

HF-HNO₃-H₂SO₄/H₂O Mixtures for Etching Multicrystalline Silicon Surfaces: Formation of NO₂⁺, Reaction Rates and Surface Morphologies

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The reaction behavior of HF-HNO₃-H₂O 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 NO₂⁺ ions have been detected by means of ¹⁴N 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 %)-HNO₃ (65 %)-H₂SO₄ (97 %) mixtures with w (40 %-HF)/w (65 %-HNO₃) ratios of 2 to 4 and w (97 %-H₂SO₄) < 0.3. For higher concentrations of sulfuric acid, H₂SO₄ can be considered as a diluent. In order to investigate the influence of the sulfuric acid at constant HF and HNO₃ quantities, fuming HNO₃ (100 %) was used and the water in the mixtures successively replaced by H₂SO₄. 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 H₂SO₄ are attributed to high solution viscosities and the formation of fluorosulfuric acid. Generally, in HF-HNO₃-H₂SO₄/H₂O etching mixtures a reduced dissociation of nitric acid, the formation of nitronium ions, the solubility of neutral nitrogen intermediates (*e. g.* NO₂, N₂O₃), 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.

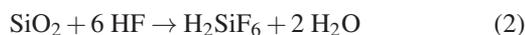
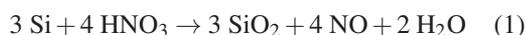
Key words: Acidic Etching, Multicrystalline Silicon, Nitronium Ions, Sulfuric Acid, Solar Cells

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-HNO₃-H₂O etching mixtures [2].

Dissolving silicon requires two simultaneous processes: the stepwise oxidation of silicon atoms by oxidants, *e. g.* HNO₃, NO₂, NO₂⁺ or NO⁺, and the formation of water-soluble complexes by fluoride containing species, *e. g.* HF, F⁻ and HF₂⁻. A simple two-step etching mechanism has been proposed [3–5]. In this

model the formation of an intermediate SiO₂ layer by nitric acid (Eq. 1) is followed by dissolving of this oxide with hydrofluoric acid (Eq. 2).

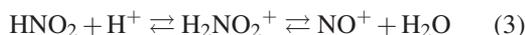


According to this early model the only reaction products are nitrous oxide, hexafluorosilicic acid and water. However, several further species including NO₂, N₂O, NH₄⁺ and H₂ were detected as additional reaction products of HF-HNO₃-H₂O etching solutions [6, 7], and the formation of an intermediate silicon 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 -SiH₂F and

-SiHF₂ 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-HNO₃-H₂O 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 NaNO₂ 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).



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-NOHSO₄-H₂SO₄ mixtures indicating a high reactivity towards crystalline silicon support this concept [13, 14]. In HF-HNO₃-H₂O etching solutions the formation of reactive N(III) species (NO⁺, N₂O₃) and the nitrosyl-nitrate ion adduct [N₄O₆²⁺] were verified by means of Raman spectroscopy. N₂O₃ has been discussed as a reservoir for nitrosyl ions [15].

In the present study the formation and effects of nitronium ions NO₂⁺ are investigated by acidification of HF-HNO₃-H₂O mixtures with sulfuric acid. This paper gives an overview of the reactivity of HF-HNO₃-H₂SO₄ 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-HNO₃-H₂SO₄ etching mixtures (before contact to silicon)

To investigate nitronium ion formation, HF-HNO₃-H₂SO₄ mixtures were analyzed by means of Raman and ¹⁴N NMR spectroscopy. Raman spectroscopic

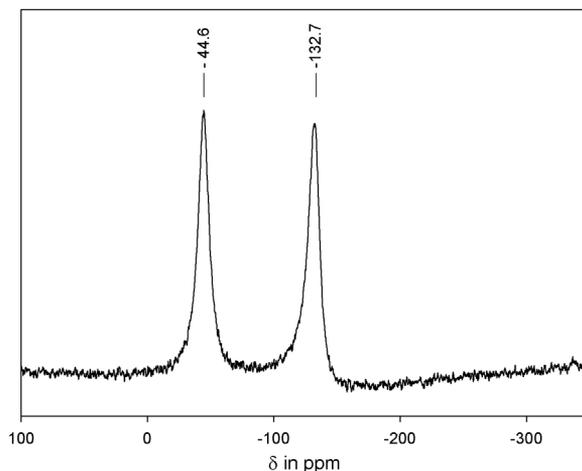
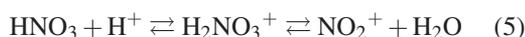


Fig. 1. ¹⁴N NMR spectrum of an HF-HNO₃-H₂SO₄ etching mixture containing nitronium ions ($c(\text{HF}) = 2.3 \text{ mol L}^{-1}$, $c(\text{N(V)}) = 1.7 \text{ mol L}^{-1}$, $c(\text{NO}_2^+) = 1.3 \text{ mol L}^{-1}$, $c(\text{H}_2\text{SO}_4) = 15.0 \text{ mol L}^{-1}$).

studies of the ternary HNO₃-H₂SO₄-H₂O system have shown that the equilibria NO₃⁻/HNO₃ (Eq. 4) and HNO₃/NO₂⁺ (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 %)-HNO₃ (65 %)-H₂SO₄ (97 %) relatively high amounts of water prohibit nitronium ion formation.



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. ¹⁴N NMR spectroscopic analysis has shown two discrete signals, which could be assigned to nitric acid at $\delta = -44.6 \text{ ppm}$ and nitronium ions at $\delta = -132.7 \text{ ppm}$ (Fig. 1).

Because alkaline solutions rapidly convert N(V) species (HNO₃, H₂NO₃⁺ and NO₂⁺) 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

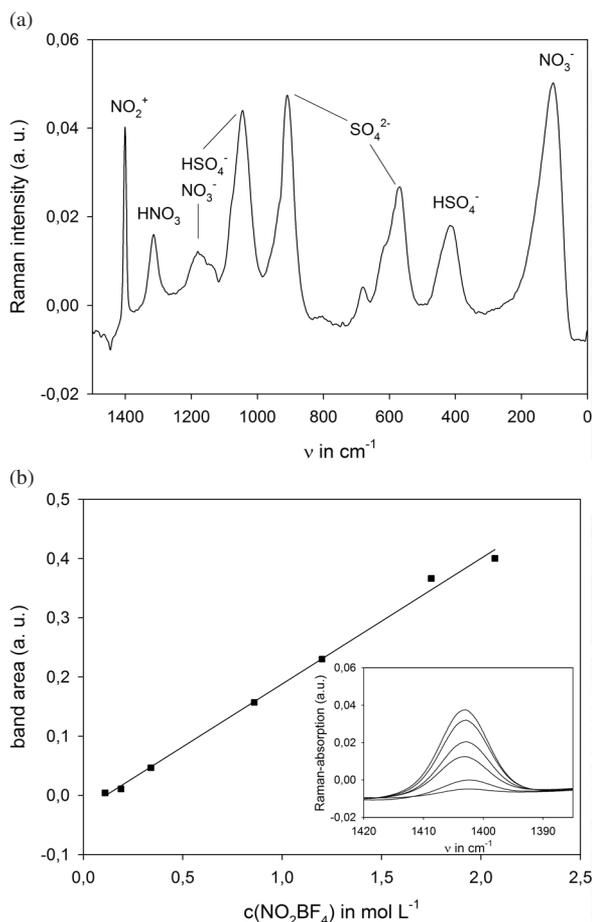


Fig. 2. a) Raman spectrum of an HF-HNO₃-H₂SO₄ etching mixture containing nitronium ions ($c(\text{HF}) = 1.6 \text{ mol L}^{-1}$, $c(\text{N(V)}) = 5.1 \text{ mol L}^{-1}$, $c(\text{H}_2\text{SO}_4) = 12.9 \text{ mol L}^{-1}$, $c(\text{NO}_2^+) = 1.9 \text{ mol L}^{-1}$); b) regression of experimentally determined Raman line intensities vs. nitronium ion concentration of NO₂BF₄/H₂SO₄ standard mixtures (insert: NO₂⁺ Raman line at 1400 cm⁻¹).

for the quantification of nitronium ions and undissociated nitric acid.

$$c(\text{N(V)}) = c(\text{NO}_3^-) + c(\text{HNO}_3) + c(\text{H}_2\text{NO}_3^+) + c(\text{NO}_2^+) \quad (6)$$

However, Raman spectroscopy allows *quantitative* NO₂⁺ analysis by evaluation of the intensity of the prominent $\nu(\text{NO})$ stretching line of nitronium ions ($\nu = 1400 \text{ cm}^{-1}$). Fig. 2a shows a typical Raman spectrum of an etching solution containing NO₂⁺ 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

Table 1. Experimentally determined nitronium ion concentrations in HF-HNO₃-H₂SO₄ etching mixtures. The nitric acid concentration is the difference of $c(\text{N(V)})$ and $c(\text{NO}_2^+)$.

Etching mixture	$c(\text{H}_2\text{SO}_4)$ in mol L ⁻¹	$c(\text{H}_2\text{O})$ in mol L ⁻¹	$c(\text{HNO}_3)$ in mol L ⁻¹	$c(\text{NO}_2^+)$ 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

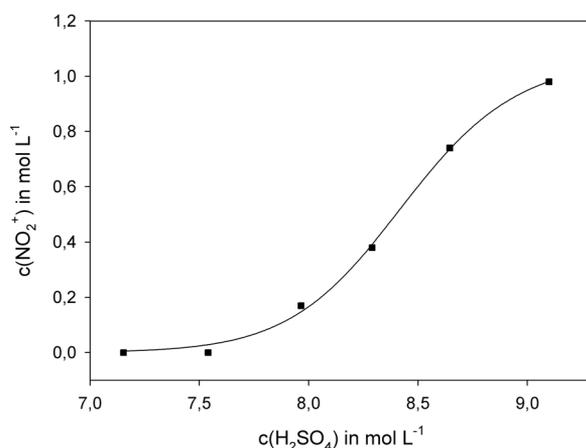


Fig. 3. Correlation between nitronium ion concentrations and sulfuric acid concentration determined by Raman spectroscopy ($c(\text{HF}) = 2.6 \text{ mol L}^{-1}$, $c(\text{N(V)}) = 8.9 \text{ mol L}^{-1}$).

was determined by plotting the $\nu(\text{NO})$ line intensity vs. the NO₂⁺ concentration of NO₂BF₄/H₂SO₄ standard mixtures. Fig. 2b illustrates a calibration plot and the $\nu(\text{NO})$ stretching lines of these NO₂⁺ standard mixtures. Due to the temperature dependence of the $\nu(\text{NO})$ intensity, all Raman measurements were performed at r. t. [17].

Table 1 summarizes nitronium ion concentrations determined in selected HF-HNO₃-H₂SO₄ etching mixtures. The hydrofluoric acid concentration $c(\text{HF}) = 2.6 \text{ mol L}^{-1}$ and the sum of N(V) species $c(\text{N(V)}) = 8.9 \text{ mol L}^{-1}$ are constant for etching mixtures 1 to 6. The total amount of water $c(\text{H}_2\text{O})$ is the sum of the respective residual water content of the concentrated acids (HF (40%) and H₂SO₄ (97%)) and the amount of water added to the etching solution. Replacement of added water by sulfuric acid causes increasing NO₂⁺ 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 NO₂⁺ and H₂SO₄ concentrations is shown in Fig. 3.

Overall reactivity of HF-HNO₃-H₂SO₄ 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: $w(40\% \text{-HF})/w(65\% \text{-HNO}_3) = 2$ to 4 and $w(97\% \text{-H}_2\text{SO}_4) < 0.3$. In the pseudo ternary system HF (40%)-HNO₃ (65%)-H₂SO₄ (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%)-HNO₃ (65%)-H₂O mixtures, the sulfuric acid-diluted system exhibits a greater tolerance for the diluent. For HF-HNO₃-CH₃COOH 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%)-HNO₃ (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%)-HNO₃ (65%)-H₂SO₄ (97%) mixtures causes a decrease in the amounts of hydrofluoric and nitric acid. However, constant HF and HNO₃ concentrations are necessary to study the effect of sulfuric acid on the silicon etching process. In HF (40%)-HNO₃ (100%)-H₂SO₄ (97%)/H₂O solutions the substitution of wa-

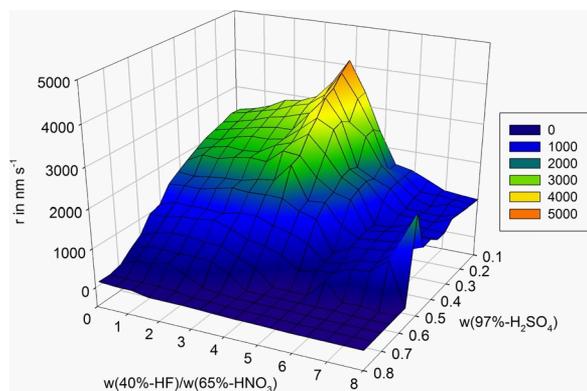


Fig. 4. Silicon etching rates found for the pseudo ternary system HF (40%)-HNO₃ (65%)-H₂SO₄ (97%). The absolute amounts of hydrofluoric and nitric acid change with sulfuric acid dilution.

ter by sulfuric acid makes systematic reactivity studies possible through a variation of the H₂SO₄ content at constant HF and HNO₃ concentrations.

Influence of the H₂SO₄ concentration on etching rates and formation of NO₂⁺ 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 N₂O₃, have been reported to be important intermediates in the silicon dissolution process. In conventional HF-HNO₃-H₂O etching mixtures the multitude of nitrogen containing compounds such as HNO₃, NO₃⁻, NO₂, NO_x⁺ and NO complicate reactivity studies of N(III) species. Recently investigated HF-NOHSO₄-H₂SO₄ 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-HNO₃-H₂O and HF-HNO₃-H₂SO₄ mixtures. Upon etching silicon with HF-HNO₃-based mixtures, N(III) species are gener-

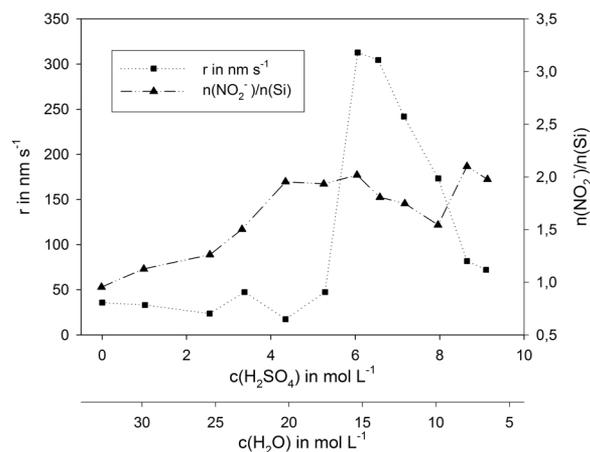
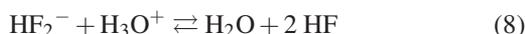
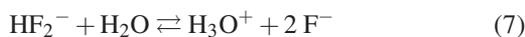


Fig. 5. Silicon etching rates *versus* sulfuric acid concentration for the reaction of multicrystalline silicon with HF-HNO₃-H₂SO₄/H₂O etching mixtures and nitrite ions generated per dissolved amounts of silicon depending on the concentration of sulfuric acid. The concentrations of hydrofluoric acid and N(V) species are kept constant ($c(\text{HF}) = 2.6 \text{ mol L}^{-1}$ and $c(\text{N(V)}) = 8.9 \text{ mol L}^{-1}$).

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 (N₂O₃, NO⁺, HNO₂) are converted into nitrite ions. The nitrite concentration thus represents a sum parameter for all N(III) species. In HF-HNO₃-H₂O etching mixtures a linear correlation between etching rates and NO₂⁻ concentrations was found for lower nitrite concentrations [15].

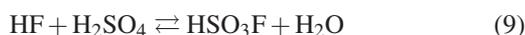
In the HF (40 %)-HNO₃ (100 %)-H₂SO₄ (97 %)/H₂O etching system increasing sulfuric acid parts (which induce a stabilization of N(III) species) do not cause a linear rise of silicon etching rates (Fig. 5). While from 0 to 5 mol L⁻¹ H₂SO₄ constant etching rates of 20–40 nm s⁻¹ are observed, a sudden increase occurs around 6 mol L⁻¹ H₂SO₄. This is unexpected, but correlates roughly with a change from colorless to green/blue of the etching solutions. At H₂SO₄ concentrations above 7 mol L⁻¹ these colors disappear, and solutions containing 9 mol L⁻¹ H₂SO₄ are also colorless. This implies that higher concentrations of colored species such as NO₂ (yellow-brown) or N₂O₃ (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-HNO₃-CH₃COOH 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 HF₂⁻) to the silicon surface. In the silicon dissolution process, HF₂⁻ ions have recently been reported to be more reactive than HF molecules and F⁻ ions [20]. The HF₂⁻ species exhibit acidic (Eq. 7) and basic properties (Eq. 8). According to Eq. 8 increasing proton activities lead to decreasing concentrations of reactive HF₂⁻ ions.



In addition to that, the formation of fluorosulfuric acid (Eq. 9), which was proven by means of ¹⁹F NMR measurements ($\delta(\text{HSO}_3\text{F}) = 36.9$ ppm) for H₂SO₄ concentrations greater than 8.3 mol L⁻¹, captivates fluoride-containing species (HF, F⁻ and HF₂⁻) in the

etching mixtures and leads to decreasing silicon etching rates.



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 N₂O₃ and NO⁺ – as well as the presence of undissociated nitric acid, NO₂ and nitronium ions leads to a high reactivity of HF-HNO₃-H₂SO₄ 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 (NO₂⁻), neutral molecules (HNO₂,

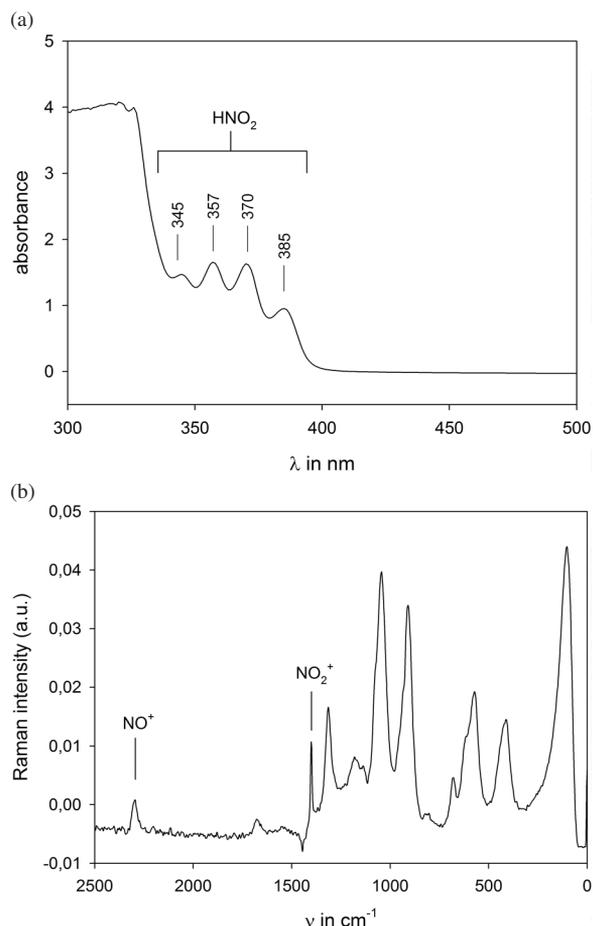


Fig. 6. a) UV/Vis spectrum of a conventional HF-HNO₃-H₂O mixture after dissolving silicon and b) Raman spectrum of a sulfuric acid-rich HF-HNO₃-H₂SO₄ mixture after dissolving silicon ($c(\text{H}_2\text{SO}_4) = 9.1$ mol L⁻¹). For both mixtures the concentrations of hydrofluoric acid and N(V) species are constant ($c(\text{HF}) = 2.6$ mol L⁻¹ and $c(\text{N(V)}) = 8.9$ mol L⁻¹).

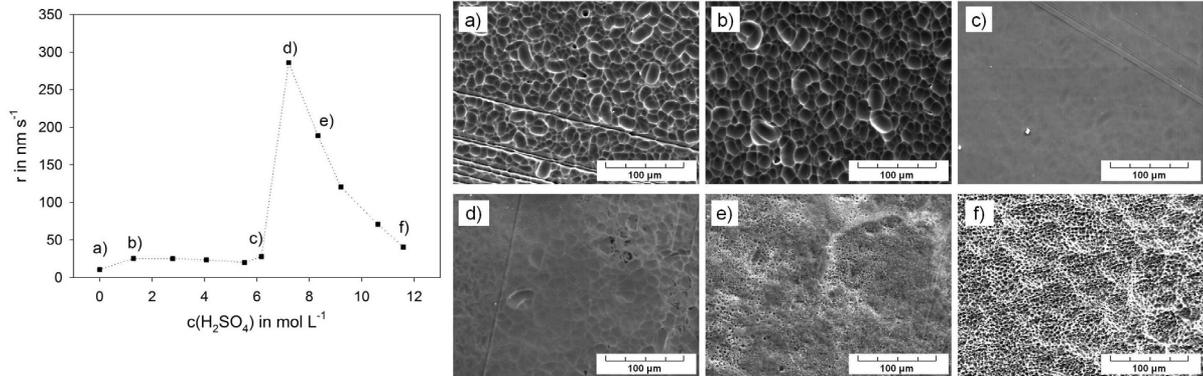
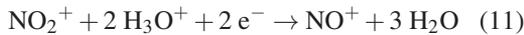
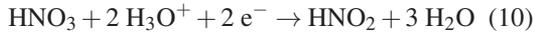
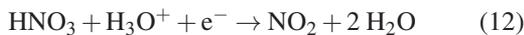


Fig. 7. SEM images of etched multicrystalline silicon surfaces. Sulfuric acid concentrations and etching rates are shown in the diagram. The concentration of hydrofluoric acid and N(V) species are equal for each etching mixture ($c(\text{HF}) = 2.6 \text{ mol L}^{-1}$ and $c(\text{N(V)}) = 5.7 \text{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

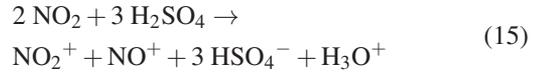
N₂O₃) or cations (H₂NO₂⁺, NO⁺). Eq. 3 illustrates the equilibrium between nitrous acid and nitrosyl ions. At r. t. and in diluted aqueous solutions nitrous acid is stable. After dissolving silicon in a diluted HF-HNO₃-H₂O mixture, nitrous acid was identified by means of UV/Vis spectroscopy as the intermediary N(III) species (Fig. 6a). The absorption maxima at 345, 357, 370 and 385 nm can be assigned to HNO₂ [21]. For high sulfuric acid concentrations the presence of nitrosyl ions was verified by means of Raman spectroscopy ($\nu(\text{NO}^+) = 2300 \text{ cm}^{-1}$, Fig. 6b). In HF-HNO₃-based etching mixtures the equilibrium between the intermediates nitrous acid and nitrosyl ions is shifted by increasing amounts of sulfuric acid.



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).



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-HNO₃-H₂SO₄ mixtures forming both NO₂⁺ and NO⁺.



Characterization of etched silicon surfaces

For conventional HF-HNO₃-H₂O 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, HF₂⁻) 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-HNO₃-H₂SO₄ 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 $c(\text{H}_2\text{SO}_4) = 0.0 - 11.6 \text{ mol L}^{-1}$. The genera-

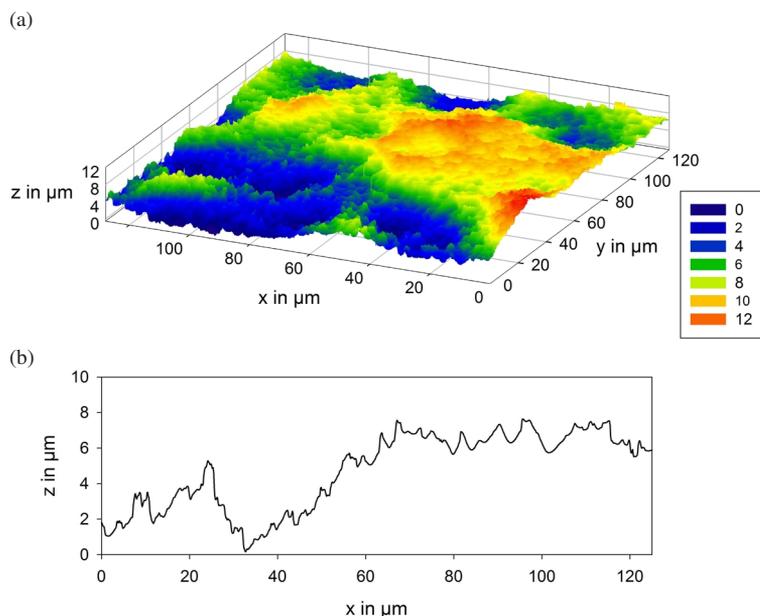


Fig. 8. a) LSM image $128 \times 128 \mu\text{m}^2$ and b) surface profile of an etched multicrystalline silicon wafer piece. Composition of the etching solution: $c(\text{HF}) = 2.6 \text{ mol L}^{-1}$, $c(\text{N(V)}) = 5.7 \text{ mol L}^{-1}$, $c(\text{NO}_2^+) = 1.3 \text{ mol L}^{-1}$ and $c(\text{H}_2\text{SO}_4) = 11.6 \text{ mol L}^{-1}$.

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 H₂SO₄-rich mixtures. Surprisingly, no polished surfaces were observed by means of SEM for sulfuric acid concentrations of $c(\text{H}_2\text{SO}_4) > 8 \text{ mol L}^{-1}$. 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 $\nu = 1400 \text{ cm}^{-1}$ confirms the formation of nitronium ions. A nitronium ion concentration of $c(\text{NO}_2^+) = 1.28 \text{ mol L}^{-1}$ was determined by evaluation of the NO₂⁺ 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 $2 \mu\text{m}$. 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-HNO₃-H₂O 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 ¹⁴N NMR and Raman spectroscopy. Integration of NO₂⁺ Raman line intensities at 1400 cm^{-1} enables the quantification of nitronium ions in HF-HNO₃-H₂SO₄ solutions.

In HF-HNO₃-H₂SO₄ etching mixtures the silicon etching rates depend on several parameters. These are the concentration of oxidizing species such as NO₂⁺, NO⁺ and N₂O₃, 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 H₂SO₄ concentration of 6 mol L^{-1} , which is caused mainly by an accelerated Si oxidation by increasing concentrations of undissociated HNO₃, nitronium ions and/or NO_x species such as NO₂. 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 HNO₂, N₂O₃ 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-HNO₃-H₂O 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-HNO₃-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-HNO₃ based solutions.

Experimental Section

Preparation of the HF-HNO₃-H₂SO₄ 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 $0.5-2 \Omega \text{ cm}^{-1}$, 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 $\text{NO}_2\text{BF}_4/\text{H}_2\text{SO}_4$ 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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