Raman spectroscopic determination of the degree of dissociation of nitric acid in binary and ternary mixtures with HF and H$_2$SiF$_6$

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**Abstract**
The oxidizing effect of nitric acid in aqueous solutions depends on the concentration of undissociated nitric acid. This makes the concentration of undissociated nitric acid an essential parameter to monitor and control the quality of silicon etching in the industrial manufacturing of solar cells. In the present study, a method known already is extended in such a way that the degree of dissociation of nitric acid can be determined by Raman spectroscopy in HF/HNO$_3$/H$_2$SiF$_6$ acid mixtures over a broad concentration range for the first time and without using an internal or external standard to compensate the typical time-dependent drift of a Raman spectrometer. The method developed requires the calculation of a peak area ratio from the areas of the unimpeded Raman signals assigned to nitrate (ν$_{N−O} )$ at 1,048 cm$^{-1}$ and to undissociated HNO$_3$ (ν$_{N−OH} )$ at 957 cm$^{-1}$. The correlation between the peak ratio and the degree of dissociation of nitric acid revealed can be described by a simple empirical equation. Using this equation, the degree of dissociation of nitric acid can be determined over a broad concentration range in binary and ternary mixtures of HNO$_3$ with HF and H$_2$SiF$_6$. The impact of the acids HF and H$_2$SiF$_6$ and the total water content in the degree of dissociation of nitric acid is discussed.

**KEYWORDS**
dissociation, nitric acid, Raman spectroscopy, silicon etching

**1 | INTRODUCTION**
The HF/HNO$_3$/H$_2$SiF$_6$ system is the acid mixture used most for wet chemical etching of silicon (Si) in microelectronics and photovoltaics. Its major application is to etch away the so-called saw damage from the surface of Si wafers.$^{[1]}$ The term “saw damage” designates a disturbed crystal lattice layer at the wafer surface with a thickness of several micrometres that is formed during wire sawing of multicrystalline Si blocks and monocrystals. On the one hand, the composition of the acid mixture determines the rate of removal of the disturbed lattice layer, and, on the other hand, it determines the final topography of the wafer after the end of the etching process.$^{[2]}$ The choice of etching...
parameters (vertical/horizontal immersion, temperature, stirring speed, and additives used) allows one to shape the topography of the wafer surface in such a way that it has a lower reflectivity, which leads to a higher efficiency of the solar cell manufactured. A recent investigation using a combination of confocal microscopy and Raman microscopy explains this phenomenon, showing that disturbed lattice areas that are under strong tensile and compressive stress are specifically attacked by acidic etching solutions.

Although numerous studies deal with the mechanism of the acid etching of Si with HF-HNO₃ mixtures, the essential step in the initial phase of the reaction is still unclear. Despite its non-noble character, Si dissolves only very slowly (0.03 nm·min⁻¹) even in concentrated hydrofluoric acid (48%). Only after the addition of an oxidizing agent (e.g., HNO₃) can etch rates of up to several thousand nm·s⁻¹ be achieved. The characteristic feature of etching Si in HF/HNO₃ mixtures is the occurrence of an induction period, which lasts up to several seconds. The end of the induction period is usually indicated by a massive etch attack and is accompanied by a massive formation of gaseous products. Which reactions occur during the induction period are still unknown, however, the major outcome of the induction period is a more or less massive etch attack and is accompanied by a massive formation of gaseous products. Which reactions occur during the induction period are still unknown, however, the major outcome of the induction period is a more or less massive formation of intermediary highly reactive N (III) species, which determine the etching process significantly and cause the high etch rate after the end of the induction period. It arises the question for the reactive species that first initiates a reaction between Si and nitric acid in freshly prepared HF/HNO₃ mixtures.

Robbins and Schwartz already assumed that undissociated nitric acid, that is the HNO₃ species, was the reactive species for the oxidation of Si in the HF/HNO₃ system. First systematic studies on the kinetics of oxidation by nitric acid were carried out by Berg, who determined the dissolution rate of copper into nitric acid at different concentrations. Berg attributes the oxidizing effect to the dissolution of copper solely to undissociated nitric acid, following the work of Briner. In addition, Berg, for the first time, established an experimentally proven kinetic relationship in which the dissolution rate of copper is linearly related to the concentration of undissociated nitric acid in a first order reaction.

In his work, Berg derived the concentrations of undissociated HNO₃ from the data of various authors. However, these authors assumed that HNO₃ only dissociates to H₃O⁺ and NO₃⁻ (Equation 1).

\[
\text{HNO}_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- \tag{1}
\]

Recent Raman spectroscopic investigations on the dissociation of nitric acid by Irish and Puzic showed that the signal of the nitrate ion at 1,046 cm⁻¹ is asymmetrically broadened at a concentration of about 3 mol·L⁻¹ and above. The asymmetric widening was attributed to the presence of an ion pair (H₂O⁺·NO₃⁻). A further signal from a concentration of 4 mol·L⁻¹ is observed at 968 cm⁻¹, which is assigned to undissociated nitric acid. Based on these findings, they formulated the equilibria of the individual species in the solution, as shown in Figure 1.

Based on the works of Irish and Puzic and Potier et al., Hlushak et al. [18,20,21] deconvoluted the Raman spectra in the range of 900...1,100 cm⁻¹ with three Gaussian-Lorentz functions. One band at 1,046 cm⁻¹ ± 2 cm⁻¹ was assigned to the nitrate ion, another band at 1,024 cm⁻¹ ± 12 cm⁻¹ to the ion pair (H₂O⁺·NO₃⁻), and another band at 961 cm⁻¹ ± 8 cm⁻¹ to the undissociated nitric acid. They derived a polynomial from a plot of the signal area of the nitrate ion band over the total concentration of nitric acid that describes the relationship between the degree of dissociation and the concentration of nitric acid. Levanov et al. determined the dissociation constant of nitric acid by a signal deconvolution of the Raman spectra in the same wave number range into three Voigt profiles and determined the activity coefficients in a concentration range of 0–18 mol·L⁻¹.

This results to the following formulation for the degree of dissociation, \(\alpha\), of nitric acid (Equation 2)

\[
\alpha = \frac{c_{\text{NO}_3^-} + c_{\text{H}_2\text{O}^+\cdot\text{NO}_3^-}}{c_{\text{HNO}_3}} \tag{2}
\]

with \(c_{\text{NO}_3^-}\) as the concentration of nitrate ions, \(c_{\text{HNO}_3}\) as the concentration of the nitric acid submitted, and \(c_{\text{H}_2\text{O}^+\cdot\text{NO}_3^-}\) as the concentration of the ion pair. The concentration of undissociated nitric acid, \(c_{\text{HNO}_3}\), is the difference between the initial concentration and the dissociated fraction described by the nitrate concentration and the concentration of the ion pair (Equation 3).

\[
c_{\text{HNO}_3} = c_{\text{HNO}_3} - \left(c_{\text{H}_2\text{O}^+\cdot\text{NO}_3^-} + c_{\text{NO}_3^-}\right) \tag{3}
\]

Using the known dissociation degree according to Equation 2, the concentration of undissociated nitric acid can be calculated from Equation 4.

\[
c_{\text{HNO}_3} = c_{\text{HNO}_3}(1 - \alpha) \tag{4}
\]
on the concentration of nitric acid. However, it is not advantageous to compensate the time-dependent signal drift of a typical Raman spectrometer by adding an internal standard to concentrated HF/HNO₃/H₂SiF₆ acid mixtures. A repeating measurement of an external standard (e.g., CCl₄[21]) is, in principle, possible, however, less applicable for continuous measurements, such as online etch bath monitoring and should, therefore, be avoided.

Consequently, the method of Levanov and Hlushak[20–22] was extended to determine the degree of dissociation of nitric acid in HF/HNO₃/H₂SiF₆ acid mixtures of unknown nitric acid concentration and the influence of HF and H₂SiF₆ on the degree of nitric acid dissociation. The total nitric acid content in such acid mixtures can be determined, for example, by ion chromatographic determination of the nitrate content in highly diluted aliquots. Knowing this, the concentration of undissociated nitric acid can be calculated, which is essential for a kinetic description of the etching reaction, which is still pending today.

2 | EXPERIMENTAL

2.1 | Chemicals, acids

Etch mixtures were prepared by mass dilution from analytical grade acids (hydrofluoric acid, HF 48 %[w/w] and nitric acid, HNO₃, 69 %[w/w], both from Merck, Darmstadt, Germany; hexafluorisilicic acid, H₂SiF₆, 45 %[w/w] from Fluorchemie Dohna, Dohna, Germany). All experiments were carried out at room temperature. All concentrations are defined as the quotient of the molar amount of the component i, nᵢ, and the total mass of the solution, m (Equation 5). According to,[23,24] this quotient is considered as specific partial quantity qᵢ having the unit mol·kg⁻¹.

\[ qᵢ = \frac{nᵢ}{m} \]  

5

2.2 | Raman spectroscopy

Raman spectra from the concentrated etch mixtures were recorded in the range from 2,500 to 230 cm⁻¹ using a DRX SmartRaman (ThermoFisher Scientific) equipped with a 532-nm excitation laser at 10-mW laser energy and a grating with a resolution of 5 cm⁻¹. Single use UV semi-micro cuvettes (d = 10 mm, 220–900 nm; Brand GmbH + Co KG, Wertheim, Germany) were found to be the most resistant against the etch mixtures. The signals were assigned as shown in Table 1.

| Species        | Wave numbers observed (cm⁻¹) | Wave numbers literature (cm⁻¹) | Vibration mode |
|----------------|------------------------------|---------------------------------|----------------|
| HNO₃           | 640[25]                      | 688[26,27]                      | δrocking(NO₂)  |
|                | 930[28,29]                   | 957                            | νs(NO₂)        |
|                | 1305[29]                     | 1,558[25]                      | 2x δOOP        |
| NO₃⁻           | 722[25]                      | 1,048[27,29]                   | ν(N-O)         |
|                | 1,036[30,31]                 | 1,036[18]                      | ν(N-O)         |
| H₂O⁺-NO₃⁻      | 1,036[20,29]                 | 1,046[25]                      | ν(N-O)         |
|                | 1,288[32]                    | 1,288[33]                      | νs(NO₂)        |
| N₂O₃           | 627[32]                      | 784                            | νwag(NO₂)      |
|                | 1,328[32]                    | 1,328[33]                      | νs(NO₂)        |
| N₂O₄           | 810[27]                      | 810[32]                        | δbending(NO₂)  |

FIGURE 2 Typical Raman spectrum of a HNO₃ solution (45% [w/w]), signal deconvolution with peak positions given in Table 1. Inset: Interferences of signals in an HF/HNO₃/H₂SiF₆ etch mixture in the range of 770–580 cm⁻¹ [Colour figure can be viewed at wileyonlinelibrary.com]
2.3 | Data evaluation

Figure 2 shows a typical Raman spectrum of a semi-concentrated nitric acid solution. The wave number ranges of 1,150...900 cm\(^{-1}\) and 750...600 cm\(^{-1}\) were deconvoluted into four individual signals with Voigt profiles.

The baseline-corrected signal areas for the Raman band of the symmetric N-O stretching vibration in the nitrate ion at 1,048 cm\(^{-1}\) with a full width of half maximum of 6.5...7.5 cm\(^{-1}\) and the N-OH stretching vibration in the molecule of undissociated nitric acid at 957 cm\(^{-1}\) (full width of half maximum = 40...45 cm\(^{-1}\)) are used to determine the degree of dissociation. The wave number range of 600...750 cm\(^{-1}\), which also contains the signals of HNO\(_3\) and NO\(_3^-\), is interfered by overlapping with the Si-F stretching vibration of the reaction product H\(_2\)SiF\(_6\) at 656 cm\(^{-1}\).[29] The HNO\(_3\) band at 1,305 cm\(^{-1}\) is also unsuitable for evaluation, despite its higher intensity, because it interferes with the signals of N\(_2\)O\(_3\) (1,288 cm\(^{-1}\)) and NO\(_2^-\) (1,328 cm\(^{-1}\)).[32] Signals of other reaction products, such as N\(_2\)O\(_4\), at 265 cm\(^{-1}\) or 810 cm\(^{-1}\) and (N\(_2\)O\(_4\))\(^+\) at 2,246 cm\(^{-1}\), do not interfere within the wave number range selected.[27]

3 | RESULTS

3.1 | Procedure to determine the degree of dissociation of HNO\(_3\)

The degree of dissociation of HNO\(_3\) in the concentration range 1...69% [w/w] was determined by Raman spectroscopy, based on the method presented by Levanov and Hlushak.[20-22] This method is based on the analysis of the baseline-corrected signal areas of the deconvoluted signals for the nitrate ion at 1,048 cm\(^{-1}\) and the ion pair (H\(_2\)O\(^+\)-NO\(_3^-\)) at 1,034 cm\(^{-1}\). The sum of the two signal areas is plotted over the total concentration of the HNO\(_3\) to determine the degree of dissociation of the nitric acid. In that case, if the area is linear to the nitrate concentration \(c_{\text{HNO}_3} < 1.8 \text{ mol·kg}^{-1}\), the nitric acid is completely dissociated, and the peak area measured \(A_{\text{measured}}\) is equal to the peak area extrapolated. This concentration range was used to determine a calibration coefficient \(k\) that is the slope of the linear relationship in Equation 6.

\[
A_{\text{measured}} = (c_{\text{NO}_3^-} + c_{\text{H}_2\text{O}^+\text{-NO}_3^-}) \cdot k \tag{6}
\]

If the nitric acid concentration increases continuously, \(A_{\text{measured}}\) is smaller than the peak area extrapolated \((c_{\text{HNO}_3} \cdot k)\). This relationship results from the association of nitrate ions with protons. The degree of dissociation can be calculated from Equation 7.

\[
\alpha = \frac{A_{\text{measured}}}{c_{\text{HNO}_3} \cdot k} \tag{7}
\]

The degree of dissociation thus determined is graphically shown in Figure 3 in the concentration range up to 69% [w/w] nitric acid.

Figure 3 compares the results obtained in this study with the values of Levanov,[22] Berg,[10] and Hlushak.[20] Even without considering the ion pair, the degrees of dissociation used by Berg show only minor deviations. The linear correlation between the dissolution rate of copper and the concentration of undissociated HNO\(_3\) by Berg[10] is an indication of the validity of the theory that HNO\(_3\) is the species in the rate determining step in the dissolution of copper.

The method developed in this work is based on the evaluation of the baseline-corrected peak areas of the Raman signals of the undissociated HNO\(_3\) at 957 cm\(^{-1}\), \(A_{\text{HNO}_3}(957 \text{ cm}^{-1})\), and the nitrate ion at 1,048 cm\(^{-1}\), \(A_{\text{NO}_3^-}(1,048 \text{ cm}^{-1})\). These were determined anew, because the peak areas of these signals are not published as a function of the nitric acid concentrations. The degrees of dissociation calculated are shown in Figure 3. The ratio of the signal areas, \(R\), is calculated from the baseline-corrected peak areas obtained, according to Equation 8.

\[
R = \frac{A_{\text{HNO}_3}(957 \text{ cm}^{-1})}{A_{\text{NO}_3^-}(1,048 \text{ cm}^{-1})} \tag{8}
\]

The peak area ratios determined for different nitric acid concentrations and the corresponding degrees of dissociation show the correlation plotted in Figure 4. Its empirical mathematical description is given by Equation 9.

![Figure 3](https://wileyonlinelibrary.com)
This empirical formula is valid for the value range \(0.15 \leq \alpha \leq 0.95\).

\[\alpha(R) = K_1 \cdot e^{-\frac{R}{k_1}} + K_2 \cdot e^{-\frac{R}{k_2}} \]  

(9)

with

\[K_1 = 0.521 \pm 0.020; \quad k_1 = 0.192 \pm 0.009;\]
\[K_2 = 0.425 \pm 0.021; \quad k_2 = 1.85 \pm 0.16\]

Using Equation 9, the degree of dissociation of nitric acid in HF/HNO\(_3\)/H\(_2\)SiF\(_6\) acid mixtures of unknown nitric acid concentration can be obtained if the baseline-corrected peak area ratio for these mixtures has been determined previously. However, the determination of the undissociated nitric acid via the band at 957 cm\(^{-1}\) is only possible from a content of 18\%[w/w] HNO\(_3\), because the intensity of the band clearly differs from the corrected background only from this content. Therefore, the upper limit of \(\alpha = 0.95\) was chosen. At this value, the relative uncertainty of \(\alpha\) is about 2%. The determination is carried out with a relative uncertainty of 10% or lower up to a peak ratio of about 1.3 and a resulting degree of dissociation of \(\alpha = 0.21\). At the lower limit of the value range, which is given by the highest experimentally measured value (w [HNO\(_3\)] = 69\%, \(R = 1.98, \alpha = 0.15\)), a result uncertainty of about 15% must be expected.

The total concentration of nitric acid in the acid mixture must be known in order to obtain the concentration of undissociated nitric acid in HF/HNO\(_3\)/H\(_2\)SiF\(_6\) acid mixtures. Only in the case of freshly prepared acid mixtures is this value known from the initial concentration of the nitric acid. In acid mixtures of unknown composition, that is after a longer etching process, the total nitrate content has to be determined, for example, by ion chromatographic measurement in high dilution, typically with factors between 2,000 and 10,000.\(^{[35]}\) The nitrate concentration determined in such highly diluted solutions corresponds to the total concentration of nitric acid, according to Equation 10.

\[c_{NO_3^−} = c_{0,HNO_3}\]  

(10)

Thus, the concentration of undissociated nitric acid in any HF/HNO\(_3\)/H\(_2\)SiF\(_6\) acid mixtures can be determined via Equation 3.

3.2 Application to etching mixtures of the HF/H\(_2\)SiF\(_6\)/HNO\(_3\) system

The degree of dissociation of nitric acid in binary and ternary mixtures with HF and H\(_2\)SiF\(_6\) can be determined using the method described. Figure 5 shows the dependence of the degree of dissociation of HNO\(_3\) on the HF content (left) and the H\(_2\)SiF\(_6\) content (right) in binary mixtures.

An increase in the HF or H\(_2\)SiF\(_6\) concentration at a constant HNO\(_3\) concentration leads to a decrease in the degree of dissociation of HNO\(_3\). At a HNO\(_3\) concentration of 5 mol·kg\(^{-1}\), the degree of dissociation decreases almost linearly with increasing HF content. This is the case in a mixture with H\(_2\)SiF\(_6\) at a HNO\(_3\) concentration of 6 mol·kg\(^{-1}\). The graphs are negatively curved with increasing HF or H\(_2\)SiF\(_6\) content at lower HNO\(_3\) concentrations. If the HNO\(_3\) concentration is higher than 5 mol·kg\(^{-1}\) (HF) or 6 mol·kg\(^{-1}\) (H\(_2\)SiF\(_6\)), the curvatures are positive.

Regarding the binary mixtures, both acids HF and H\(_2\)SiF\(_6\), each reduce the degree of dissociation of the nitric acid. This reduction for HF is significantly smaller for the same HNO\(_3\) concentrations due to the lower acid strength of HF (pKa = 3.16)\(^{[36]}\) than for H\(_2\)SiF\(_6\), whose acidity corresponds approximately to that of H\(_2\)SO\(_4\).\(^{[37]}\)

This tendency also continues in the ternary acid mixtures in Figure 6. The composition range of typical acidic etching mixtures is covered with an HNO\(_3\) concentration of 4 mol·kg\(^{-1}\) (25\%[w/w]), HF concentrations between 1.5 and 3.5 mol·kg\(^{-1}\) (3–7\%[w/w]) and H\(_2\)SiF\(_6\) concentrations between 0.2 and 1.3 mol·kg\(^{-1}\) (3–19\%[w/w]).

The increase of the H\(_2\)SiF\(_6\) concentration again shows a significantly stronger impact on the degree of dissociation than a change in the HF content. However, the functions do not show exactly the same curvature. It is, therefore, not straightforward to develop an empirical
A very interesting relationship is obtained if the degrees of dissociation of the differently concentrated HNO₃ of the binary mixtures (HF/HNO₃; H₂SiF₆/HNO₃) and the ternary mixtures (HF/H₂SiF₆/HNO₃) are plotted over the total water content of the respective mixture (Figure 7). The resulting plot shows that the degree of dissociation of the HNO₃ is essentially dependent on the concentration of the water in the acid mixture in a first approximation.

The resulting empirical relationship between the water concentration and the degree of dissociation is given by Equation 11.

$$\alpha = a \cdot q_{H_2O}^4 + b \cdot q_{H_2O}^3 + c \cdot q_{H_2O}^2 + d \cdot q_{H_2O} + e$$

with

$$a = (3.54 \pm 2.01) \times 10^{-6} \text{ kg}^4 \cdot \text{mol}^{-4};$$
$$b = (-5.28 \pm 2.83) \times 10^{-3} \text{kg}^3 \cdot \text{mol}^{-3};$$
$$c = (0.0275 \pm 0.0149) \text{kg}^2 \cdot \text{mol}^{-2};$$
$$d = (-0.551 \pm 0.343) \text{kg} \cdot \text{mol}^{-1}; \quad e = 3.65 \pm 2.95$$

This dependence provides a useful approach for a simplified kinetic description of the etching reaction. The influence of the concentrations of HF and H₂SiF₆ on the concentration of undissociated HNO₃ (Equation 4) in a formalized kinetic model can now be simplified, described by the water content of the acid mixture.
A method for the Raman spectroscopic determination of the degree of dissociation of HNO₃ in HF/HNO₃/H₂SiF₆ acid mixtures was developed. This method is based on the determination of the peak area ratio of the Raman signals of the undissociated HNO₃ at 957 cm⁻¹ and the nitrate ion at 1,048 cm⁻¹. The degree of dissociation of nitric acid in each acidic mixture can be calculated by means of an empirical correlation between the peak area ratios and the degree of dissociation. The only preconditions are that the Raman bands required for the determination of the peak ratio (a) are not interfered with by other Raman bands and (b) have sufficient intensities. The concentration of undissociated nitric acid is obtained either by knowing the initial content of nitric acid or after the determination of the total nitrate concentration by ion chromatography, as in highly diluted etch solutions.

The impact of HF or H₂SiF₆ on the dissociation of nitric acid is basically correlated to the dissociation strength of the two acids. However, it could be shown that the degree of dissociation of HNO₃ in the ternary etch mixtures is a function of the total water content in the respective mixtures (Figure 7), providing a simplified approach for a later formalized kinetic description of the etch reaction.

The method presented can be applied independently on the Raman device used and without the use of internal or external standards to compensate for the typical device drift. This provides a further important parameter for characterizing acid etching mixtures, which can be continuously determined and used as an instrument for controlling etching baths in industrial production lines for the manufacture of solar cells.

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How to cite this article: Langner T, Rietig A, Acker J. Raman spectroscopic determination of the degree of dissociation of nitric acid in binary and ternary mixtures with HF and H₂SiF₆. J Raman Spectrosc. 2020;51:366–372. https://doi.org/10.1002/jrs.5769