# **Reactive Species Generated during Wet Chemical Etching of Silicon in HF/HNO<sub>3</sub> Mixtures**

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The role of intermediate species generated during wet chemical etching of silicon in a HF-rich HF/HNO<sub>3</sub> mixture was studied by spectroscopic and analytical methods at 1 °C. The intermediate N<sub>2</sub>O<sub>3</sub> was identified by its cobalt blue color and the characteristic features in its UV-vis and Raman spectra. Furthermore, a complex N(III) species  $(3NO^+ \cdot NO_3^-)$  denoted as  $[N_4O_6^{2+}]$  is observed in these solutions. The time-dependent decay of the N(III) intermediates, mainly by their oxidation at the liquid-air interface, serves as a precondition for the study of the etch rate as function of the intermediate concentration measured by Raman spectroscopy. From a linear relationship between etch rate and  $[N_4O_6^{2+}]$  concentration, NO<sup>+</sup> is considered to be a reactive species in the rate-limiting step. This step is attributed to the oxidation of permanent existing Si-H bonds at the silicon surface by the reactive NO<sup>+</sup> species. N<sub>2</sub>O<sub>3</sub> serves as a reservoir for the generation of NO<sup>+</sup> leading to a complete coverage of the silicon surface with reactive species at high intermediate concentrations. As long as this condition is valid (plateau region), the etch rate is constant and yields a smooth silicon surface by NO<sup>+</sup>, the etch rate decreases linearly with the N<sub>2</sub>O<sub>3</sub> concentration and results in a roughening of the etched silicon surface (slope region).

#### 1. Introduction

The HF/HNO<sub>3</sub> etching system is perhaps the mostly widely used isotropic etchant for silicon.<sup>1</sup> Applications, e.g., the removal of work damage or roughness (after sawing of ingots) or the texturing of surface, can be found in the semiconductor industry as well as in a production step for solar cell fabrication.<sup>2,3</sup>

A systematic study of the etching mechanism was done by Robbins and Schwartz.<sup>4–6</sup> According to these authors, the etching of silicon in HF/HNO<sub>3</sub> mixtures follows a chemical process with two basic reaction steps. In the first step, silicon is formally oxidized by HNO<sub>3</sub> (eq 1) followed by the dissolution of formed SiO<sub>2</sub> by HF (eq 2). The overall reaction is written as eq 3.

 $3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O$ (1)

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$
 (2)

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O \quad (3)$$

The crucial step in this reaction is the oxidation of silicon by nitric acid. The electrochemical nature of the process was first mentioned by Turner,<sup>7</sup> who described the simultaneous dissolution of silicon at local anodic sites and reduction of the oxidizing agent at local cathodic sites. Kooij et al.<sup>1</sup> also assumed the electrochemical behavior of silicon etching because of the creation of holes which are injected into the valence band due to the reduction of HNO<sub>3</sub>.

Yet unresolved is the question about the nature and the role of intermediates formed by the reduction of HNO<sub>3</sub>. Equilibria of nitrogen oxides and nitrous acid were discussed by Abel et al.<sup>8–10</sup> Robbins et al. concluded that nitrous acid is acting as an active oxidizing agent because of the following observations. Traces of added NaNO<sub>2</sub> increase the etch rate due to the formation of nitrous acid<sup>4,5</sup> and prevent a commonly observed induction period. This period is characterized by an initially lower etch rate because the oxidizing agent nitrous acid has to be generated by the etch process itself.<sup>6</sup>

However, neither an identification of the assumed intermediates nor their relevance for the kinetics of etching has been experimentally proven so far. This paper is devoted to the intermediates in the etching of silicon in HF-rich, concentrated HF/HNO<sub>3</sub> mixtures. The spectroscopic identification of the intermediate nitrogen species, trapped when the etching is performed at 1 °C, as well as their impact on the etch rate of silicon is presented. Additionally, XPS measurements were performed for characterization of the wafer surface after etching. The presented results give new insight into the reaction mechanism of isotropic acidic etching of silicon, particularly, the nature of the rate-limiting step.

### 2. Experimental Section

Analytical-grade nitric acid (65 wt %, 14.45 M) and hydrofluoric acid (40 wt %, 22.77 M) were used for all etch mixtures reported herein as volume percentage [% (v/v)]. An overall volume of 50 mL of etch solution after HF and HNO<sub>3</sub> were mixed was filled in wide-mouthed bottles of HDPE (highdensity polyethylene) and thermostated during the series of experiments to the reaction temperature by using a cryostat (Polystat K12-2, Huber Kältemaschinen GmbH).

Each etch solution was then pre-aged by dissolving a defined amount of silicon (e.g., 1.4 g of Si). To prevent the loss of SiF<sub>4</sub> and an uncontrollable warming of the solution, silicon slices of approximately 70 mg (boron-doped, thickness of 675  $\mu$ m,

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resistivity of 24–36 W cm) were dissolved successively. Not until one piece of Si had been dissolved completely was the next one added to the etch solution. This pre-aging process dissolved the entire amount of silicon in  $\sim$ 2 h.

For the etch rate determination, a 10 mm  $\times$  10 mm silicon specimen [(111) orientation, boron-doped, thickness of 325  $\mu$ m, resistivity of 10 W cm, arithmetic average roughness of 1.1 nm] was held between the ends of a tweezers and immersed in the etch solution for 5–180 s. The reaction was quenched by immersing the sample in a beaker filled with a large volume of deionized water and rinsing thereafter. The etch rate (*r*) was obtained by differential weighing.

To perform a series of experiments at a quasi-constant silicon content, the time of etching had to be fitted to the etch rate in such a way that for any etch rate measurement only 1-7 mg of silicon was dissolved additionally. For the interpretation of surface morphology photographs, it is important to notice that with a decreasing etch rate a smaller silicon content was dissolved that can be attributed to the constant etch time during a series of experiments.

The concentrations of nitrite, nitrate, and fluoride ions in the etch solution were determined by ion chromatography (Deutsche METROHM GmbH & Co. KG) by dilution of an aliquot of 0.5 mL of the etch mixture with deionized water to a factor of 1:5000. The UV-vis measurements were carried out with a Specord 210 spectrometer (Analytik Jena AG) using UV semimicro cuvettes (d = 10 mm, 220–900 nm; Brand GmbH & Co. KG). The same cuvettes were used for Raman measurements.

Time-dependent Raman scattering of etch solutions was excited by 514.5 nm laser radiation of an Innova 305  $Ar^+$  ion gas laser (Coherent). The laser power was 25 mW. The scattered light was collected in a 180° backscattering geometry, analyzed by a T 64000 triple monochromator spectrometer (Jobin Yvon) set to a spectral band-pass of 2 cm<sup>-1</sup>, and detected using a liquid nitrogen-cooled CCD camera.

XPS measurements were carried out at a PHI 5600 CI (Physical Electronics) system using a hemispheric energy analyzer. Typical measurement parameters were as follows: excitation with monochromatic Al K $\alpha$  X-rays at 350 W, measuring area ~800  $\mu$ m in diameter, pass energy of 12 eV, and base pressure of 2 × 10<sup>-10</sup> mbar. The samples were measured immediately after drying, however, after a short (minutes) transport on air.

Surface morphology studies of etched silicon wafers were carried out with an optical depth profilometer [MicroProf, Fries Research & Technology GmbH (FRT)] receiving roughness parameters, photographs, three-dimensional pictures, and surface profiles. The sample area of 3 mm  $\times$  3 mm was profiled with 200  $\times$  200 points. The roughness of the polished wafers was measured using a Dektak 3030 surface profilometer (Veeco Instruments Inc.).

All species that appear in brackets in the text or figures denote concentrations in units of grams per liter.

### 3. Results and Discussion

**3.1. Etch Rate as a Function of the Nitrite Concentration.** A high concentration of reactive intermediates relieves their detection and enables the investigation of their influence on the reaction mechanism of silicon dissolution over a long period. This condition is achieved by predissolving a certain amount of silicon in a freshly prepared mixture of concentrated HF and  $HNO_3$  at 1 °C to stabilize the intermediate nitrogen species (visible as blue- or green-colored etch solutions) and to slow their decomposition into NO and/or NO<sub>2</sub>. The starting point for



**Figure 1.** (a) Correlation among etch rate *r*, nitrite concentration, and arithmetic average roughness ( $R_a$ ) of the etched silicon surfaces [ $\vartheta = 1 \,^{\circ}$ C, *m*(Si)<sub>diss</sub> = 1.40 g, 50 mL of 70% (v/v) HF and 30% (v/v) HNO<sub>3</sub>]. (b) XPS profiles of the Si2p region of the silicon surface after etching. The use of a monochromator results in Si2p<sub>3/2</sub> and Si2p<sub>1/2</sub> splitting. Selected samples are numerated; the numeration is valid throughout this paper.

the kinetic measurements is the nitrite concentration measured immediately after the last piece of silicon had been dissolved. If one begins from that maximum value within a given experimental series, the nitrite concentration decreases with time following first-order kinetics. <sup>11</sup>

Figure 1 shows the etch rate as a function of the nitrite concentration. To follow the series of experiments on a time scale, the *x*-axis of Figure 1 has to be read from right (high nitrite concentration) to left (low nitrite concentration). The region of high nitrite concentrations, where the etch rate is independent of the nitrite content, is denoted as a plateau region. Below a certain value, a linear relationship to the etch rate was observed and denoted as the slope region. These two remarkable dependencies between etch rate and nitrite concentration were reproducibly found for (i) different temperatures ( $T \le 15$  °C), (ii) various amounts of predissolved silicon, and (iii) different etch bath compositions with a hydrofluoric acid content of >70% (v/v).

Activation energies of 41 kJ/mol for the plateau region and 44 kJ/mol for the slope region, each at a constant nitrite concentration for different temperatures, are an indication that the reaction mechanism is the same in both regions and independent of nitrite concentration.<sup>11</sup>

XPS studies of the etched silicon surfaces show a complete hydrogen termination also, which is also independent of the nitrite concentration of the etch mixture (Figure 1). Neither Si-O bonds nor Si-F or Si-O-F bonds (103.3-105 eV) were detected. If Si-F bonds were formed during etching of silicon, a replacement with Si-OH bonds would occur during water rinsing and a change in the Si2p peak should occur.<sup>12,13</sup> Only a complete hydrogen termination of the silicon surface and its resistivity against oxidation explains that no native oxide was observed in the Si2p spectra. This shows that any changes in the etch rate must originate by species in the etch solution.

We supposed earlier<sup>11</sup> that the nitrite ion is not the reactive species in the etching process but rather a sum parameter for all intermediate nitrogen species in the +3 oxidation state such as NO<sup>+</sup>, N<sub>2</sub>O<sub>3</sub>, and  $[N_4O_6^{2+}]$  [in the following denoted as N(III) species] in the concentrated etch solution. Only the dilution of the concentrated etch solutions by a factor of 1:5000 for the ion chromatographic analysis causes the full conversion of all N(III) species to nitrite ions.

**3.2. UV–Vis and Raman Spectroscopy of Intermediates in Colored Etch Solutions.** UV–vis spectra of blue or greenblue etch solutions exhibit, independent of the mixing ratio of



**Figure 2.** UV-vis spectra of blue-colored etch solutions that differ in composition.

HF and HNO<sub>3</sub>, a broad peak at 638 nm (Figure 2). With an increasing nitric acid content, the peak maximum at 638 nm increases due to an enhancement (darkening) of the blue color. Simultaneously, the nitrite concentration increases from 21.5 to 28.7 g/L and then to 32.0 g/L for 50% (v/v) HNO<sub>3</sub>.

The blue and green colors are originated by  $N_2O_3$ , according to a UV-vis study of  $N_2O_3$  in aqueous solutions by Doherty et al.<sup>14</sup> The formation of  $N_2O_3$  is confirmed by Raman spectra of various colored etch solutions showing a broad peak at 258 cm<sup>-1</sup>.

According to a Raman study on different isomers of  $N_2O_3$  in NO/O<sub>2</sub> matrices by Nour et al., this line is assigned to the  $\nu_6$  N–N stretch mode of the asymmetric nitrogen(III) oxide (as-N<sub>2</sub>O<sub>3</sub>).<sup>15</sup> This line is the strongest Raman line of as-N<sub>2</sub>O<sub>3</sub> at all. Further characteristic N<sub>2</sub>O<sub>3</sub> vibrations were detected at 195, 623, 784, and 1288 cm<sup>-1</sup>. The generation of green and blue-green etch solutions might be ascribed to a superposing of blue (N<sub>2</sub>O<sub>3</sub>) and yellow brown (nitrous gases) (Figure 3).

A second N(III) species was identified by Raman spectroscopy by a peak at 2240 cm<sup>-1</sup>. According to the work by Harrar et al.,<sup>16</sup> this peak can be associated with the species ( $3NO^+\cdot NO_3^-$ ) (2246 cm<sup>-1</sup>), further denoted as [ $N_4O_6^{2+}$ ]. Moreover, a very weak band corresponding to the NO<sup>+</sup> ion at 2382 cm<sup>-1</sup> was detected. These Raman results confirm the work of Kelly et al., who suggested the formation of NO<sup>+</sup> in a HF/HNO<sub>3</sub> etch mixture.<sup>17</sup> Further relevant Raman bands of colored etch solutions are attributed to nitric acid, nitrate, dissolved N<sub>2</sub>O<sub>4</sub>, and the hexafluorosilicic anion (Figure 3), as listed in Table 1.

Other nitrogen species in the +5 oxidation state, for instance, NO<sub>2</sub><sup>+</sup>, whose strongest Raman line would have been observed at 1400 cm<sup>-1</sup> were not found.<sup>16</sup> Moreover, the Raman spectra did not reveal any hint on the presence of nitrite ions, since the strongest Raman line ( $\nu_1$ ) at 1329 cm<sup>-1</sup> in aqueous solution was not observed.<sup>27</sup>

**3.3. Etch Rate versus N(III) Intermediates.** The etch rate measurements using the concentrated, blue-colored etch solution from Figure 1 were followed by Raman spectroscopy. The inset in Figure 4 shows the evolution of the 258 cm<sup>-1</sup> Raman band attributed to  $N_2O_3$  as function of time, i.e., the nitrite ion concentration. If the etch solution is exposed to air, the N(III) intermediates undergo an oxidative decay.<sup>11</sup> The signal intensity decreases as the initially dark blue solution fades out and vanishes finally if the solution becomes transparent. The plot of the  $N_2O_3$  Raman peak area versus the nitrite concentration (Figure 4) shows a linear relationship between the amount of  $N_2O_3$  dissolved in the concentrated etch solution and the nitrite concentration measured in a 1:5000 dilution by ion chromatography.



**Figure 3.** (a) Raman spectrum of a blue-colored etch solution after silicon dissolution [ $\vartheta = 1$  °C,  $m(Si)_{diss} = 1.4$  g, 50 mL of 70% (v/v) HF and 30% (v/v) HNO<sub>3</sub>]. (b) Raman spectrum a after exposure of the sample to air for several hours. (c) Difference Raman spectrum (a – b). (d) Raman band profile analysis of spectrum c for the low-energy wavenumber range. (e) Raman band profile analysis of spectrum c in the NO stretching range; the intensity axis was extended by a factor of 20 compared to that of panel d.

The correlation of Raman peak area for the second N(III) species,  $[N_4O_6^{2+}]$ , versus nitrite concentration shows a completely distinct behavior as seen in Figure 5. At high nitrite concentrations, the  $[N_4O_6^{2+}]$  Raman peak area is more or less constant; however, with a certain nitrite concentration, a linear dependence between the amount of  $[N_4O_6^{2+}]$  in concentrated etch solution and the nitrite concentration measured in a dilute solution exists. The right-hand side of Figure 5 shows a linear dependence between the kinetic parameter etch rate and the  $[N_4O_6^{2+}]$  Raman peak area and identifies the reactive species in the rate-limiting step. It is supposed that the NO<sup>+</sup> ion is the essential constituent in the  $[N_4O_6^{2+}]$  complex ion rather than the nitrate ions, which are present in a manifold excess and considered to stabilize the nitrosonium cation in form of the  $[N_4O_6^{2+}]$  complex species.

On the basis of the results that were obtained, the following interpretation can be given.

(i) By the dilution of concentrated etch solutions, the intermediate N(III) species  $N_2O_3$  and  $[N_4O_6^{2+}]$  are fully converted into nitrite ions. A quantification is given by the relationship in eq 4, introduced by Doherty et al.,<sup>14</sup> and expanded by the species nitrosonium ion, NO<sup>+</sup>. Even if the other species mentioned in eq 4 were not spectroscopically identified, their presence at low concentrations should not be ruled out.

$$([NO_2^{-}])_{\text{diluted solution}} = ([N_2O_3] + [NO^+] + [HN_2O_3^+] + [H_2NO_2^+] + [HNO_2])_{\text{concentrated solution}}$$
(4)

TABLE 1: Wavenumbers of the Raman Lines Which Are Characteristic for the Species Found in HF/HNO<sub>3</sub> Etch Solutions

species	observed wavenumbers (cm <sup>-1</sup> )	literature wavenumbers (cm <sup>-1</sup> )
HNO <sub>3</sub>	$929^{a}$	928, <sup>16</sup> 925, <sup>18,19</sup> 92620
	1305	1294, <sup>16</sup> 1300, <sup>18,19</sup> 1303 <sup>20</sup>
	$690^{b}$	680 <sup>19</sup>
$NO_3^-$	722	72018
	1038, 1047	105016,18
$N_2O_4$	812	810, <sup>16</sup> 809 <sup>21</sup>
	1384	1380 <sup>16,21</sup>
$[N_4O_6^{2+}]$	2240	2246 <sup>16</sup>
$NO^+$	2382	238722
$N_2O_3$	195	20515
	257	258, <sup>16</sup> 260, <sup>23</sup> 253, <sup>21</sup> 266 <sup>15</sup>
	623	62715
	784	78415
	1288	128815
cis-N <sub>2</sub> O <sub>2</sub>	1869	1866 <sup>24</sup>
$SiF_6^{2-}$	404	$395 - 400^{25}$
	654	656 <sup>25,26</sup>
$H_2O$	1640	
	956	cuvette
	1447	cuvette

<sup>*a*</sup> This Raman band results from the symmetric stretching vibration of HNO<sub>3</sub> and coincides with a signal from the employed plastic cuvette. <sup>*b*</sup> The Raman band at 690 cm<sup>-1</sup> is also observed for HF/HNO<sub>3</sub> mixtures without dissolved silicon and is attributed to the NO<sub>2</sub> bending vibration of HNO<sub>3</sub> (680 cm<sup>-1</sup>). The shift is considered to be a consequence of interaction between both acids, e.g., hydrogen bonds.



**Figure 4.** Relationship between the Raman peak area of  $N_2O_3$  at 258 cm<sup>-1</sup> and the nitrite concentration obtained by ion chromatography. The inset shows the time-dependent  $N_2O_3$  Raman signal (top curve, maximum nitrite concentration; bottom curve, nitrite concentration near 0 g/L).

The complete conversion of the N(III) species, mainly  $N_2O_3$ and  $[N_4O_6^{2+}]$ , to nitrite ions by dilution of concentrated etch solutions underlines the importance of the nitrite concentration as a useful sum parameter (eq 4) in characterizing the reactivity of etch mixtures in industrial applications.

(ii) The correlation between the peak area of  $[N_4O_6^{2+}]$  and the nitrite ion concentration in Figure 5 does not yield a linear dependence like that for N<sub>2</sub>O<sub>3</sub> in Figure 4. The region with a constant NO<sup>+</sup> concentration with a large amount of nitrite, i.e., high N<sub>2</sub>O<sub>3</sub> concentration (plotted as a function of nitrite concentration and time in Figures 5 and 7, respectively), leads to the assumption that N<sub>2</sub>O<sub>3</sub> serves as a reservoir for the generation of NO<sup>+</sup>. A plausible method of NO<sup>+</sup> formation can



**Figure 5.** Correlation between the Raman peak area of  $[N_4O_6^{2+}]$  at 2246 cm<sup>-1</sup> and the nitrite concentration obtained by ion chromatography (a) and etch rate dependence on  $[N_4O_6^{2+}]$  concentration (b).

be given by the following series of equilibria between the different N(III) species in concentrated etch solutions (eq 5).

$$HN_{2}O_{3}^{+} \xrightarrow[+H^{+}]{+H^{+}} N_{2}O_{3} \xrightarrow[-H_{2}O]{} 2HNO_{2} \xrightarrow[-2H^{+}]{+2H^{+}} 2H_{2}NO_{2}^{+} \xrightarrow[-2H^{+}]{+2H^{+}} 2H_{3}O^{+} + 2NO^{+}$$
(5)

In the plateau region, the concentration of  $N_2O_3$  is sufficiently high to establish a high concentration of NO<sup>+</sup> (the concentration of  $N_2O_3$  is found to be proportional to the square of the NO<sup>+</sup> concentration, in agreement with eq 5) that completely covers the silicon surface, yielding a region with a constant NO<sup>+</sup> concentration and a uniform etch rate. From a certain concentration of N<sub>2</sub>O<sub>3</sub>, the generated NO<sup>+</sup> concentration is insufficient for a complete surface coverage and the etch rate decreases linearly to the surface concentration of NO<sup>+</sup>. The right plot of Figure 5 showing a linear correlation between etch rate and [N<sub>4</sub>O<sub>6</sub><sup>2+</sup>] Raman peak area is considered as evidence for the assumed coverage phenomena and shows that NO<sup>+</sup> is involved as the reactive species in the rate-determining step of the dissolution of silicon. The similar activation energies for the plateau and slope region, the always present hydrogen termination of the silicon surface, and the linear relationship between the  $[N_4O_6^{2+}]$  concentration and the etch rate are seen as evidence of a uniform reaction mechanism that is independent of the concentration of the N(III) intermediates.<sup>11</sup>

**3.4. Morphology of Etched Silicon Surfaces as a Function of Nitrite Concentration.** A characteristic feature of this etching system is the evolution of the surface morphology and roughness parameters after etching of initially polished silicon samples (with an initial arithmetic average roughness of 0.7 nm) in the dependence on the N(III) concentration. The arithmetic average roughness ( $R_a$ ) values for a 3 mm × 3 mm area are shown as function of the nitrite concentration in the left plot of Figure 1. The corresponding micrographs of the surface as well as the three-dimensional views of samples 1, 3, and 5 are depicted in Figure 6. The plot of the  $R_a$  values versus the nitrite concentration gives two different regions in analogy to the already found etch rate dependence as a function of the nitrite concentration.

This finding points to the previously proposed coverage phenomena as an explanation of the etch rate and surface morphology evolution shown in Figure 1. The reactive N(III) species are generated at the silicon surface due to the reduction of nitric acid. This can be visibly observed in an unstirred solution having a high content of already dissolved silicon by the evolution of a blue-green-colored cloud covering a piece of silicon after its immersion in the etch mixture. This leads to a high and localized concentration of reactive N(III) species near



Figure 6. Micrographs of etched silicon pieces (top row) and corresponding three-dimensional views (bottom row).



**Figure 7.** Time-dependent decomposition of N(III) species, nitrite concentration obtained by ion chromatography, and  $[N_4O_6^{2+}]$  and  $N_2O_3$  concentration obtained by Raman spectroscopy.

the silicon surface and therefore to a full coverage of all possible surface reaction sites. This situation remains unchanged as long as the local N(III) species concentration is sufficiently high and results in the observed plateau region in Figure 1. The concentration of the reactive species decreases with time mainly via an oxidative degradation (see the next section). At a certain concentration, indicated by the transition from the plateau to slope region, the full coverage is no longer given, leading to a linear relationship between the N(III) concentration and  $R_a$  value. Stirring experiments underline this hypothesis.<sup>11</sup> It was found that the etch rates in both the slope and plateau regions are dramatically lowered by stirring. The linear relationship between the etch rate and nitrite concentration in the former slope region remains; however, the slope  $\Delta r / \Delta [NO_2^-]$  decreases with an increase in the stirring speed. The former plateau region is turned into a slope region with a linear relationship between the etch rate and nitrite concentration that decreases with an increase in the stirring rate.

Such unusual behavior can be explained only by stirring the species involved in the rate-limiting step away from the surface. As a consequence, species from the bulk solution, such as nitric or hydrofluoric acid, are transported to the surface. Then, the surface reactive sites are faced with different solution species with distinct reactivity. However, at present, it is not possible to decide whether the observed pitting is caused mainly by a simple absence of N(III) species or by a facilitated attack of nitric or hydrofluoric acid.

**3.5. Fate of the Intermediates.** Exposing the etch solution to air causes a time-dependent decay of all N(III) species as illustrated in Figure 7. The decay of the nitrite concentration was shown to follow first-order kinetics, whereas the nitrate concentration increases identically with the same reaction order and rate.<sup>11</sup> Furthermore, evidence for a direct oxidation of the N(III) species by oxygen from the air was found, since the molar ratios between the amounts of decomposed nitrite and of formed nitrate for given time intervals amount to values ranging from 0.9 to close to unity. The deviation from unity can be explained by outgassing caused by the disproportionation of N<sub>2</sub>O<sub>3</sub> into NO and NO<sub>2</sub>. The oxidation of the N(III) intermediates on air is easily underlined by the following observation. (i) A concentrated colored etch solution stored without oxygen, e.g., in a tightly sealed reaction vessel, can hold its color at 1 °C for several days. (ii) If the bottle is opened, a decoloration of the solution starts from the liquid-gas interface and proceeds slowly into the bulk solution. (iii) Stirring accelerates the nitrite decay via an increase in the area of the liquid-gas interface and faster oxygen uptake. The rate constants of nitrite decay and nitrate increase were found to be almost identical with different stirring rates.11

In light of the Raman studies, these findings could be explained by a direct oxidation of  $N_2O_3$  (as the major contribution to the nitrite concentration) to  $NO_3^-$  by air oxygen formally described by eq 6.

$$N_2O_3 + O_2 + H_2O \rightarrow 2HNO_3 \tag{6}$$

Furthermore, the absence of nitrous acid and nitrite ions in the Raman spectra is seen as an indication that the commonly assumed disproportionation reaction of nitrous acid into nitric acid and NO in eq 7 does not occur or occurs to an only negligible extent.

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$
 (7)

## 4. Conclusions

Performing the etch experiments at 1 °C instead of at room temperature leads to a stabilization of nitrogen intermediates because of reduction of nitric acid. Another important advantage for kinetic investigations can be seen in the decrease of the etch rate. As the etch rate is lowered, the reaction heat can be removed from the silicon surface more efficiently, leading to a better controllability of etching.

On the basis of the spectroscopic identification of  $N_2O_3$  and  $(3NO^+ \cdot NO_3^-)$  (denoted as  $[N_4O_6^{2+}]$ ) as intermediary species and the linearity between the  $[N_4O_6^{2+}]$  concentration and the etch rate, the following mechanistic model is established.

Assuming the simplified formalism of eqs 1 and 2 as a valid description of the isotropic etching of silicon in HF-rich solutions, the oxidation of the silicon surface by nitric acid (eq 1) is the rate-limiting step while the subsequent dissolution of SiO<sub>2</sub> (eq 2) proceeds much faster.<sup>28–31</sup> According to Robbins et al.,<sup>4,5</sup> the diffusion of the minority component (HF or HNO<sub>3</sub>) to the silicon surface limits the overall reaction.

The reduction of nitric acid as an oxidant from the +5 to +2 oxidation state with NO as the final gaseous product proceeds in two consecutive steps: (i) the fast reduction of N(V) to N(III) and (ii) the rate-limiting step of the reduction of N(III) to N(II). Both partial reactions are illustrated by the very simplified reaction scheme (eqs 8 and 9):

initiation: 
$$HNO_3 \xrightarrow{+Si}{-Si(IV)} N_2O_3 + NO^+$$
 (8)

propagation: 
$$Si(0) \xrightarrow{+N0^+} Si(I)$$

 $0) \xrightarrow{+\mathrm{NO}^+} \mathrm{Si}(\mathrm{IV}) \xrightarrow{+4\mathrm{F}^-} \mathrm{SiF}_4 \xrightarrow{+2\mathrm{HF}} \mathrm{H}_2\mathrm{SiF}_6$ (9)

XPS measurements of the silicon surface after etching reveal a hydrogen-terminated silicon surface as result of a preceding dissolution of oxidic silicon surface species by  $HF^{.32-34}$  The hydrogen-terminated silicon surface possesses a hydridic character and is therefore stable in acidic solution in chemical analogy to SiH<sub>4</sub>. The rate-limiting step is now assumed as the attack of NO<sup>+</sup>, a small and positively charged ion capable of approaching the hydridic surface, either under formation of intermediate Si–OH surface moieties or by an oxidative cleavage of the Si–Si back-bonds of the Si–H surface species.

This gives rise to two main questions. (i) How does the fast reduction of HNO<sub>3</sub> to the N(III) intermediates proceed, and with which steps in the oxidation of silicon can be associated? A possible answer can be given with respect to the model by Turner,<sup>7</sup> where the reduction of nitric acid is an electrochemical process. According to Lehmann,<sup>35</sup> the etching of silicon using concentrated HF/HNO<sub>3</sub> mixtures is analogous to the anodic oxidation of silicon in HF solutions at high current densities. The injection of holes into the valence band of silicon can cause a cleavage of Si–Si bonds which may further react with water molecules, yielding a Si–O–Si bond. Such a quite unspecific reaction step might account for the isotropic character of the acidic etching.<sup>36</sup>

(ii) Yet unresolved is the question of the final state of NO<sup>+</sup> after its reaction with silicon. The evolution of brown gas as a consequence of the oxidation of NO by air is broadly attenuated at 1 °C compared with that at  $\geq 25$  °C. A quantitative analysis of the gas atmosphere during the acidic etching of a multi-crystalline silicon with a HF/HNO<sub>3</sub>/H<sub>2</sub>O mixture gave a considerable amount of N<sub>2</sub>O as the reaction product.<sup>37</sup> Furthermore, N<sub>2</sub>O was identified as the major reaction product in the electrochemical oxidation of silicon in HF/HNO<sub>3</sub> mixtures.<sup>1</sup> It has to be concluded that eq 3 is an insufficient description of

the etching reaction because the mentioned observations make clear the fact that the reduction of nitric acid does not end with NO as the final product.

To clarify the mechanism of wet chemical etching of silicon in HF/HNO<sub>3</sub> mixtures, further detailed investigations of the liquid phase and the gas phase are needed to characterize the reduction of nitric acid to the final reduction products.

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