at 2200 cm^{-1} by referencing the spectrum for a Si_3N_4-coated IRE to that of a bare IRE (all in a dry N_2 ambient). However, no SiH_x is detectable on the chemically treated Si_3N_4 surface under conditions for which it can be seen on elemental Si. This is true for the initial HF treatment of the as-received sample and for removal of either the native oxide or of an oxide formed, as above, by exposure to aqueous H_2O_2. In view of the evidence given above for the presence of surface SiOH, this result is consistent with the rapid hydrolysis of Si-H sites on the Si_3N_4 surface, as noted elsewhere.[11,13,17]

Proceeding now to the question of surface amine sites, Table I summarizes the reported[45-56] mode frequencies for various NH_x^+ and NH_x species. The NH_x^+ values were obtained from IR and Raman data for crystalline salts containing methyl- or ethylammonium cations, and the NH_x data are from IR spectra of aminosilanes. It is noted that the ν(N-H) modes for NH_x^+ are lower in energy than those of the neutral NH_x species and generally lie below the region of strong H_2O absorption (cf. Fig. 1). Hence, NH_x^+ species should be observable if the ν(N-H) bands are sufficiently intense. For a 0.01-0.02 M HF solution (pH ≈ 2.7) the results of Knotter and Denteneer[5] suggest that any surface NH_x sites should be protonated; hence, NH_x^+ species are more likely than the neutral analogs. In the bulk of the film an N-H stretching mode due to H remaining from LPCVD growth was seen,[30] as described above, at 3335 cm^{-1}.

Table I. Vibrational frequencies (cm^{-1}) for NH_x^+ and NH_x groups.[a]

	ν_a	ν_s	δ_1	δ_2
$CH_3NH_3^+$ [b]	3080-3231	2993-3159	1578-1632	1534-1575
$(CH_3)_2NH_2^+$ [c]	3049-3233	3034-3216	1536-1574	1433-1444
$(CH_3)_3NH^+$ [d]		2760	1215	
$R_3Si\text{-}NH_2$ [e]	3474-3483	3401-3405	1536-1552	
$(R_3Si)_2NH$ [f]		3351-3382	1164-1179	

[a] ν_a = antisymmetric stretch; ν_s = symmetric stretch; $\delta_{1,2}$ = deformation. The description of $\delta_{1,2}$ as bending, scissoring, rocking, or wagging varies for different studies and depends on the chemical species. Other deformations, which fall below 900 cm^{-1}, have been omitted.
[b] Reference 45-47. The values given represent the ranges reported in different studies for various compounds.
[c] Reference 48-52. The values given represent the ranges reported in different studies for various compounds.
[d] Reference 53. The data are for $[(CH_3)_3NH]_2SiF_6$ in which strong -N-H$^+$-F$^-$ hydrogen bonding shifts ν_s to a low value. For $[(C_2H_5)_3NH]SbCl_6$, Ref. 54, ν_s = 2703 cm^{-1} with (3164 cm^{-1} without) NH$^+$-Cl$^-$ hydrogen bonding.
[e] Reference 55, 56; R = alkyl group. For HSA Si_3N_4 following evacuation at high temperature, the corresponding frequencies for this species are reported (Ref. 17) to be 3510, 3450, and 1550 cm^{-1}.
[f] Reference 55. For HSA Si_3N_4 following evacuation at high temperature, the corresponding frequencies for this species are reported (Ref. 17) to be 3350 and 1470 cm^{-1}.

Observation of the NH_x or NH_x^+ bending modes under the present conditions is difficult due to interference from the strong H_2O absorption (cf. Fig. 1) and from the additional effect of a slight miscancellation of the Si multiphonon absorptions in the 1250-1500 cm^{-1} range. The latter effect could be eliminated by the use of a Ge IRE. Although thick (0.3 μm) Si_3N_4 films have been grown[57] on Ge by PECVD, Ge has not to our knowledge been evaluated as a substrate for the growth of thin films (such as those used here) by LPCVD which requires a higher substrate temperature than does PECVD.

An attempt was made to observe NH_x species by taking advantage of the protonation-induced shift in ν(N-H) noted above. Data were taken while flowing a 0.3 M HCl solution through the cell (after having displaced the dilute HF solution). The HCl was used to increase the H_3O^+ concentration without incurring the higher etch rate that would result from a concentrated HF solution. No NH_x^+ signatures were observed (Fig. 4b) in the 2700-3200 cm^{-1} range (cf. Table I) above the $\delta R/R$ detection limit of ~1 × 10^{-5} per reflection. The same is true in the absence of HCl, *i.e.*, for a dilute HF etching solution. In H_2O solution, both HCl and HF give broad absorption bands, with somewhat different structure,[39] in the ~2500-3700 cm^{-1} range which contribute to $\delta R/R$ in Fig. 4b.

This null result suggests that, under steady-state conditions in dilute aqueous HF, (-N-)$_3$SiOH (probably H-bonded to H_2O) is the dominant surface species and that the attack on NH_x^+ sites is too rapid to permit formation of a sufficiently high concentration of these species to be detectable in the present experiment. A further implication is that the rate-limiting step under these conditions may be an attack on the Si-N back bond at the (-N-)$_3$SiOH site. It is difficult to estimate how low the relative NH_x^+ surface coverage would have to be in order to be undetectable. However, IR data for

HSA powders[16,17] show that the integrated intensity for the $(\text{-Si-})_2\text{N-H}$ stretching mode is considerably greater than that of the $(\text{-N-})_3\text{SiO-H}$ mode. Assuming that the coverages of the two species are about the same on the HSA powders *in vacuo* then, based on the present $\delta R/R$ detection limit and on the observed SiO-H intensity (Fig. 4a,b), a conservative estimate indicates that the NH_x^+ coverage would have to be at least a factor five lower than that of SiOH in order to escape detection. This upper limit estimate is further reduced if one recalls that the SiO-H band in Fig. 4a,b reflects only the fraction of SiOH sites not H-bonded to H_2O.

Conclusions

Infrared attenuated total reflection spectroscopy has been used to observe the surface chemistry of Si_3N_4 films under steady-state conditions during exposure to dilute aqueous HF solutions. Surfaces etched in HF do not exhibit rapid growth of an SiO_2 layer when subsequently exposed to either humid room air at room temperature or to liquid H_2O. However, some evidence is found for the formation of an ultrathin oxide-like layer when the etched surface is rinsed in deionized H_2O. Removal of this layer in HF results in no detectable signal in the Si-H stretching region, unlike the case for Si subjected to a similar oxide-removal treatment. However, surface SiOH is observed via reaction with acetic acid or HCl solution, suggesting that SiH_x sites on the Si_3N_4 surface are rapidly hydrolyzed. Protonation of surface NH_x, to form NH_{x+1}^+ sites, should shift the ν(N-H) stretching modes to lower energy and away from the region of strong H_2O absorption. However, no NH_x was detectable by this means which indicates a low steady-state coverage.

These results have implications for chemical processes aimed at the functionalization of (*i.e.*, the attachment of organic ligands to) Si_3N_4 surfaces following exposure to aqueous HF treatment, since they suggest SiOH, and not SiH_x or NH_x, as the reactive species remaining after such treatment. In this context, it is noted that several groups have reported the functionalization of HF-treated Si_3N_4 surfaces using alkyl bromides[58] or alkyl chlorosilanes.[59-61] In analogy with SiO_2 surfaces,[62] these reactions could occur at SiOH sites on the Si_3N_4 surface, via elimination of HBr or HCl, or even by direct attack at strained Si-N-Si bridges. One study[63] reported reaction with 1-alkenes (*i.e.*, $H_2C = CH\text{-}R$, where R is a long-chain *n*-alkyl ligand) which almost certainly involves surface SiH_x sites.[64] However, the Si_3N_4 used in that work was thought to be Si-rich with, possibly, a surface chemistry more like that of pure Si than of Si_3N_4.

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