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Mass and Electron Balance for the Oxidation of Silicon during the Wet Chemical Etching in HF/HNO₃ Mixtures

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ABSTRACT: The stoichiometry of the wet-chemical etching of silicon in concentrated HF/HNO₃ mixtures has been studied. By quantifying the major reaction products in solution, the established model that 3 mol of Si are oxidized by 4 mol of HNO₃ to yield 4 mol of NO could not be confirmed. In HNO₃-rich HF/HNO₃ mixtures, approximately 1.1 mol of HNO₃ are required to oxidize 1 mol of Si. Excess HNO₃ leads to massive accumulation of N(III) species in the etchants and massive formation of nitrous oxides due to incomplete reduction of the HNO₃. An excess of HNO₃ leads to higher consumption and poorer utilization indicated by the massive accumulation of N(III) species in the etchants. In HF-rich mixtures, only 0.9 mol of HNO₃ are needed to oxidize 1 mol of

Si yielding a lower accumulation of N(III) species and a higher utilization of the HNO₃. Two parallel pathways contribute to the oxidation of silicon in such solutions: (i) via the oxidation by HNO₃ and reactive intermediates generated by the reduction of HNO₃ and (ii) via the formation of hydrogen. A comprehensive treatment covering alkaline etching, electrochemical etching in HF media, and etching in concentrated HF/HNO₃ mixtures is proposed based on the reactivity of the hydrogen terminated silicon surface against the applied oxidizing agent.
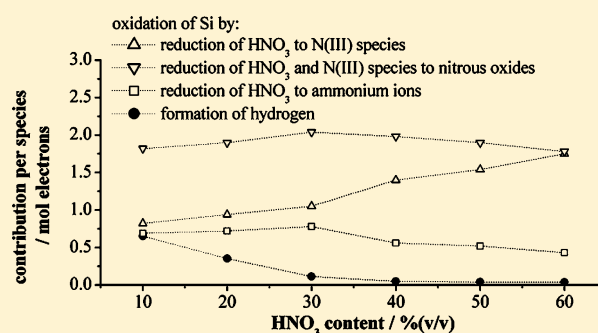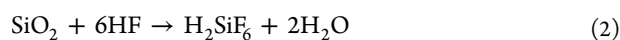
1. INTRODUCTION

Wet-chemical etching of multicrystalline silicon wafers using HF/HNO₃ mixtures in solar cell manufacturing removes saw-damage and conditions the wafer surface to achieve low reflectivity. The etching step plays an important role in the economical and ecological production of solar wafers. Modern bleed-and-feed etch lines utilize only a small volume of acid in order to remove saw damage from the wafer surface. Most of the acid is required to maintain the etch regime and produce a certain etch rate. More efficient management of acid use requires a deeper understanding of the etch mechanism as well as comprehensive knowledge of the etching stoichiometry and the nature of the reaction products.

Since the pioneering work done by Robbins and Schwartz,[1−4] the mechanistic picture of silicon etching in HF/HNO₃ mixtures is commonly described as a two step chemical process including (i) the formal oxidation of silicon to SiO₂ by nitric acid (eq 1)

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

and (ii) the subsequent dissolution of SiO₂ by HF (eq 2).

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

The overall reaction (eq 3) shows that the only reaction products are water, nitrogen monoxide, and hexafluorosilicic acid.

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O \qquad (3)$$
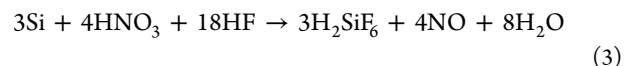
Turner described the etching of silicon as an electrochemical process consisting of anodic and cathodic reactions at different sites on the silicon surface.[5] Anodic oxidation of silicon (eq 4) is induced by injection of m holes (h⁺). Parameter m can range from 2 to 4, depending on the current multiplication factor (i.e., divalent or tetravalent electrochemical oxidation).[6] Again, formation of SiO₂ is assumed which is subsequently dissolved by HF according eq 2.

$$Si + 2H_2O + mh^+ \rightarrow SiO_2 + 4H^+ + (4 - m)e^- \qquad (4)$$
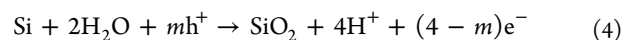
The cathodic reaction in eq 5 shows the reduction of nitric acid to form NO.

$$HNO_3 + 3H^+ \rightarrow NO + 2H_2O + 3h^+ \qquad (5)$$
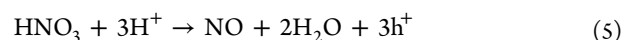
Equations 4 and 5 can be combined to give the overall reaction of eq 4. Of particular interest is Turner's essential conclusion that the main function of the oxidizing agent is not to oxidize silicon but provide an agent that is easily reduced in the cathode reaction.

Although there is general agreement with these descriptions, there are many details which are still unclear and under debate. This study is focused on one of the still unresolved questions regarding the reaction products and, in general, the stoichiometry of the etching reaction. There are many experimental results showing species other than nitric acid are involved in the etching of silicon and products other than NO are formed. The following compilation draws a picture of how complex the process is.

(i)   The dissolution of silicon by a mixture containing 70% (v/v) HF and 30% (v/v) HNO_3 above room temperature causes a vigorous evolution of brown NO_2 gas.[7] The etch solution turns brown after a short while, if a sufficiently high concentration of the gas is dissolved. The formation of brown NO_2 gas and brown coloration of the etchant are also observed if the reaction is carried out under an argon atmosphere.[7] This identifies NO_2 as a direct reaction product of silicon etching.

(ii) If the reaction is performed at 1 °C, the generation of nitrogen oxide gases is dramatically reduced and the etch mixture turns blue due to the formation of dissolved N_2O_3.[7,8] Brown NO_2 gas evolves by disproportionantion of N_2O_3 to NO_2 and NO, without etching, during warming to room temperature.[7,8] A detailed study by Raman spectroscopy revealed the presence of a complex N(III) species $(3NO^+ \cdot NO_3^-)$ denoted as $[N_4O_6^{2+}]$ in these blue etch solutions.[8] The linear relationship between etch rate and $[N_4O_6^{2+}]$ concentration suggests NO^+ is a reactive species in the rate-limiting step.[8] This confirms the theory of the reactive species in silicon etching proposed by Kelly et al.[9]

(iii) N_2O was also identified as a gaseous reaction product.[10,11]

(iv) Ammonium ions have been identified as a reaction product in the etching of silicon.[12] The formation of ammonium from nitric acid can be explained only by four successive two-electron reduction steps. This implies the existence of several dissolved intermediary and reactive nitrogen compounds which are involved in the oxidation of silicon. This confirms Turner's conclusion that any species with a proper redox potential is able to oxidize silicon. Furthermore, Patzig et al. identified ammonium ions as a product of silicon etching using a nitrosyl salt/HF etchant.[13]

(v)   Kooij et al. used mass spectrometry to analyze the gas produced during silicon etching from a mixture consisting of 6 M HF and 6 M HNO_3.[10] They found the gas phase consisted of 80.0% H_2, 18.3% N_2O, 1.0% NO, and 0.7% NO_2. Kooji et al. suggested the mechanism of silicon oxidation via nitric acid occurred by injection of three holes into the valence band of silicon and one hole from the formation of hydrogen. The colorless bubbles observed in stain etching might be accounted for by the formation of N_2O or H_2.[14]

(vi) Recently, the amount of hydrogen formed during the etching of silicon in HF/HNO_3 mixtures was quantified using a modified glow discharge system with optical emission detection.[15] The amount of hydrogen was found to depend on the HF/HNO_3 mixing ratio and temperature independent.

(vii) In contradiction to eq 4, no oxidized species could be detected on the surface of etched wafers, even at high nitric acid or $[N_4O_6^{2+}]$ concentrations. Silicon surfaces were always found to be completely hydrogen terminated after etching.[16]

The final conclusion from these facts is that there is no validated mass balance on the acid etching of silicon. We do not know how much nitric acid is consumed or what products are formed during the reaction. However, it is unlikely reaction products can be quantified at various stages of the reaction simultanelously. Such an analysis would have to cover all evolved gases, all ionic species, dissolved gases in the etching mixtures, and any reactive intermediates.

To overcome this, we have chosen two different approaches. The first is of general interest, and the second can be performed in any lab or production site. Validation of the overall etching reaction stoichiometry described by eq 3 is characterized by the first approach, in which small pieces of silicon were very slowly dissolved in a series of HF/HNO_3-etch mixtures over a period of several weeks. The stoichiometry of the etch reaction was calculated from the composition of silicon in the saturated solutions. The second approach was to determine the stoichiometry of silicon etching during the initial phase of the reaction by dissolving a small piece of silicon in a HF/HNO_3-etch mixture and immediately measuring the concentrations of nitrate, nitrite, and ammonium ions using ion chromatography. After capturing a sample, the process was continued by dissolving the next piece of silicon.

The major disadvantage of the procedure was that no gas phase composition information could be made. However, evolved gases could be quantified by the difference between the consumed nitric acid and all nitrogen species detected in solution. The reaction was carried out at 1 °C to minimize the impact from nitrous gases. At this temperature, the nitrous gases remain dissolved in the etch solution primarily as N_2O_3 (see at ii). After dilution of concentrated etch mixtures, dissolved N_2O_3, as well as the intermediate $[N_4O_6^{2+}]$, are converted into nitrite ions which are easily detected.[7,8] Furthermore, at temperatures below 8 °C, ammonium ions were found to be stable against disproportionation with intermediates and dissolved gases that have a nitrogen atom in the +3 oxidation state (e.g., N_2O_3 or $[N_4O_6^{2+}]$).[12] Under these conditions, formation of nitrogen is expected to be suppressed, and reduce the formation of NO_2, NO, and N_2 to a minimum, causing the evolved gases to consist mainly of N_2O and H_2.

At the same time we performed parallel measurements of the amount of hydrogen formed by the etching of silicon under the conditions described here. The experimental procedure and the results have been previously published.[15] The combined results from quantitative analysis of etch solutions and the hydrogen content provide the first mass and electron balance of the wet-chemical etching of silicon by HF/HNO_3 mixtures.

2. EXPERIMENTAL SECTION

All experiments were carried out under isothermal conditions using a cryostat (Polystat K12-2, Huber Kältemaschinen GmbH, Offenburg, Germany). Wide-mouthed HDPE (high-density polyethylene) bottles with tight-sealing screw caps were

used as reaction vessels. The reaction vessels were mounted into a sample holder and then immersed into the cryostat. HF/HNO$_3$-acid mixtures were prepared from aliquots of analytical grade acids (HF 40% (w/w), nitric acid 65% (w/w), Merck, Darmstadt, Germany). A volume of 50 mL of each mixture was dispensed into a reaction vessel and thermostatted to 1 °C. For the sake of simplicity, etch mixtures were named using their volume acid mixing ratios. In spite of this simplification in the notation, all mixture components were weighed and all analytical results are based on the mass of the individual compound. This approach was taken due to the considerable volume contraction observed when mixing concentrated HF with concentrated HNO$_3$.
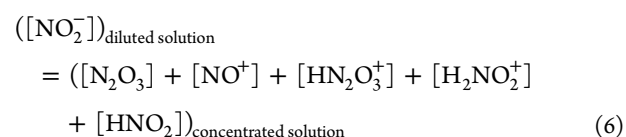
In order to determine the maximum solubility of silicon, weighed pieces of p-conducting silicon ranging from 50 to 200 mg (diameter 4 in., polished, thickness 675 μm, resistivity 24−36 Ω cm; Wacker Siltronic, Freiberg, Germany) were very slowly dissolved in acid mixtures at a temperature of 1 °C. After placing the silicon into the solution, the reaction vessels were tightly sealed. The next piece of silicon was added after the previous one was completely dissolved. We defined the end of the reaction when the silicon remained for 7 days without changes in shape and without producing gas bubbles. This piece was removed and weighed to determine the amount dissolved. Depending on the composition of the HF/HNO$_3$ mixtures, the duration of the saturation experiments ranged between 7 and 10 weeks.

The described procedure minimizes the loss of silicon as SiF$_4$. Solutions were analyzed by ICP-OES for Si (IRIS intrepid II XUV, Thermo Electron Corp, U.K.) using an established procedure.[17] The amount of dissolved silicon measured from ICP-OES measurements agreed to within 2% of the weighed amounts of silicon added to the etchants. These values agreed with the results of an earlier study[18] showing the concentration of dissolved silicon can be calculated from the weighed amount of silicon.

Concentrations of nitrate ions and total fluoride ions (from HF and H$_2$SiF$_6$) in the etch solutions were determined by ion chromatography (761 compact IC, Deutsche METROHM GmbH & Co. KG).[19] Ammonium ion concentrations in the etch solutions were found to be negligibly low (at the detection limit). Hexafluorosilicic acid is known to dissolve additional silicon. In order to determine the content of dissolved silicon present only as H$_2$SiF$_6$ a gravimetric method by precipitation of K$_2$SiF$_6$ in ethanolic solution was applied.[19]

The procedure to determine the consumption of nitric acid in the initial phase of the reaction was almost identical. After dissolution of 50−70 mg of silicon in the respective acid mixture at a temperature of 1 °C, a 0.5 mL aliquot of each concentrated etch mixture was diluted with deionized water by a factor of 500 for the ammonium determination.[12] Another 0.5 mL aliquot of each etch mixture was diluted by a factor of 5000 to measure the concentrations of nitrite, nitrate, and fluoride by ion chromatography.[7] The mean uncertainty in the determination of these anions is about 1.2%.

By dilution of an aliquot of the original concentrated etch solution by a factor of 5000 all nitrogen species in the +3 oxidation state (e.g., N$_2$O$_3$, NO$^+$ in [N$_4$O$_6$$^{2+}$]), in the following denoted as N(III)-species, are fully converted into nitrite ions, as expressed by the following relationship:[7]

$([NO_2^-])_{\text{diluted solution}}$

$$= ([N_2O_3] + [NO^+] + [HN_2O_3^+] + [H_2NO_2^+]$$
$$+ [HNO_2])_{\text{concentrated solution}} \tag{6}$$

A commercial GD-OES instrument (GDS 750 LECO Germany, Munich, 1992) with monochromator (Digikröm DK480, Spectral Products, Albuquerque, USA) and an unchanged Grimm type glow discharge chamber was used to quantify the amount of hydrogen.[15] A small fraction of the reaction gases from HF/HNO$_3$ etching of approximately 300 mg of silicon in a Teflon apparatus under argon atmosphere was fed with a constant argon flow via a drying column into the discharge chamber. Reaction gases were excited by the plasma of a continuously DC sputtered iron sample. Hydrogen atom emission intensities at 121.5 and 656.3 nm were used for quantification. The emission intensities of oxygen and nitrogen atoms were recorded at 130.2 and 174.2 nm, respectively, but not quantified. The estimated uncertainty of this procedure is about 5%.[15]

3. RESULTS AND DISCUSSION

3.1. Overall Stoichiometry of Si Etching in Concentrated HF/HNO$_3$ Mixtures. The first series of experiments were conducted to answer the question if eq 4 is a valid description of the etching process in general. Silicon was dissolved until saturation in etch solutions of different compositions and the mass balances were compared with the predictions of eq 3.

Figure 1 shows the theoretical maximum amount of silicon that can be dissolved in 50 mL of HF/HNO$_3$ etch solutions of
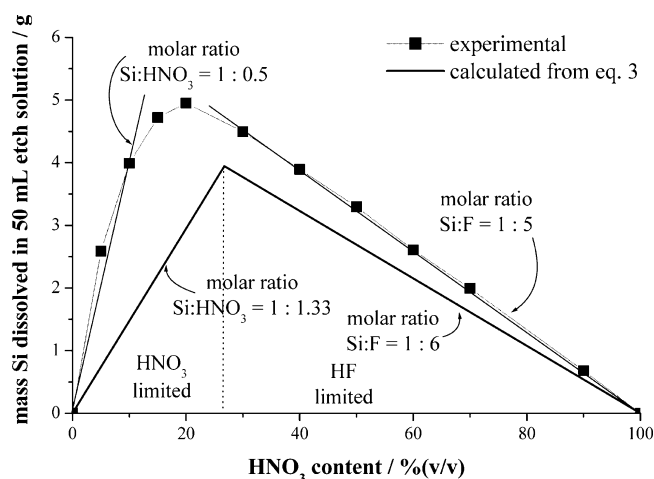

Figure 1. Maximum solubility of silicon in 50 mL of HF/HNO$_3$ etch solutions of different compositions after a period of 7 to 10 weeks at 1 °C in comparison to the calculated maximum silicon solubility according to eq 3.

different compositions calculated using eq 3 (assuming the HF/HNO$_3$ mixtures behave as ideal solutions). Since HF and HNO$_3$ are necessary to dissolve silicon, maximum solubility is always limited by the minority compound. In etchants with more than 26.75% (v/v) HNO$_3$ (the maximum value from the calculated curve) the oxidizer (HNO$_3$) is present in excess (eq 1) so that the solubility of silicon is limited by the amount of HF according to eq 2. The theoretical slope in this region represents the molar ratio Si/HF = 1:6 as stated in eq 3. In

etchants having less than 26.75% (v/v) HNO_3 the HNO_3 concentration determines the maximum solubility of silicon according to eq 1. Again, the theoretical slope in this region is derived from eq 3 as the molar ratio Si/HNO_3 = 1:1.33.

The experimental values plotted in Figure 1 show that the maximum solubility of silicon dramatically exceeds that predicted from eq 3 over the entire range of mixing ratios. Equation 3 fails to describe the net reaction of silicon etching in two different ways: (i) Hydrofluoric acid is able to dissolve more silicon than predicted from the molar ratio Si/F = 1:6 (derived from SiF_6^{2-} in eq 2 as the predicted reaction product). (ii) Nitric acid is able to oxidize much more silicon than expected. Therefore, the change in the oxidation state of nitrogen from +5 (HNO_3) to +2 (NO) according to eq 1 must be higher so that reaction products other than NO must be formed.

The higher solubility of Si in an HF-rich mixture corresponds to a molar ratio of Si/F = 1:5 as derived from the slope of the experimental data in the region above 30% (v/v) HNO_3 (Figure 1). The nature of the water-soluble Si complex is obtained by chemical analysis of the etch solutions. In the first analysis, aliquots of the concentrated etch solution were titrated with NaOH using phenolphthalein to indicate the end point. The titrated sample solutions were analyzed for F^- after dilution by ion chromatography.[19] This procedure yields the total fluoride concentration due to complete decomposition of the SiF_6^{2-} complex at a pH above 9.[17] In a second analysis Si bound as SiF_6^{2-} was quantitatively precipitated from the concentrated etch solutions as K_2SiF_6. The precipitates were redissolved and the contents of Si and fluoride analyzed by ICP-OES and ion chromatography, respectively.[17,19] The results in Figure 2 show that in etch solutions with more
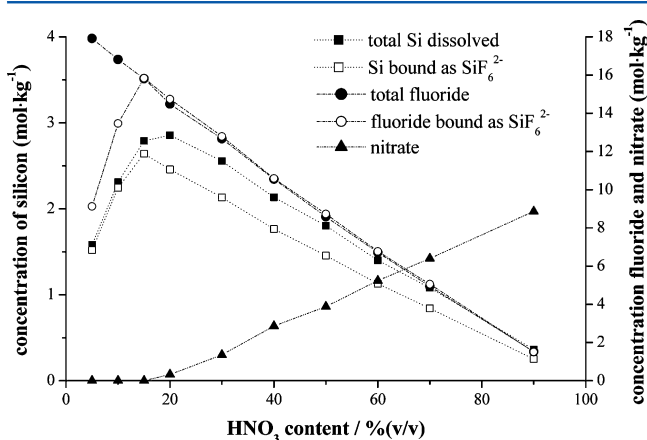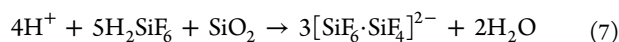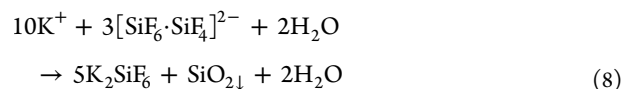

Figure 2. Results from chemical analysis of etch solutions after saturation experiments. The concentrations of the elements and anions refer to the amounts of the undiluted etch mixtures.

than 20% (v/v) HNO_3 all of the fluoride, but only 80% of the totally dissolved Si can be precipitated as K_2SiF_6. These findings correspond to the so-called high-silica fluorosilicic acid as described by Thomsen.[20] According to Thomsen, hexafluoro-silicic acid is able to dissolve an extra 20% SiO_2 according to eq 7

$$4H^+ + 5H_2SiF_6 + SiO_2 \rightarrow 3[SiF_6 \cdot SiF_4]^{2-} + 2H_2O \qquad (7)$$

After precipitation of K_2SiF_6 the extra silicon remains in solution as silicic acid (as in the present case) or precipitates very slowly as colloidal SiO_2 (eq 8).[20]

$$10K^+ + 3[SiF_6 \cdot SiF_4]^{2-} + 2H_2O$$
$$\rightarrow 5K_2SiF_6 + SiO_{2\downarrow} + 2H_2O \qquad (8)$$

The experimental data in Figure 1 suggest a higher oxidizing power than predicted by eq 3. The stoichiometric ratios for the oxidation of silicon were calculated from the moles of nitric acid consumed and the moles of dissolved silicon and plotted in Figure 3. In the region with HNO_3 as minority compound, the
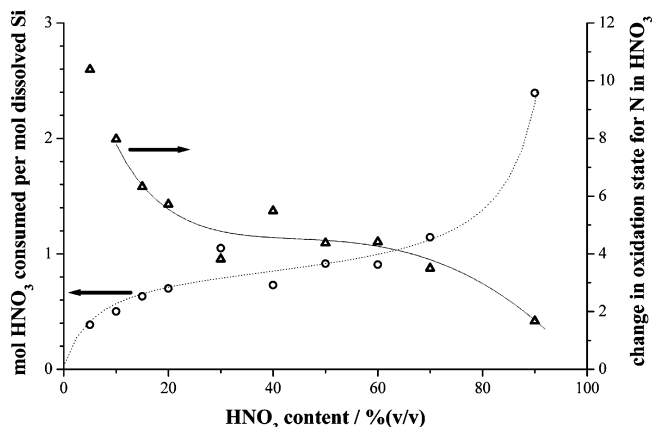

Figure 3. Changes in consumption of HNO_3 per mol of dissolved Si in concentrated HF/HNO_3 etch solutions of different compositions over a period of about 10 weeks at 1 °C. Left axis: number of moles HNO_3 required to oxidize 1 mol Si; right axis: formal change in the oxidation state of N starting from HNO_3. The calculated change in the oxidation state of 10 units is unrealistic high.

oxidation of 1 mol silicon requires approximately 0.5 mol HNO_3. This increases to approximately 2.5 mol in HNO_3-rich etch mixtures showing that nitric acid is much more utilized when present as the minority compound. With 4 mols of electrons needed to oxidize 1 mol of silicon, the formal number of mole electrons transferred from nitric acid to silicon is estimated from the formal change in the oxidation state of nitrogen in nitric acid (Figure 3). In HNO_3-poor mixtures, HNO_3 should be entirely consumed with formation of NH_4^+ via the transfer of 8 mol electrons according to Figure 3.

The presented results should be seen as trends; however, an overinterpretation of the results should be avoided because of the 10 week duration of the experiments. Notably, the calculated change of the oxidation states for HNO_3 of 10 units in a mixture containing 5% (v/v) HNO_3 (Figure 3) is not real. Furthermore, the predicted complete reduction of HNO_3 to ammonium ions via the exchange of 8 mol electrons is unrealistic, too. A previous study showed that nitric acid is only partially reduced to ammonium ions.[12] In the present series, practically no ammonium or nitrite ions were found. To explain their absence, the stability of ammonium ions in etch solutions has to be considered. Ammonium ions were found to be stable for hours in the presence of N(III) intermediates at temperatures below 8 °C.[12] Therefore, it is reasonable to expect that over a time of 7 to 10 weeks even the very slow synproportionation of $\overset{+3}{N}$ and $\overset{-3}{N}$ can result in a complete decomposition of the ammonium ions. Finally, it was shown that N_2O_3 as well as other nitrous oxides dissolved in the etch mixtures either outgas from the solutions or are oxidized by air to nitrate respectively nitric acid.[7,12,16]
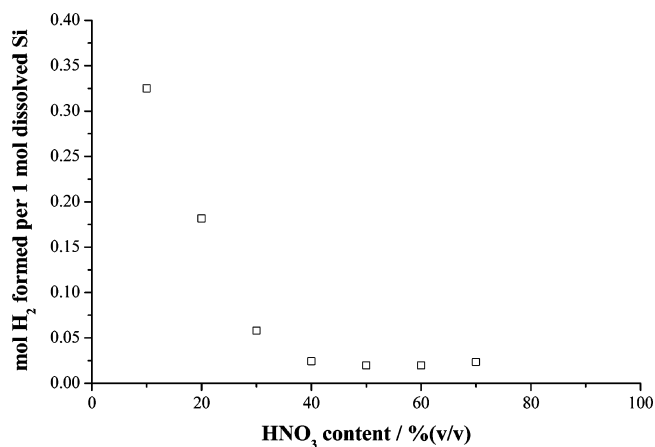
Table 1. Mass Balance of Consumed and Formed Species during the Continuous Dissolution of Si in Concentrated HF/HNO$_3$ Mixtures at 1 °C Normalized to the Dissolution of 1 mol Si

| composition HNO$_3$ | consumption of HNO$_3$ | formation of | | | |
		N(III) intermediates[a]	NH$_4^+$	H$_2$[b]	not detected N-species[c]
% (v/v)		mol per 1 mol Si			
10	0.8916 ± 0.0266	0.417 ± 0.0070	0.0862 ± 0.0008	0.3262	0.3885 ± 0.0275
20	0.8607 ± 0.0178	0.5123 ± 0.0108	0.0899 ± 0.0010	0.1771	0.2586 ± 0.0209
30	0.8623 ± 0.0252	0.5297 ± 0.0247	0.098 ± 0.0005	0.0562	0.2346 ± 0.0353
40	1.143 ± 0.0436	0.7037 ± 0.0103	0.0706 ± 0.0006	0.0241	0.3687 ± 0.0448
50	1.104 ± 0.0366	0.772 ± 0.0273	0.065 ± 0.0003	0.0196	0.267 ± 0.0456
60	1.1731 ± 0.0466	0.8762 ± 0.0205	0.0538 ± 0.0005	0.0189	0.2431 ± 0.0509

[a]Measured as nitrite ion concentration in 1:5000 dilutes solution[7] [b]Values were taken from ref 15; the relative uncertainty is estimated to 5% [c]The amount of nondetected N-species is calculated from the difference between the total consumed HNO$_3$ and the sum of nitrite and ammonium ions; the uncertainty of the amount of nondetected N-species is calculated as propagation from the uncertainties of the involved species.

In summary, a number of general conclusions can be drawn. There is no unique reaction equation that sufficiently describes the stoichiometry between Si and HNO$_3$ over the entire concentration range. There is considerable variation in the consumption of HNO$_3$. Broad variation can be expected for the gaseous reaction products (i.e., different nitrous oxides). The higher the nitric acid concentration in the etch mixture; the extent of nitric acid reduction is lower. In HNO$_3$-poor mixtures, there are other oxidizing reagents that contribute to the oxidation of silicon. Finally, the long duration favors side-reactions, so that neither ammonium nor nitrite ions were found at significant concentrations.

3.2. Formation of Hydrogen during Si Etching in Concentrated HF/HNO$_3$ Mixtures. Recently, we studied the amount of hydrogen formed by dissolution of approximately 300 mg Si in different etch mixtures at different temperatures by optical emission spectroscopy.[15] The results given in Table 1 and in Figure 4 show that considerable amounts of hydrogen

Figure 4. Formation of hydrogen during the dissolution of silicon in concentrated HF/HNO$_3$ mixtures at 1 °C and normalized to 1 mol dissolved Si. Data were taken from ref 15.

are formed in HNO$_3$-poor etch mixtures. Results revealed that the formation of hydrogen is independent of temperature between −10 and +35 °C.[15] The evolution of hydrogen contributes to the oxidation of silicon parallel with the oxidation by nitric acid as described in the previous section.

3.3. Mass Balance of the Initial Period of Si Etching. To establish the mass balance of silicon etching, silicon pieces with masses between 50 and 200 mg were dissolved in 50 mL

of etch mixtures at 1 °C. Immediately after the piece completely dissolved, aliquots of the solutions were analyzed. Measured concentrations of the ions formed are plotted against the silicon concentration (both quantities in mol L^{-1}) calculated from the weights of the dissolved silicon pieces (Figure 5a−c). Only the slopes of the graphs (plotted as solid lines) were used for further calculations in order to minimize uncertainties of single measurements.

The dissolution process is remarkably reproducible as shown by the linear behavior. In other words, for each mixing ratio of HF and HNO$_3$, there exists a relationship between the conversion of the educts (silicon and nitric acid) and the products formed (nitrite and ammonium) at a given temperature. However, the linear ranges for the different species expand over different amounts of dissolved silicon. The widest linear range was found for the consumption of nitric acid up to approximately 3 g of dissolved silicon in 50 mL of etch mixture. The linear range is shorter for ammonium (approximately 2.5 g) and much shorter for nitrite at approximately 0.75 g. (The linear section turns in a descending curvature due to a beginning decomposition as already shown for nitrite[7,16] and ammonium.[12]) Table 1 summarizes the stoichiometric ratios of consumed and formed species normalized to 1 mol silicon.

From Table 1, it is clear that the chemical analysis is not able to detect all reaction products. There is a considerable difference between the amount of consumed nitric acid and the sum of detected nitrite and ammonium ions in solution. Although it is not possible to make any statements about the nature of the nondetected species, some general comments can be made. The most likely explanation is the direct liberation of gaseous products formed by the reduction of nitric acid and N(III) intermediates. Plausible candidates are N$_2$O, NO, and NO$_2$. Another possible source for gaseous compounds is the synproportionation between intermediates in the +3 oxidation state (N$_2$O$_3$, NO$^+$, and N$_4$O$_6^{2-}$) and ammonium ions in the −3 oxidation state to yield nitrogen.[12] It should be noted that at the chosen low reaction temperature of 1 °C, the evolving gases had only a slight brown color so that the colorless gases N$_2$O, H$_2$, and even N$_2$ can be assumed as the major gaseous reaction products. Second, it cannot ruled out that there are other intermediary species or dissolved gases (e.g., N$_2$O$_4$ or N$_2$O$_2$) in the concentrated acid mixtures which were not fully converted to ammonium, nitrite, and nitrate by the dilution. However, their contribution is considered small compared to the quantified species.[8]

Figure 6 compiles the results of Table 1. At 40% (v/v) HNO$_3$ and above 1.1 mol, HNO$_3$ is consumed in the reaction

Figure 6. Mass balance of consumed and formed species during the continuous dissolution of Si in concentrated HF/HNO₃ mixtures at 1 °C normalized to the dissolution of 1 mol Si.
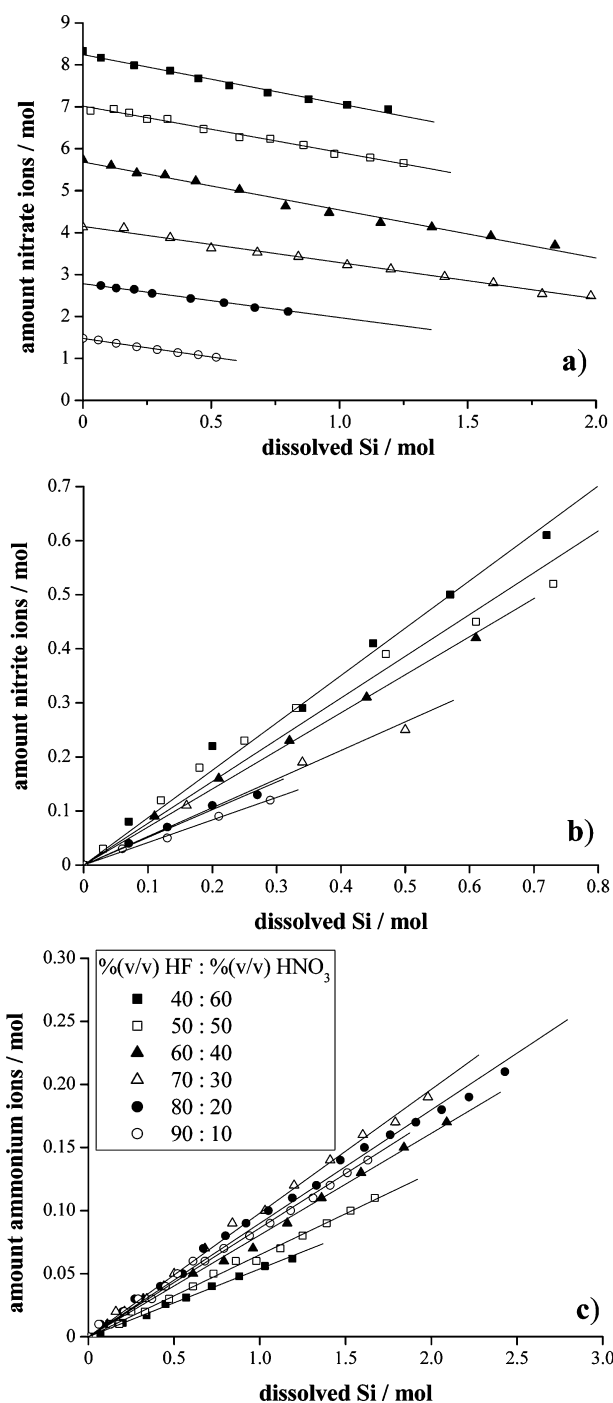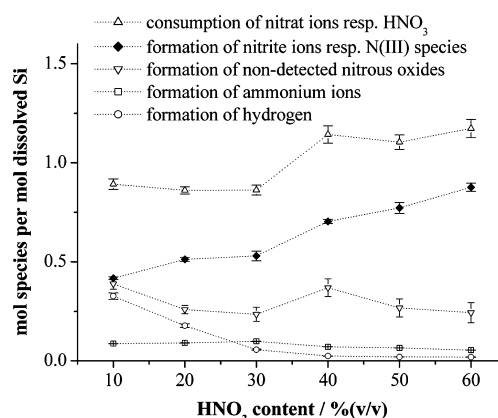

Figure 5. Consumption and formation of species formed during the continuous dissolution of silicon in concentrated HF/HNO₃ mixtures at 1 °C. (a) Consumption of HNO₃ (calculated from the nitrate ion concentration), (b) formation of nitrite ion concentration (as sum of intermediary N(III) species), (c) formation of ammonium ions. The quantities and their uncertainties in Table 1 were calculated form the slopes of the linear fits (plotted as solid lines).

intermediates and the formation of hydrogen contribute to the oxidation of silicon. Silicon oxidation via hydrogen formation is insignificant and the oxidation of silicon proceeds almost completely from HNO₃. At 30% (v/v) HNO₃ and below the oxidation of 1 mol of silicon, approximately 0.87 mol of HNO₃ is required whereas in etchants with 40% (v/v) HNO₃ and above the utilization of nitric acid increases and now 1.1 mol HNO₃ are consumed. These results differ significantly from the long-term experiments in section 3.1. Figure 3 shows the 5% (v/v) HNO₃ etch mixture consumes approximately 0.5 mol HNO₃ per 1 mol silicon, while in the 60% (v/v) HNO₃ mixture, 0.9 mol are required. In general, HNO₃ consumption in the continuous etching process is always higher than found for the saturation experiments. To explain this behavior, the long time scale of the experiments described in section 3.1 has to be considered. It can be assumed that there is enough time to reoxidize a fraction of the N(III) intermediates formed during the etching to nitric acid.[7] The concentration of N(III) intermediates increases with HNO₃ concentration in agreement with earlier results showing the N(III) intermediates in HNO₃-rich etchants have a higher solubility and higher stability against oxidation.[16] The very reactive N(III) intermediates undergo further reduction as shown by their involvement in the rate determining step in HF-rich etchants.[8]

Finally, the formation of ammonium ions should be discussed. Ammonium ions are a product of the reduction of nitric acid in agreement with studies on the electrochemical reduction of nitrate ions.[21−23] In contradiction to other reaction products intermediate ammonium ions are formed without significant correlation to the HF/HNO₃ mixing ratio and, more surprisingly, independent of the concentration of N(III) intermediates present in the etchant. Following the electrochemical reaction pathway, ammonium ions are formed by the reduction of N(+I) intermediates. However, Kooij et al.[10] and Weinreich[11] identified N₂O as the most important gaseous reaction product of silicon etching. Due to the almost constant formation of ammonium ions, we prefer to assume an almost constant, quite low solubility of these N(+I) intermediates in HF/HNO₃ mixtures at any mixing ratios. Exceeding this solubility limit leads to the liberation of N₂O and an almost constant concentration of N(+I) intermediates is available for a further reduction to ammonium ions. The nature of these intermediates (e.g., hyponitrous acid, $H_2N_2O_2$, nitrosohydrogen, HNO, or the nitroxyl anion, NO^-) is merely

with silicon resulting in higher concentrations of reactive N(III) intermediates as shown by a former study on HNO₃-rich etch mixtures.[16] At 30% (v/v) HNO₃ and below the oxidation of 1 mol silicon requires approximately 0.87 mol of HNO₃ yielding the typically lower concentration of N(III) intermediates in HF-rich etch mixtures.[7] In etchants with HNO₃ as minority compound, both nitric acid and the N(III)

speculation since there is no spectroscopic evidence for any of them.[8]

3.4. Electron Balance of Si Etching in the HF/HNO$_3$ Mixtures. To establish an electron balance of silicon etching in HF/HNO$_3$ mixtures requires calculation of the individual contribution from each species with the abstraction of 4 mol electrons per mol dissolved silicon. The formation of 1 mol each of the species N(III), NH$_4$$^+$, and H$_2$ requires the transfer of 2, 8, and 2 electrons, respectively, from silicon to nitric acid. The multiplication of these numbers with the stoichiometric ratios of Table 1 yields their individual contribution to the oxidation of silicon in Table 2. The resulting difference to the required 4 mol electrons is attributed to the oxidation of silicon by the nondetected N-species.

Table 2. Electron Balance of the Oxidation of Si during the Etching in Concentrated HF/HNO$_3$ Mixtures at 1 °C

composition	contribution to the oxidation of 1 mol silicon			
HNO$_3$	N(III) intermediates	NH$_4$$^+$	H$_2$	nondetected N-species
% (v/v)	mol electrons per 1 mol Si			
10	0.84	0.69	0.65	1.82
20	1.03	0.72	0.35	1.90
30	1.06	0.78	0.11	2.05
40	1.41	0.56	0.05	1.98
50	1.54	0.52	0.04	1.90
60	1.75	0.43	0.04	1.78

Figure 7 leads in principle to the same conclusions as discussed for Figure 6. It shows the considerable importance of
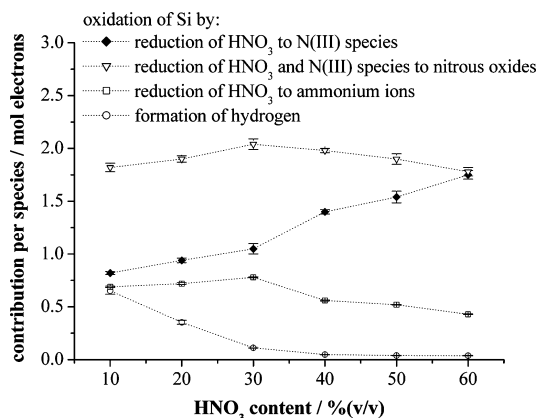

Figure 7. Electron balance of the oxidation of Si calculated for the etching in concentrated HF/HNO$_3$ mixtures at 1 °C. The individual contributions of the species (in mol electrons) refer to 1 mol dissolved Si.

the formation of hydrogen that contributes approximately 0.65 mol of electrons to the oxidation of silicon in the 5% (v/v) HNO$_3$ mixture.

The contribution of hydrogen formation decreases exponentially with increasing HNO$_3$ content. This is compensated by a higher contribution of N(III) species, i.e., more HNO$_3$ is consumed and more N(III) intermediates are formed (Figure 6). As the amount of consumed HNO$_3$ increases, more Si is oxidized by formation of N(III) intermediates. These intermediates are enriched in the etchant and only a certain fraction undergoes further reaction. Therefore, the utilization of HNO$_3$ is less efficient. Furthermore, the contribution of the
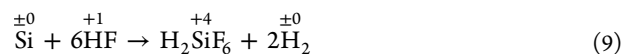
nondetected N-species amounts to approximately 2 mol of electrons independent of the HF/HNO$_3$ mixing ratio. Because of the different amounts of nondetected N-species (Figure 6), these species have to be reduced to different extents.
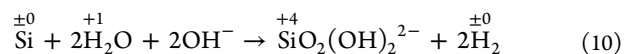
4. CONCLUSION

Up to now there is no uniform base for a general treatment of the different types of silicon etching. On one hand, there is the comprehensive mechanistic model by Kolasinski that covers the alkaline etching, the di- and tetravalent electrochemical etching in HF media, the (photo-) electrochemical etching in HF solution, as well as the photochemical etching in HF media with a unified mechanistic model.[24] On the other hand, the etching of silicon in HF/HNO$_3$ mixtures does not fit either Kolasinski's model or others. There is a general agreement that the oxidation of silicon in such mixtures is basically the same as for anodic oxidation with a silicon surface that behaves randomly as localized anodes and cathodes.[6,25−27] Particularly, the tetravalent anodic oxidation in hydrofluoric media is seen as a suitable model for silicon etching in HF/HNO$_3$ mixtures. Key features of the tetravalent anodic dissolution are the formation of an oxide layer at the surface and the absence of hydrogen. However, recent results have put this assumption in jeopardy: No oxide layer was detected, and moreover, the formation of hydrogen was found to depend on the HF/HNO$_3$ mixing ratio.

Based on the results presented in this work, a first step to close this gap can be accomplished by comparing the types of silicon etching in different media and the different oxidizing agents with respect to the formation of hydrogen and the applied oxidation potential. For this purpose, the following simplified reaction equations are sorted by decreasing hydrogen formation.
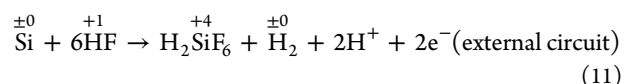
According to its standard electrode potential silicon is a less noble element (M) that should dissolve in water or in any diluted acid by formation of hydrogen (e.g., Na or K) according to eq 9.[28] However, this reaction is not observed. Etching with hydrofluoric acid in the absence of any oxidizing agent removes only the protective native oxide layer and yielding a hydrogen-terminated silicon surface. The hydridic Si−H surface exhibits chemical behavior similar to silane, SiH$_4$, that is stable in acidic media, however, readily attacked in alkaline media.

$$\overset{\pm 0}{Si} + 6\overset{+1}{H}F \rightarrow H_2\overset{+4}{Si}F_6 + 2\overset{\pm 0}{H}_2 \tag{9}$$

In alkaline media silicon behaves as a less noble element. Dissolution proceeds with 2 mol of H$_2$ formed per 1 mol of dissolved Si according to eq 10. Silicon is formally oxidized with the loss of the electron pair in the Si−H bond by reaction of protons with the hydridic hydrogen of the Si−H bond.

$$\overset{\pm 0}{Si} + 2\overset{+1}{H}_2O + 2OH^- \rightarrow \overset{+4}{Si}O_2(OH)_2^{2-} + 2\overset{\pm 0}{H}_2 \tag{10}$$
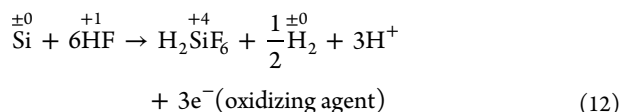
Anodic dissolution of silicon in diluted aqueous HF solution at low current densities produces 1 mol of hydrogen (eq 11). A total of 2 mol of electrons per mol of dissolved silicon are removed by hydrogen formation, the other 2 mol by the external circuit.

$$\overset{\pm 0}{Si} + 6\overset{+1}{H}F \rightarrow H_2\overset{+4}{Si}F_6 + \overset{\pm 0}{H}_2 + 2H^+ + 2e^-(external\ circuit) \tag{11}$$
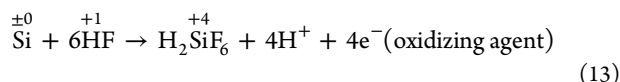
The contribution of hydrogen formation to the oxidation of silicon is reduced to 1 mol of electron and less if HF-rich HF/HNO$_3$ mixtures are used. The remaining 3 mol of electrons are
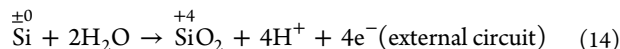
removed by the chemical oxidizing agent. Equation 12 can be seen as idealized description for etching with mixtures of 90% (v/v) HF and above.
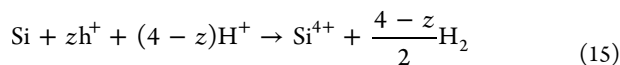
$$\overset{\pm 0}{Si} + 6\overset{+1}{HF} \rightarrow H_2\overset{+4}{SiF_6} + \frac{1}{2}\overset{\pm 0}{H_2} + 3H^+$$
$$+ 3e^-(\text{oxidizing agent}) \tag{12}$$

In HNO_3-rich HF/HNO_3 mixtures with more than 60% (v/v) HNO_3, practically no hydrogen is formed. The oxidation of silicon is achieved by the chemical oxidizing agent only as written in the idealized eq 13.

$$\overset{\pm 0}{Si} + 6\overset{+1}{HF} \rightarrow H_2\overset{+4}{SiF_6} + 4H^+ + 4e^-(\text{oxidizing agent}) \tag{13}$$

Finally, electrochemical etching at high current densities (eq 14) produces Si–O species to a considerable extent, even in the presence of hydrofluoric acid.[25−27] Only in this case does silicon etching proceeds by the two consecutive steps of silicon oxide formation and silicon oxide dissolution by HF (eqs 1−3). Equation 14 describes the oxidation of silicon and the generation of an oxide layer, formally written as SiO_2.

$$\overset{\pm 0}{Si} + 2H_2O \rightarrow \overset{+4}{SiO_2} + 4H^+ + 4e^-(\text{external circuit}) \tag{14}$$
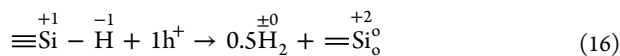
The order of these dissolution models is identical to the order of increasing external oxidation power. In alkaline solution, silicon behaves fully like a less noble metal that is oxidized by the attack of the very weak oxidizing agent water with formation of the equivalent moles of hydrogen (eq 10).[29−31] With increasing oxidation power the noble character gets lost as indicated by the descending formation of hydrogen (eqs 11−13). Further increase of the oxidation power leads finally to tetravalent anodic oxidation in aqueous HF media and formation of massive oxide films in the absence of hydrogen evolution (eq 14). The gradual transition between the two pathways of eqs 10 and 14 is formalized to eq 15

$$Si + zh^+ + (4 - z)H^+ \rightarrow Si^{4+} + \frac{4 - z}{2}H_2 \tag{15}$$

Parameter z is equivalent to the dissolution valence that is defined by the ratio of the number of exchanged carriers per dissolved silicon atom.[6] In other words, it defines the number of electrons that are removed by an external oxidation source (external current, oxidizing agent) in competition with the oxidation of silicon (i.e., electron removal) by the formation of hydrogen. Parameter z increases with increasing oxidation power either due to higher concentrations of an oxidizing agent or by an external current.

From this formalized explanation the following mechanistic picture is drawn: A key step to the reactivity of silicon in acidic solution is the kinetically determined reactivity of the hydrogen-terminated silicon surface. These hydridic species are either moderately oxidized via a one electron step with formation of hydrogen (eq 16) or oxidized in a two electron step to H^+ under strong oxidizing conditions.

$$\overset{+1}{\equiv Si} - \overset{-1}{H} + 1h^+ \rightarrow 0.5\overset{\pm 0}{H_2} + \overset{+2}{= Si_o^o} \tag{16}$$

or by a two electron step under formation of protons (eq 17).

$$\overset{+1}{\equiv Si} - \overset{-1}{H} + 2h^+ \rightarrow H^+ + \overset{+2}{= Si_o^o} \tag{17}$$
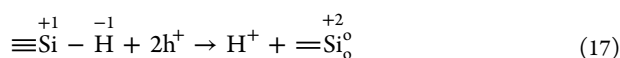
The presented results might be seen as a support of a statement made by Kolasinski.[24] The dissolution of silicon atoms from the bulk silicon proceeds by a quite uniform mechanism. Any findings on the reduction of HNO_3, the formed intermediary species and their reactivity, or on the formation and absence of hydrogen rely solely on the chemistry of the chemical oxidation reagent.

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Notes

The authors declare no competing financial interest.

■ DEDICATION

Dedicated to Prof. Dr. Klaus Bohmhammel (Technische Universität Bergakademie Freiberg) on the occasion of his 70th anniversary.

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