HF-HNO_3-H_2SO_4/H_2O Mixtures for Etching Multicrystalline Silicon Surfaces: Formation of NO_2^+, Reaction Rates and Surface Morphologies

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The reaction behavior of HF-HNO_3-H_2O etching mixtures, which are frequently used for texturing silicon surfaces, is significantly influenced by the addition of sulfuric acid. For high concentrations of sulfuric acid, nitronium ions NO_2^+ ions have been detected by means of ^{14}N NMR spectroscopy, and results of Raman spectroscopic investigation have allowed the quantification of the nitronium ions. Maximum etching rates of 4000 – 5000 $nm\,s^{-1}$ are reached for HF (40 %)-HNO_3 (65 %)-H_2SO_4 (97 %) mixtures with w (40 %-HF)/w (65 %-HNO_3) ratios of 2 to 4 and w (97 %-H_2SO_4) < 0.3. For higher concentrations of sulfuric acid, H_2SO_4 can be considered as a diluent. In order to investigate the influence of the sulfuric acid at constant HF and HNO_3 quantities, fuming HNO_3 (100 %) was used and the water in the mixtures successively replaced by H_2SO_4. A sudden increase of etching rates was found for sulfuric acid concentrations around 6 $mol\,L^{-1}$ correlating with the characteristic color of the etching solutions. Decreased reaction rates at > 7 $mol\,L^{-1}$ H_2SO_4 are attributed to high solution viscosities and the formation of fluorosulfuric acid. Generally, in HF-HNO_3-H_2SO_4/H_2O etching mixtures a reduced dissociation of nitric acid, the formation of nitronium ions, the solubility of neutral nitrogen intermediates (*e. g.* NO_2, N_2O_3), as well as other effects influence the attack of silicon surfaces. The structure of etched silicon surfaces was investigated by means of scanning electron (SEM) and laser scanning microscopy (LSM). The morphologies are influenced most significantly by the relative amounts of sulfuric acid. Unexpectedly, in nitronium ion-containing mixtures rough surfaces with pore-like etching pits are generated.

Key words: Acidic Etching, Multicrystalline Silicon, Nitronium Ions, Sulfuric Acid, Solar Cells

Introduction

Wet chemical etching is of enormous relevance to silicon solar cell processing. Conventional acidic etching mixtures consist of hydrofluoric acid, nitric acid and water. These solutions are widely utilized for saw damage removal, texturing of silicon surfaces for reducing light reflection and recycling of used solar modules. In addition to these solar material applications, the usage for nanostructured devices has attracted much attention, such as fabrication of silicon nanowires by metal-assisted chemical etching of silicon [1] or tuning the size of silicon nanocrystals with HF-HNO_3-H_2O etching mixtures [2].

Dissolving silicon requires two simultaneous processes: the stepwise oxidation of silicon atoms by oxidants, *e. g.* HNO_3, NO_2, NO_2^+ or NO^+, and the formation of water-soluble complexes by fluoride containing species, *e. g.* HF, F^- and HF_2^-. A simple two-step etching mechanism has been proposed [3 – 5]. In this model the formation of an intermediate SiO_2 layer by nitric acid (Eq. 1) is followed by dissolving of this oxide with hydrofluoric acid (Eq. 2).

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

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

According to this early model the only reaction products are nitrous oxide, hexafluorosilicic acid and water. However, several further species including NO_2, N_2O, $NH_4^+$and H_2 were detected as additional reaction products of HF-HNO_3-H_2O etching solutions [6, 7], and the formation of an intermediate silicon dioxide layer was excluded by means of XPS measurements [8, 9]. Instead, after etching in HF-containing solutions silicon surfaces are completely hydrogen-terminated, and in a few cases F atoms have been detected on the silicon surface. For example, fluorine-containing endgroups such as -SiH_2F and

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-SiHF$_2$ were identified by means of real-time, *in situ* infrared studies [10].

Due to the complexity of the chemical system and to the multitude of transport processes at the surface/etchant interface, several reaction steps have remained unidentified, and the precise oxidation of surface silicon atoms by nitric acid and/or various nitrogen containing species is subject of dispute. According to Turner, the dissolution of silicon should be described as an electrochemical process in which silicon is dissolved at local anodic sites while oxidants are reduced at local cathodic sites [11].

A well-known phenomenon in diluted HF-HNO$_3$-H$_2$O etching mixtures is a so-called induction period with considerably lower etching rates at the beginning of a typical experiment. This delay time is reduced, and etching rates are increased, by addition of NaNO$_2$ as a “stimulating agent” [3]. The nitrite ions can be protonated twice in highly acidic etching mixtures leading to the formation of nitrosyl ions NO$^+$ (Eq. 3).

$$HNO_2 + H^+ \rightleftarrows H_2NO_2^+ \rightleftarrows NO^+ + H_2O \qquad (3)$$

Nitrosyl ions were supposed to be strong oxidants for silicon surfaces by Kelly *et al.* [12]. Several studies have shown that N(III) intermediates, especially nitrosyl ions, are involved in the rate-determining step of the silicon etching reactions. Recent studies with HF-NOHSO$_4$-H$_2$SO$_4$ mixtures indicating a high reactivity towards crystalline silicon support this concept [13, 14]. In HF-HNO$_3$-H$_2$O etching solutions the formation of reactive N(III) species (NO$^+$, N$_2$O$_3$) and the nitrosyl-nitrate ion adduct [N$_4$O$_6$$^{2+}$] were verified by means of Raman spectroscopy. N$_2$O$_3$ has been discussed as a reservoir for nitrosyl ions [15].

In the present study the formation and effects of nitronium ions NO$_2$$^+$ are investigated by acidification of HF-HNO$_3$-H$_2$O mixtures with sulfuric acid. This paper gives an overview of the reactivity of HF-HNO$_3$-H$_2$SO$_4$ etching solutions depending on the sulfuric acid concentrations, focusing on silicon etching rates, formation of N(III) species and morphologies of etched surfaces.

Results and Discussion

Characterization of pristine HF-HNO$_3$-H$_2$SO$_4$ etching mixtures (before contact to silicon)

To investigate nitronium ion formation, HF-HNO$_3$-H$_2$SO$_4$ mixtures were analyzed by means of Raman and ^{14}N NMR spectroscopy. Raman spectroscopic studies of the ternary HNO$_3$-H$_2$SO$_4$-H$_2$O system have shown that the equilibria NO$_3$$^-$/HNO$_3$ (Eq. 4) and HNO$_3$/NO$_2$$^+$ (Eq. 5) are shifted by addition of sulfuric acid [16]. However, nitronium ions are generated only in highly acidic solutions with strictly limited water contents [17, 18]. In the pseudo ternary system HF (40 %)-HNO$_3$ (65 %)-H$_2$SO$_4$ (97 %) relatively high amounts of water prohibit nitronium ion formation.

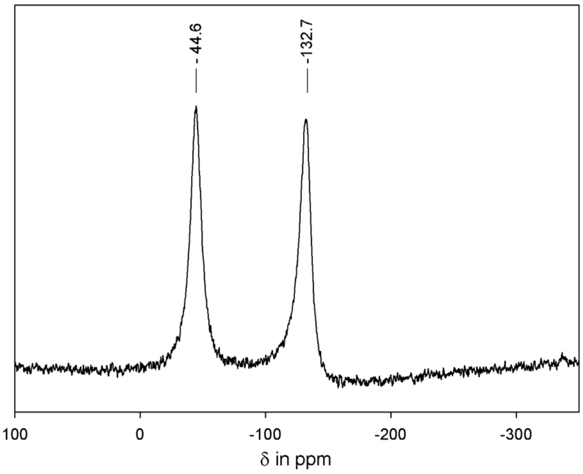

Fig. 1. ^{14}N NMR spectrum of an HF-HNO$_3$-H$_2$SO$_4$ etching mixture containing nitronium ions (c(HF) = 2.3 mol L^{-1}, c(N(V)) = 1.7 mol L^{-1}, c(NO$_2$$^+$) = 1.3 mol L^{-1}, c(H$_2SO_4$) = 15.0 mol L^{-1}).

$$HNO_3 \rightleftarrows H^+ + NO_3^- \qquad (4)$$

$$HNO_3 + H^+ \rightleftarrows H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O \qquad (5)$$

The water concentration is reduced by using fuming nitric acid (100 %) instead of concentrated nitric acid (65 %). High amounts of concentrated sulfuric acid (97 %) additionally bind the water of the concentrated hydrofluoric acid (40 %) and stabilize nitronium ions in these solutions. NMR *and* Raman spectroscopic investigations have clearly proven the formation of nitronium ions in etching mixtures with high sulfuric acid concentrations. ^{14}N NMR spectroscopic analysis has shown two discrete signals, which could be assigned to nitric acid at $\delta = -44.6$ ppm and nitronium ions at $\delta = -132.7$ ppm (Fig. 1).

Because alkaline solutions rapidly convert N(V) species (HNO$_3$, H$_2$NO$_3$$^+$ and NO$_2$$^+$) into nitrate ions, quantitative analysis of nitrate ions by ion chromatography yields only a sum parameter for N(V) species (Eq. 6). Therefore, ion chromatography is not suitable

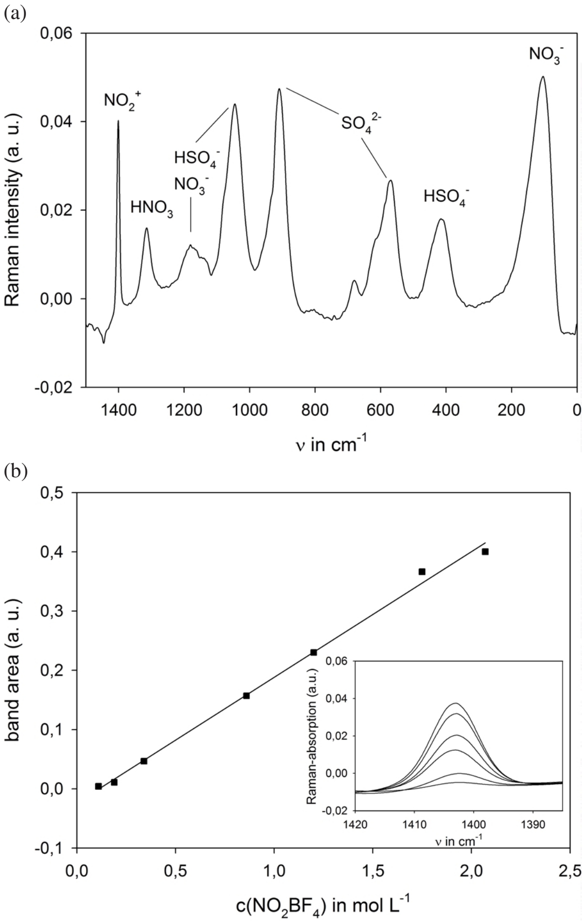

Fig. 2. a) Raman spectrum of an HF-HNO$_3$-H$_2$SO$_4$ etching mixture containing nitronium ions (c(HF) = 1.6 mol L^{-1}, c(N(V)) = 5.1 mol L^{-1}, c(H$_2$SO$_4$) = 12.9 mol L^{-1}, c(NO$_2^+$) = 1.9 mol L^{-1}); b) regression of experimentally determined Raman line intensities *vs.* nitronium ion concentration of NO$_2$BF$_4$/H$_2$SO$_4$ standard mixtures (insert: NO$_2^+$ Raman line at 1400 cm^{-1}).

for the quantification of nitronium ions and undissociated nitric acid.

$$c(\mathrm{N(V)}) = c(\mathrm{NO_3}^-) + c(\mathrm{HNO_3}) + c(\mathrm{H_2NO_3}^+) + c(\mathrm{NO_2}^+) \qquad (6)$$

However, Raman spectroscopy allows *quantitative* NO$_2^+$ analysis by evaluation of the intensity of the prominent ν(NO) stretching line of nitronium ions (ν = 1400 cm^{-1}). Fig. 2a shows a typical Raman spectrum of an etching solution containing NO$_2^+$ ions. Along with nitronium ions, nitric acid and nitrate ions were identified as nitrogen containing species. The regression line for quantitative analysis of the nitronium ions was determined by plotting the ν(NO) line intensity *vs.* the NO$_2^+$ concentration of NO$_2$BF$_4$/H$_2$SO$_4$ standard mixtures. Fig. 2b illustrates a calibration plot and the ν(NO) stretching lines of these NO$_2^+$ standard mixtures. Due to the temperature dependence of the ν(NO) intensity, all Raman measurements were performed at r. t. [17].

Table 1. Experimentally determined nitronium ion concentrations in HF-HNO$_3$-H$_2$SO$_4$ etching mixtures. The nitric acid concentration is the difference of c(N(V)) and c(NO$_2^+$).

Etching mixture	c(H$_2$SO$_4$) in mol L^{-1}	c(H$_2$O) in mol L^{-1}	c(HNO$_3$) in mol L^{-1}	c(NO$_2^+$) in mol L^{-1}
1	7.15	12.12	8.90	0.00
2	7.54	10.95	8.90	0.00
3	7.97	9.86	8.73	0.17
4	8.29	8.81	8.52	0.38
5	8.65	7.90	8.16	0.74
6	9.10	6.50	7.92	0.98

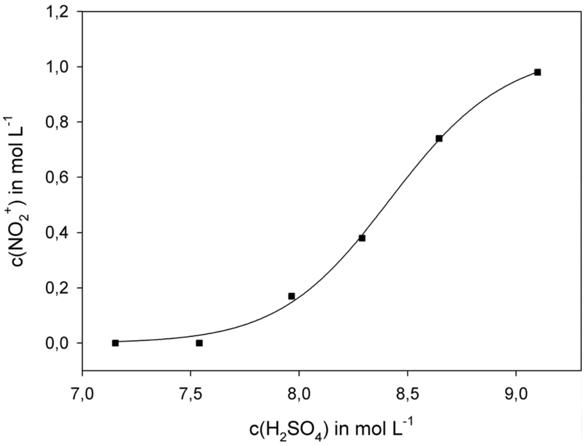

Fig. 3. Correlation between nitronium ion concentrations and sulfuric acid concentration determined by Raman spectroscopy (c(HF) = 2.6 mol L^{-1}, c(N(V)) = 8.9 mol L^{-1}).

Table 1 summarizes nitronium ion concentrations determined in selected HF-HNO$_3$-H$_2$SO$_4$ etching mixtures. The hydrofluoric acid concentration c(HF) = 2.6 mol L^{-1} and the sum of N(V) species c(N(V)) = 8.9 mol L^{-1} are constant for etching mixtures 1 to 6. The total amount of water c(H$_2$O) is the sum of the respective residual water content of the concentrated acids (HF (40 %) and H$_2$SO$_4$ (97 %)) and the amount of water added to the etching solution. Replacement of added water by sulfuric acid causes increasing NO$_2^+$ concentrations. For etching mixtures 1 and 2 a qualitative and quantitative analysis of nitronium ions was not possible because of too high water concentrations. However, the presence of low concentrations cannot be excluded. The correlation between NO_2^+ and H_2SO_4 concentrations is shown in Fig. 3.

Overall reactivity of HF-HNO$_3$-H$_2$SO$_4$ etching mixtures towards crystalline silicon surfaces

The investigated etching mixtures are highly reactive towards multicrystalline silicon surfaces. Fig. 4 illustrates etching rates depending on the etching mixture composition. Maximum etching rates of 4000–5000 nm s^{-1} were obtained for the following compositions: w (40 %-HF)/w (65 %-HNO$_3$) = 2 to 4 and w (97 %-H$_2$SO$_4$) < 0.3. In the pseudo ternary system HF (40 %)-HNO$_3$ (65 %)-H$_2$SO$_4$ (97 %), the sulfuric acid acts as a diluent. Therefore, silicon etching rates decrease with increasing amounts of sulfuric acid (Fig. 4). In comparison to the etching rates of HF (40 %)-HNO$_3$ (65 %)-H$_2$O mixtures, the sulfuric acid-diluted system exhibits a greater tolerance for the diluent. For HF-HNO$_3$-CH$_3$COOH solutions it was proposed that hampering the nitric acid dissociation is responsible for this effect [4]. Due to high water concentrations, nitronium ions were not detectable in HF (40 %)-HNO$_3$ (65 %)-rich etching mixtures. In addition to a less pronounced nitric acid dissociation, the formation of other reactive nitrogen intermediates may induce the intensive surface attack in these mixtures.

Increasing the sulfuric acid amounts in HF (40 %)-HNO$_3$ (65 %)-H$_2$SO$_4$ (97 %) mixtures causes a decrease in the amounts of hydrofluoric and nitric acid. However, constant HF and HNO$_3$ concentrations are necessary to study the effect of sulfuric acid on the silicon etching process. In HF (40 %)-HNO$_3$ (100 %)-H$_2$SO$_4$ (97 %)/H$_2$O solutions the substitution of water by sulfuric acid makes systematic reactivity studies possible through a variation of the H$_2$SO$_4$ content at constant HF and HNO$_3$ concentrations.

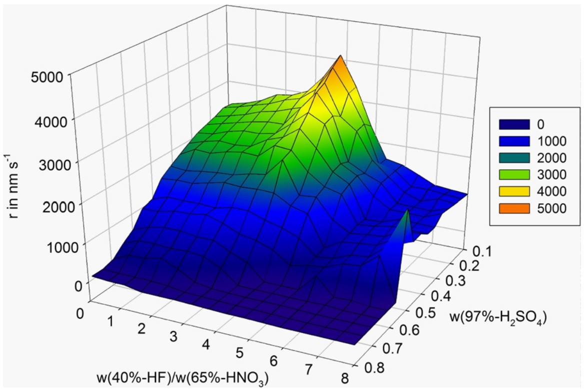

Fig. 4. Silicon etching rates found for the pseudo ternary system HF (40 %)-HNO$_3$ (65 %)-H$_2$SO$_4$ (97 %). The absolute amounts of hydrofluoric and nitric acid change with sulfuric acid dilution.

Influence of the H$_2$SO$_4$ concentration on etching rates and formation of NO$_2^+$ and N(III) species

Fig. 5 shows the correlation between silicon etching rates, sulfuric acid concentration and the amount of nitrite ions generated per dissolved silicon quantities for etching mixtures with constant parts of hydrofluoric acid and nitric acid. N(III) species are stabilized by increasing sulfuric acid concentrations. As mentioned in the introduction, nitrogen species with oxidation state + 3, *e. g.* NO$^+$ or N$_2$O$_3$, have been reported to be important intermediates in the silicon dissolution process. In conventional HF-HNO$_3$-H$_2$O etching mixtures the multitude of nitrogen containing compounds such as HNO$_3$, NO$_3^-$, NO$_2$, NO$_x^+$ and NO complicate reactivity studies of N(III) species. Recently investigated HF-NOHSO$_4$-H$_2$SO$_4$ etching mixtures are suitable model etching systems, since N(V) and N(IV) species are *a priori* not present. For these mixtures it was found that increasing nitrosyl ion concentrations cause increasing silicon etching rates [14]. According to these results high amounts of N(III) species accelerate the reaction rates in HF-HNO$_3$-H$_2$O and HF-HNO$_3$-H$_2$SO$_4$ mixtures. Upon etching silicon with HF-HNO$_3$-based mixtures, N(III) species are gener-

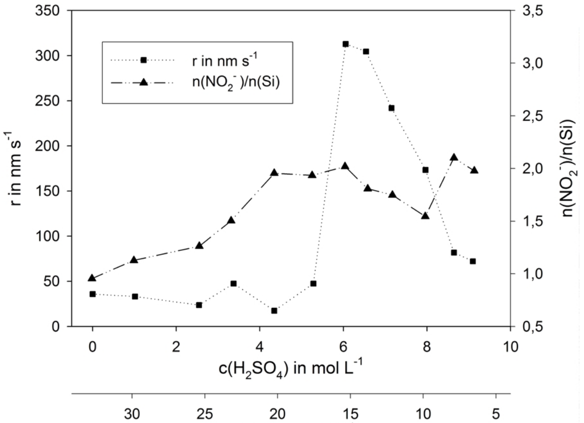

Fig. 5. Silicon etching rates *versus* sulfuric acid concentration for the reaction of multicrystalline silicon with HF-HNO$_3$-H$_2$SO$_4$/H$_2$O etching mixtures and nitrite ions generated per dissolved amounts of silicon depending on the concentration of sulfuric acid. The concentrations of hydrofluoric acid and N(V) species are kept constant (c(HF) = 2.6 mol L^{-1} and c(N(V)) = 8.9 mol L^{-1}).

ated by reduction of nitric acid. Therefore, the concentration of N(III) species may be taken as a measure for the velocity of silicon oxidation. In alkaline solutions all N(III) species (N_2O_3, NO^+, HNO_2) are converted into nitrite ions. The nitrite concentration thus represents a sum parameter for all N(III) species. In HF-HNO_3-H_2O etching mixtures a linear correlation between etching rates and NO_2^- concentrations was found for lower nitrite concentrations [15].

In the HF (40 %)-HNO_3 (100 %)-H_2SO_4 (97 %)/ H_2O etching system increasing sulfuric acid parts (which induce a stabilization of N(III) species) do not cause a linear rise of silicon etching rates (Fig. 5). While from 0 to 5 mol L^{-1} H_2SO_4 constant etching rates of 20 – 40 nm s^{-1} are observed, a sudden increase occurs around 6 mol L^{-1} H_2SO_4. This is unexpected, but correlates roughly with a change from colorless to green/blue of the etching solutions. At H_2SO_4 concentrations above 7 mol L^{-1} these colors disappear, and solutions containing 9 mol L^{-1} H_2SO_4 are also colorless. This implies that higher concentrations of colored species such as NO_2 (yellow-brown) or N_2O_3 (blue) are responsible for the sudden increase of the etching rates. The decrease of the etching rates with a further increase of the sulfuric acid concentration above 7 mol L^{-1} is also unexpected and may be explained by the assumption that effects of the stabilization of N(III) species and of a reduced nitric acid dissociation are compensated by an increasing etching mixture viscosity. In HF-HNO_3-CH_3COOH mixtures, etching rates decrease with increasing viscosities [19].

Very high sulfuric acid concentrations also increase the viscosity and impede the diffusion of fluoride-containing species (HF, F^- and HF_2^-) to the silicon surface. In the silicon dissolution process, HF_2^- ions have recently been reported to be more reactive than HF molecules and F^- ions [20]. The HF_2^- species exhibit acidic (Eq. 7) and basic properties (Eq. 8). According to Eq. 8 increasing proton activities lead to decreasing concentrations of reactive HF_2^- ions.

$$HF_2^- + H_2O \rightleftarrows H_3O^+ + 2\,F^- \tag{7}$$

$$HF_2^- + H_3O^+ \rightleftarrows H_2O + 2\,HF \tag{8}$$

In addition to that, the formation of fluorosulfuric acid (Eq. 9), which was proven by means of ^{19}F NMR measurements ($\delta(HSO_3F)$ = 36.9 ppm) for H_2SO_4 concentrations greater than 8.3 mol L^{-1}, captivates fluoride-containing species (HF, F^- and HF_2^-) in the etching mixtures and leads to decreasing silicon etching rates.

$$HF + H_2SO_4 \rightleftarrows HSO_3F + H_2O \tag{9}$$

In summary, the attack of silicon surfaces is affected by several parameters. Maximum etching rates are obtained for sulfuric acid concentrations between 5.5 and 8.0 mol L^{-1} (Fig. 5). The stabilization of N(III) species – especially N_2O_3 and NO^+ – as well as the presence of undissociated nitric acid, NO_2 and nitronium ions leads to a high reactivity of HF-HNO_3-H_2SO_4 etching mixtures. High viscosities and the formation fluorosulfuric acid cause decreasing etching rates.

Depending on the pH value, N(III) species are existent as anions (NO_2^-), neutral molecules (HNO_2,

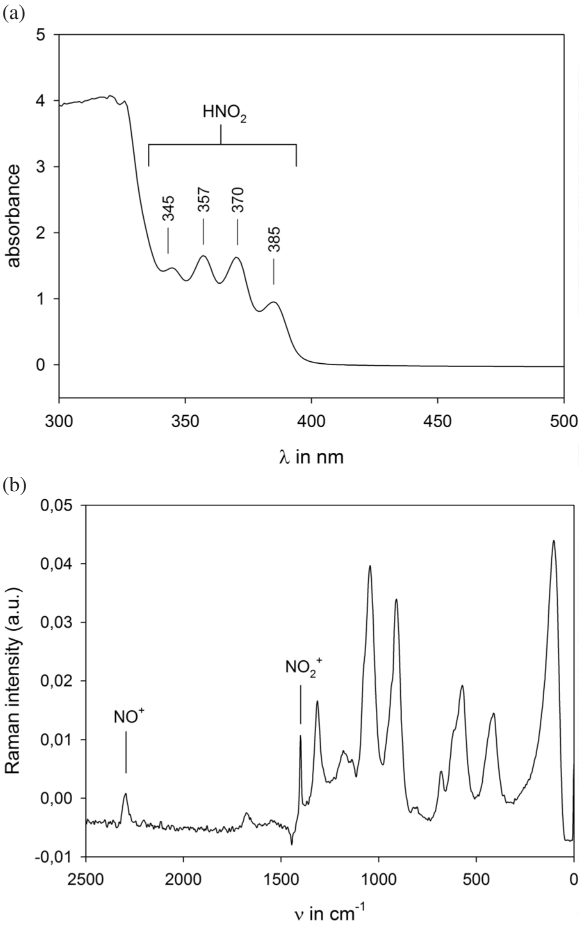

Fig. 6. a) UV/Vis spectrum of a conventional HF-HNO_3-H_2O mixture after dissolving silicon and b) Raman spectrum of a sulfuric acid-rich HF-HNO_3-H_2SO_4 mixture after dissolving silicon ($c(H_2SO_4)$ = 9.1 mol L^{-1}). For both mixtures the concentrations of hydrofluoric acid and N(V) species are constant (c(HF) = 2.6 mol L^{-1} and c(N(V)) = 8.9 mol L^{-1}).

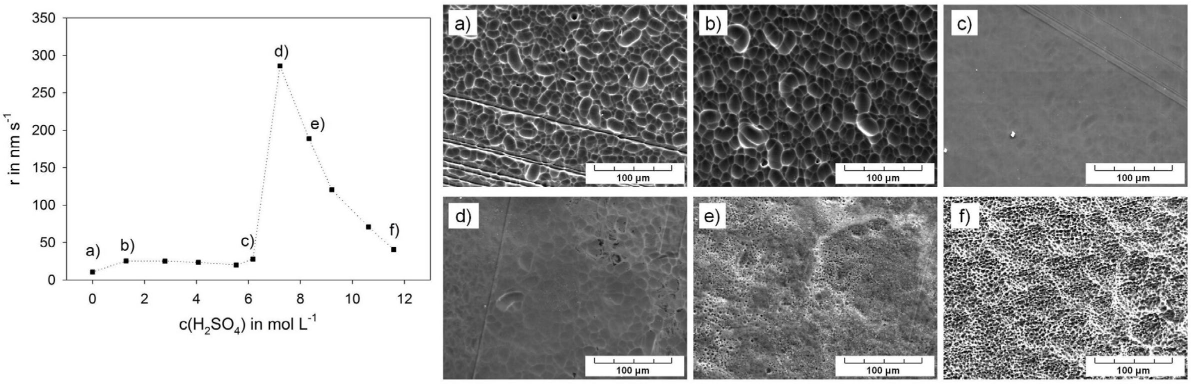

Fig. 7. SEM images of etched multicrystalline silicon surfaces. Sulfuric acid concentrations and etching rates are shown in the diagram. The concentration of hydrofluoric acid and N(V) species are equal for each etching mixture ($c(\mathrm{HF}) = 2.6\ \mathrm{mol\,L^{-1}}$ and $c(\mathrm{N(V)}) = 5.7\ \mathrm{mol\,L^{-1}}$).

N_2O_3) or cations ($H_2NO_2^+$, NO^+). Eq. 3 illustrates the equilibrium between nitrous acid and nitrosyl ions. At r. t. and in diluted aqueous solutions nitrous acid is stable. After dissolving silicon in a diluted HF-HNO$_3$-H$_2$O mixture, nitrous acid was identified by means of UV/Vis spectroscopy as the intermediary N(III) species (Fig. 6a). The absorption maxima at 345, 357, 370 and 385 nm can be assigned to HNO_2 [21]. For high sulfuric acid concentrations the presence of nitrosyl ions was verified by means of Raman spectroscopy ($\nu(NO^+) = 2300\ \mathrm{cm^{-1}}$, Fig. 6b). In HF-HNO$_3$-based etching mixtures the equilibrium between the intermediates nitrous acid and nitrosyl ions is shifted by increasing amounts of sulfuric acid.

$$HNO_3 + 2\,H_3O^+ + 2\,e^- \rightarrow HNO_2 + 3\,H_2O \quad (10)$$

$$NO_2^+ + 2\,H_3O^+ + 2\,e^- \rightarrow NO^+ + 3\,H_2O \quad (11)$$

According to Eqs. 10 and 11 the reduction of nitric acid and nitronium ions may proceed *via* 2e$^-$ steps from N(V) to N(III). In addition to such a simultaneous transfer of two electrons from the silicon surface atoms to N(V) species, a stepwise reduction is possible by two consecutive 1e$^-$ steps. Therefore, nitrogen dioxide could be an intermediate reaction product, as shown in Eqs. 12 and 13. The 1e$^-$ step from N(V) to N(IV) should be kinetically favored. A further transfer of an electron to adsorbed nitrogen dioxide reduces this substrate to N(III) compounds (Eq. 14).

$$HNO_3 + H_3O^+ + e^- \rightarrow NO_2 + 2\,H_2O \quad (12)$$

$$NO_2^+ + e^- \rightarrow NO_2 \quad (13)$$

$$NO_2 + H_3O^+ + e^- \rightarrow HNO_2 + H_2O \quad (14)$$

In sulfuric acid nitrosyl and nitronium ions are generated by disproportionation of nitrogen dioxide according to Eq. 15 [22]. Thus high sulfuric acid concentrations should cause the decomposition of nitrogen dioxide in HF-HNO$_3$-H$_2$SO$_4$ mixtures forming both NO_2^+ and NO^+.

$$\begin{aligned}&2\,NO_2 + 3\,H_2SO_4 \rightarrow\\ &NO_2^+ + NO^+ + 3\,HSO_4^- + H_3O^+\end{aligned} \quad (15)$$

Characterization of etched silicon surfaces

For conventional HF-HNO$_3$-H$_2$O mixtures the structures of the etched silicon surface depends on the composition of the mixture. In HF-rich solutions, reaction-controlled processes result in the formation of characteristic oval etching pits. Surface defects, *e. g.* grain boundaries or dislocation lines, act as starting points for etching reactions. The acceleration of the silicon oxidation by higher amounts of nitric acid leads to smooth surfaces. In these mixtures the diffusion of fluoride-containing species (F^-, HF, HF_2^-) to the silicon surface is considered to be the rate-limiting step. Therefore, regions of inhomogeneity are etched preferentially leading to polished surfaces.

For HF-HNO$_3$-H$_2$SO$_4$ mixtures the surface structures of etched silicon wafers were investigated by means of SEM and laser scanning microscopy. Fig. 7 shows SEM images of etched multicrystalline silicon surfaces obtained with several different concentrations of sulfuric acid. The surface structures are considerably influenced by increasing sulfuric acid concentrations $c(H_2SO_4) = 0.0-11.6\ \mathrm{mol\,L^{-1}}$. The genera-

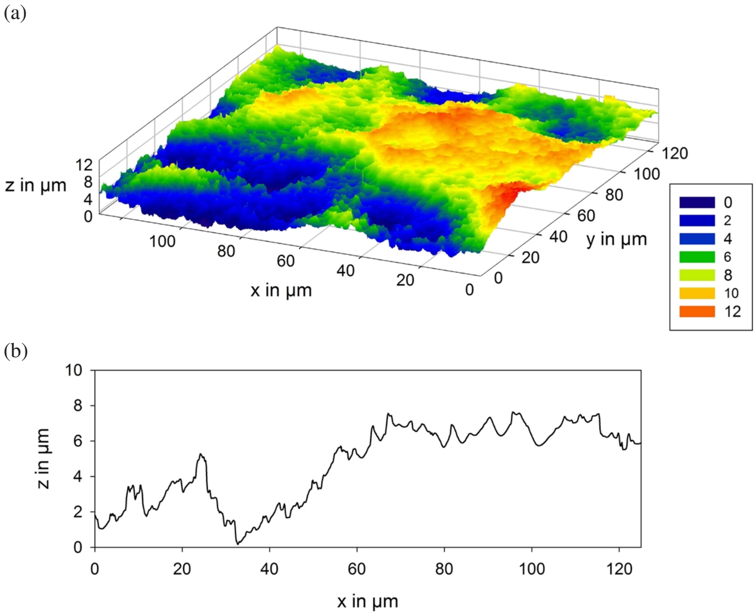

Fig. 8. a) LSM image 128 × 128 μm^2 and b) surface profile of an etched multicrystalline silicon wafer piece. Composition of the etching solution: $c(HF)$ = 2.6 mol L^{-1}, $c(N(V))$ = 5.7 mol L^{-1}, $c(NO_2^+)$ = 1.3 mol L^{-1} and $c(H_2SO_4)$ = 11.6 mol L^{-1}.

tion of oval etching pits was found for mixtures a) and b). Areas with surface defects were etched especially by mixture a). Hampering of the nitric acid dissociation by increasing amounts of sulfuric acid accelerates etching rates and leads to smooth surfaces (Figs. 7c and d).

The transport of hydrofluoric acid to the silicon/electrolyte interface is expected to be the rate-limiting process in very H_2SO_4-rich mixtures. Surprisingly, no polished surfaces were observed by means of SEM for sulfuric acid concentrations of $c(H_2SO_4) > 8$ mol L^{-1}. Pore-like etching pits are generated upon etching of silicon wafers with these mixtures (Figs. 7e and f). In etching mixture f) the Raman line ν = 1400 cm^{-1} confirms the formation of nitronium ions. A nitronium ion concentration of $c(NO_2^+)$ = 1.28 mol L^{-1} was determined by evaluation of the NO_2^+ line intensity (*vide supra*).

Three-dimensional images of etched pore-like surface structures were recorded by means of LSM. The results are depicted in Fig. 8. Nitronium ion-containing etching mixtures attack the silicon surface irregularly. Larger depressions are covered with numerous small etching pits. The radius of the small pits amounts to 2 μm. This so far unknown surface structure cannot be classified in the formalism of diffusion-controlled and/or reaction-controlled etching processes described in the literature [23].

Conclusions

The addition of sulfuric acid to conventional HF-HNO_3-H_2O etching mixtures leads to a reduced dissociation of nitric acid and to the formation of nitronium ions. For high sulfuric acid concentrations and low water contents nitronium ion formation was verified by means of ^{14}N NMR and Raman spectroscopy. Integration of NO_2^+ Raman line intensities at 1400 cm^{-1} enables the quantification of nitronium ions in HF-HNO_3-H_2SO_4 solutions.

In HF-HNO_3-H_2SO_4 etching mixtures the silicon etching rates depend on several parameters. These are the concentration of oxidizing species such as NO_2^+, NO^+ and N_2O_3, the viscosity of the solution and the concentration and availability of fluoride-containing species acting as ligands for silicon complexation. Silicon dissolution suddenly increases at a H_2SO_4 concentration of 6 mol L^{-1}, which is caused mainly by an accelerated Si oxidation by increasing concentrations of undissociated HNO_3, nitronium ions and/or NO_x species such as NO_2. For very high sulfuric acid concentrations increasing solution viscosities and the generation of fluorosulfuric acid lower the silicon etching rates. The formation of N(III) species, such as HNO_2, N_2O_3 or NO^+, was proved by ion chromatography. Besides, the presence of nitrous acid was proved by means of UV/Vis spectroscopy as an additional reaction product in diluted HF-HNO_3-H_2O mixtures.

Nitrous acid and nitrosyl ions can be generated by a simultaneous 2e$^-$ transfer from the silicon surface to nitric acid and nitronium ions, respectively. Alternatively, nitrogen dioxide can be formed as an intermediate product *via* 1e$^-$ reduction of NO$_2$$^+$ and/or dissociation of N_2O_3. A detection and quantification of nitrogen dioxide at or close to the silicon surface in future studies should allow to identify possible reaction pathways of N(V) species.

The etched silicon surface structures were investigated by means of SEM and LSM. Surprisingly, pore-like etching pits are formed in H_2SO_4-rich solutions. This disagrees with the well known principles for silicon etching modes with HF-HNO$_3$-based solutions. Obviously, the individual reaction steps at the silicon/electrolyte interface are significantly influenced by high sulfuric acid concentrations. Analysis of silicon surface terminations and model reactions performed with hydrogen terminated silicon surfaces are currently used to resolve single reaction steps of the overall etching process in HF-HNO$_3$ based solutions.

Experimental Section

Preparation of the HF-HNO$_3$-H$_2$SO$_4$ etching mixtures

Caution: Suitable safety precautions have to be taken into account when performing etching experiments with concentrated mineral acids. All experiments were performed in an HF-approved fume hood and HF-approved laboratory equipment.

Analytical-grade hydrofluoric acid (40 w-%), analytical grade nitric acid (65 w-%), freshly distilled nitric acid (100 w-%) and sulfuric acid (97 w-%) were used for the preparation of the etching mixtures. For distilling nitric acid, 200 mL sulfuric acid (97 w-%) was added to 100 mL analytical-grade nitric acid (65 w-%) under cooling. The mixture was distilled at 2 kPa. After adding the double volume of sulfuric acid to the distillate the mixture was distilled once again. The fuming nitric acid was stored in a refrigerator.

A volume of 25 mL etching solution was prepared by mixing the acids in a PP beaker under ice/NaCl cooling. During etching experiments the temperature was kept constant at 20 °C by application of a cryostat.

Silicon material and etching procedure

After weighing multicrystalline silicon wafer pieces (boron doped, thickness 330 μm, resistivity $0.5-2\ \Omega\ \mathrm{cm}^{-1}$, Deutsche Solar AG Freiberg) were placed in the etching bath for 10 – 600 s. The reactions were stopped by removing the silicon wafer pieces from the etching bath and rinsing them with deionized water. The etching rates were calculated from the mass loss of the silicon wafer pieces.

Characterization of the etching mixtures

The NMR measurements were performed using a Bruker DPX-400 spectrometer and Teflon inserts. The standard for the ^{14}N nucleus was CH_3NO_2 (28.92 MHz). CCl_3F was used as a standard for ^{19}F NMR spectroscopy (376.50 MHz).

The Raman spectra were measured in Brandt cells with a Bruker RVS 100/S spectrometer. The solutions were excited by 1064 nm radiation of a Nd:YAG laser. The laser power was 200 mW. The scattered light was collected in 180° back scattering geometry and detected by a liquid nitrogen-cooled Ge detector. The calibration plot for quantitative analysis of the nitronium ion concentration was determined by evaluation of the NO$_2$$^+$ Raman line intensities. Nitronium tetrafluoroborate (Alpha Aesar, purity: 96 %) and NO_2BF_4/H_2SO_4 standard mixtures are hygroscopic and were handled under an argon atmosphere.

The concentrations of anions (fluoride, nitrate, nitrite, sulfate) were determined by ion chromatography (Dionex ICS-2000, column: AS 11-HC, eluent: 22 mM KOH, electrical conductivity measurement). A volume of 0.1 mL etching mixture was diluted with deionized water to a factor of 1 : 5000. N(III) species were converted to nitrite ions by the addition NaOH (10 w-%).

Characterization of the etched silicon surfaces

The SEM measurements of etched silicon surfaces were carried out with a VEGA TESCAN TS 5130 SB, and three-dimensional laser scanning microscopy (LSM) images of etched structures were measured by an Olympus LEXT OLS3000 instrument.

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