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Titrimetric determination of silicon dissolved in concentrated $HF–HNO_3$-etching solutions

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Abstract

The wet chemical etching of silicon by concentrated $HF–HNO_3$ mixtures in solar and semiconductor wafer fabrication requires the strict control of the etching conditions. Surface morphology and etch rates are mainly affected by the amount of dissolved silicon, that is continuously enriched in the etching solution with each etching run. A fast and robust method for the titrimetric determination of the total dissolved silicon content out of the concentrated etching solution is presented. This method is based on the difference between the two equivalence points of the total amount of acid and the hydrolysis of the hexafluorosilicic anion. This approach allows a silicon determination directly from the etching process in spite of the presence of dissolved nitric oxides in the etching solution. The influences of different acid mixing ratios and of the etching solution density depending on the silicon content is considered and discussed in detail.
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Keywords: $HF–HNO_3$-etching mixtures; Isotropic etching; Potentiometric titration; Silicon; H_2SiF_6

1. Introduction

Isotropic wet chemical etching of silicon by $HF–HNO_3$ acid mixtures is an essential step in the processing of semiconductor and solar grade silicon. The dissolution of silicon is described by the following net equation (according to ref. [1]):

$$3Si + 18HF + 4HNO_3 \rightarrow 3H_2SiF_6 + 4NO + 8H_2O. \quad (1)$$

Main applications are the removal of surface roughness of wafers after slicing from silicon ingots (saw damage) and the texturing of silicon wafer surfaces for solar cells.

In practice, etching solutions of varying acid contents are used. In order to obtain a certain etch rate or texturing effect either freshly prepared mixtures from concentrated acids are diluted with water or already used etching solutions are refreshed several times by the addition of concentrated acids. The challenge is to find the optimum compromise between maximum utilization of the etching mixtures and economically reasonable etching rates. Among other parameters like the acid concentrations, acid mixing ratio, and temperature, the content of dissolved silicon affects mainly the etching rate. Therefore, fast and precise determination of the silicon in the etching solution independently on the acids contents is required for technical application.

From the analytical point of view, the acids act as a heavy matrix that prevents or complicates the analysis as in the case of the photometric determination of H_2SiF_6 as silicomolybdic acid [2], which is applicable only for low silicon contents up to 0.3% H_2SiF_6 in HF. A silicon determination by AAS [3,4] requires a time consuming calibration and several dilution steps of the concentrated samples. The methods based on precipitation of K_2SiF_6 and subsequent titration of the acid and later of K_2SiF_6 are time consuming as well and affected by the efficiency of K_2SiF_6 precipitation (e.g. in organic solvents or in the cold) [5–7].

The present paper describes a robust determination of silicon by potentiometric titration in synthetic $HF–HNO_3$-

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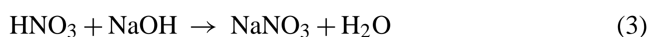
etching solutions regardless of the concentrations of HF and HNO_3 and their mixing ratio. The H_2SiF_6 content can be obtained for any etching solution, which is unsaturated with respect to silicon according to Eq. (1).

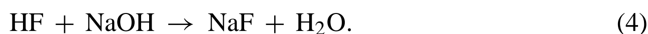
The titration of complex acid mixtures is characterized by an overlap of the equivalent points. As a general rule, pK_s values for two acids should differ more than four units to separate their equivalence points by titration [8]. Potentiometric titration of HF–HNO_3-mixtures yields only to a single equivalence point due to the close pK_s values of 3.17 at 20 °C for HF [9] and −1.34 at 30 °C for HNO_3 [9]. In HF–HNO_3-mixtures containing dissolved silicon after etching, silicon is present as dissociated species of H_2SiF_6. H_2SiF_6 has a complex and widely unresolved speciation [10]. H_2SiF_6 is considered as a strong acid comparable to sulphuric acid. The second dissociation constant $pK_{s,2}$ is estimated as 0.22 [10].

The titration of all the mentioned acids according to the net simplified Eqs. (2)–(4) in one mixture should result in a common, irresolvable equivalence point.

$$H_2SiF_6 + 2NaOH \rightarrow Na_2SiF_6 + 2H_2O \quad (2)$$



$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O \quad (3)$$



$$HF + NaOH \rightarrow NaF + H_2O. \quad (4)$$

In the second step, the hexafluorosilicic ion reacts with NaOH under formation of silicid acid at a pH around 8 [11].

$$Na_2SiF_6 + 4NaOH \rightarrow Si(OH)_4 + 6NaF. \quad (5)$$

2. Experimental

HF–HNO_3-acid mixtures were prepared from analytical grade acids (HF 40% (w/w), HNO_3 65% (w/w), Merck, Darmstadt, Germany). Pieces of p-type silicon wafers (4 in. diameter, polished, 675 μm thickness; Silchem GmbH, Freiberg, Germany) were slowly dissolved in 50 mL of a mixture of 70% (v/v) HF and 30% (v/v) HNO_3 at 1 °C. During dissolution the reaction vessels were covered with a Teflon cap. Immediately after dissolution of the silicon, the etching solution was warmed within 20 min to a temperature of 20 °C. For titration, 0.5–1 mL aliquotes were pipetted and diluted with water to a total volume of 60 mL. For time dependent studies, all samples were produced and stored in high density polyethylene (HDPE) bottles with screwtop.

The densities of the silicon containing acid mixtures were determined by weighing (AT 200, Mettler-Toledo AG, Schwerzenbach, Switzerland) the mass of five defined volumes (ranging from 1 to 3 mL with a precision of ± 0.3%) of the carefully thermostatted samples of each mixture. For comparing titration studies, a stock solution of $(NH_4)_2SiF_6$ (99.999%, Alfa Aesar, Karlsruhe, Germany) was prepared by dissolution of 2.7774 g in 500 mL deionised water (18 MΩ, Seral, Ransbach-Baumbach, Germany). For titration 0.35 mL 40% (w/w) HF, 0.15 mL 65% (w/w) HNO_3 and 8–40 mL stock solution were pipetted into a polyethylene titration vessel and diluted with water to a total volume of 60 mL.

Table 1
ICP-OES measuring conditions

Generator power (W)	1150
Ar plasma flow ($L\,min^{-1}$)	16
Ar auxiliary flow ($L\,min^{-1}$)	0.5
Ar nebulizer pressure (MPa)	0.2
Maximum integration time (s)	Low wavelength range 15 s; high wavelength range 15 s
Sample rinsing time (s)	60
Washing time (s)	15
Pump rate ($mL\,min^{-1}$)	1.85
Repeating measurements	4

Titrant is 0.5 or 1 mol L^{-1} NaOH (Titrisol, Merck). The titer of this solution was steadily determined by titration of 1 mol L^{-1} HCl (Titrisol, Merck). The titrations were performed by computerized titrator of the type DL 70 using a HF resistant electrode InLab 429 (Mettler-Toledo AG) for pH measurements. The maxima of the first derivative of titration curve were used as equivalence points.

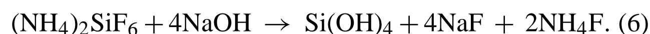
For comparison, the silicon content of the samples was determined by ICP-OES (IRIS, Thermo Jarrell Ash Corp., Franklin, MA, USA) equipped with a HF resistant spray chamber and concentric nebulizer. The measuring parameters are summarized in Table 1. The samples were diluted to a total acid concentration of 3% (v/v) HF for one series and with a NaOH concentration of 0.05 mol L^{-1} for the other series. The results for both series agree within 1.5% R.S.D.

3. Results and discussion

3.1. Titration of HF–HNO_3–$(NH_4)_2SiF_6$ solutions

The complex behavior of HF–HNO_3 mixtures after dissolution of Si can be approached by titration of HF–HNO_3 mixtures of known acid concentrations with defined volumes of a $(NH_4)_2SiF_6$ stock solution added to. Using synthetic HF–HNO_3–$(NH_4)_2SiF_6$ mixtures the titration of the HF and HNO_3 protons is clearly separated from the titration of the hexafluorosilicate anion in the titration curve.

The titration curves show two equivalence points (Fig. 1). The titrant volume of the first equivalence point is independent on the silicon concentration in the solution and represents exclusively the sum of protons of HF and HNO_3 according to Eqs. (3) and (4). The titrant volume at the second equivalence point increases linearly with the silicon concentration as described by Eq. (6):



$$(NH_4)_2SiF_6 + 4NaOH \rightarrow Si(OH)_4 + 4NaF + 2NH_4F. \quad (6)$$

Therefore, the volume difference between the first and the second equivalence point is a measure of the silicon content in the acid mixtures as demonstrated in Fig. 2. The slope of the straight line amounts to 4.04 ± 0.02 representing the stoichiometry of Eq. (6).

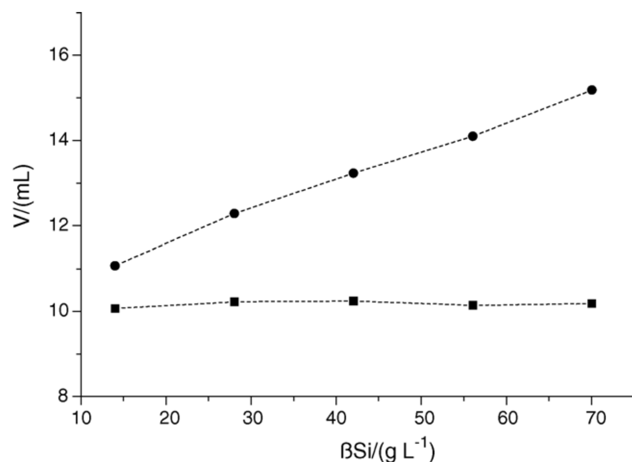


Fig. 1. Titration series of mixtures consisting of 0.35 mL 40% (w/w) HF, 0.15 mL 65% (w/w) HNO_3, and varying Si content, added as $(NH_4)_2SiF_6$, titrated with $1\,mol\,L^{-1}$ NaOH. Titrant volume at the first (■) and second (●) equivalence point.

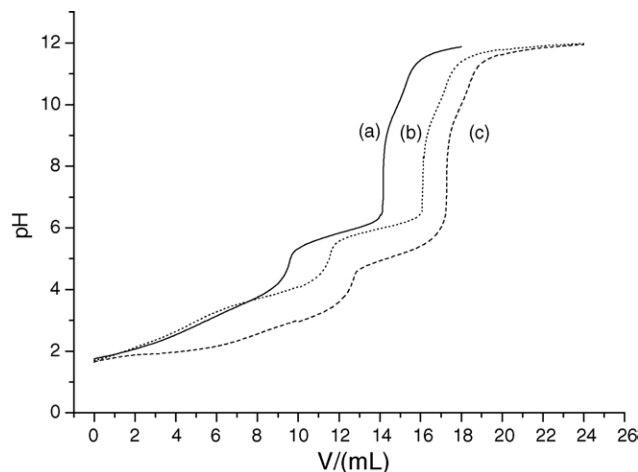


Fig. 3. Titration of synthetic etching solutions with $0.5\,mol\,L^{-1}$ NaOH. (a)One milliliter synthetic etching solution (2.1094 g silicon dissolved in an acid mixture of initially 35 mL 40% (w/w) HF and 15 mL 65% (w/w) HNO_3); (b) with 1 mL $1\,mol\,L^{-1}$ HF added to (a); (c) with 1.5 mL $1\,mol\,L^{-1}$ HNO_3 added to (a).

3.2. *Titration of synthetic HF–HNO$_3$-etching solutions with known silicon content*

A typical titration curve of a synthetic etching solution is shown as trace (a) in Fig. 3. The presence of dissolved silicon results in a strongly asymmetric curve with two separated equivalent points. The addition of either HF ((curve b) in Fig. 3) or HNO_3 ((curve c) in Fig. 3) shifts both equivalence points linearly to a higher titrant volume according to the amount of added acid.

In Fig. 4, the titrant volume of $1.0\,mol\,L^{-1}$ NaOH at the first and second equivalence points, respectively, is shown for a series of initially 70% (v/v) HF and 30% (v/v) HNO_3 with increasing silicon content. The first equivalence point is continuously shifted to lower titrant volumes due to the consumption of free acid by the dissolution of silicon according to Eq. (1). The titrant volume at the second equivalence point increases slightly with increasing silicon content and drops suddenly around $74\,g\,L^{-1}$ Si when the maximum solubility with respect to Eq. (1) is reached. This drop, which is less pronounced for the first equivalence point, arises from the full consumption of HF in the etching solutions. At maximum saturation, the mixture of 70% (v/v) HF and 30% (v/v) HNO_3 contains a slight excess of HNO_3. Any excess of HNO_3 oxidizes silicon formally to SiO_2 which is subsequent very slowly dissolved by H_2SiF_6 [12]. The drop in the density of such over-saturated solutions (Fig. 5) may origin from the loss of HF hydrogen bridge bonds in the etching solution that leads to an increase of the volume.

As a second feature, the titration curves of HF–HNO$_3$-etching solutions exhibit a complex time dependency. Fig. 6

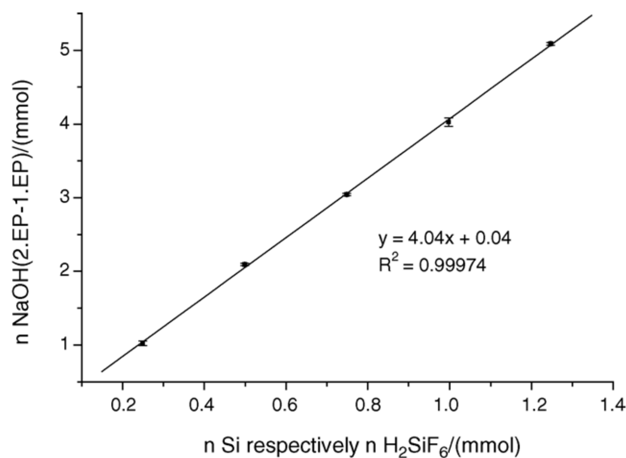


Fig. 2. Plot of the molar amount of silicon ($(NH_4)_2SiF_6$) added to the HF–HNO$_3$ acid mixture vs. the titrated molar amount of NaOH derived from the difference between the equivalence points (EP: equivalence point). The molar amounts are referred to 1 mL etching solution.

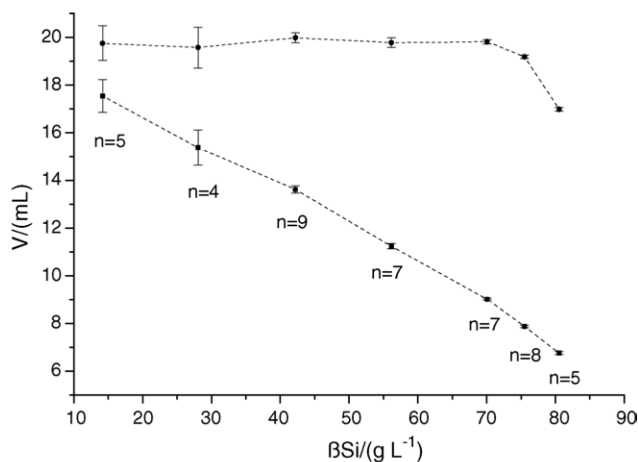


Fig. 4. Titrant volume of $1.0\,mol\,L^{-1}$ NaOH at the first (■) and second (●) equivalence points as function of the mass concentration of silicon. The plot covers titrations carried out immediately after preparation as well as time-dependent titrations continued up to 10 days after preparation ($P = 0.95$).

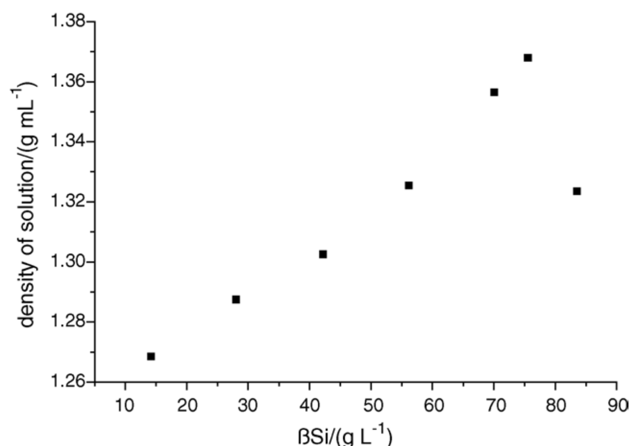


Fig. 5. Densities of synthetic etching solutions of initially 35 mL 40% (w/w) HF, 15 mL 65% (w/w) HNO_3, and different amounts of dissolved Si.

shows a shift for the titrant volume of both equivalence points to higher volumes by ageing, however, the difference between the equivalent points remains unchanged. This aging effect causes the wide confidence intervals for low silicon contents in Fig. 4. It had been found that the shifts of equivalence points are caused by the aging of the etching solution, in which dissolved nitrogen oxides (giving a yellow to brown color to the solution) are partially converted into nitric acid. An increase of the nitrate ion concentration during the aging period was proven by ion chromatography [13].

Fig. 7 represents the titration of synthetic mixtures of varying silicon content which were titrated between four and nine times each within a period of 10 days. The narrow confidence intervals, calculated for $P = 0.95$, proves the reaction of $[SiF_6]^{2-}$ with 1.0 mol L^{-1} NaOH (volume between first and second equivalence point) as time independent. The slope of 4.40 ± 0.03 in Fig. 7, which significantly deviates from the

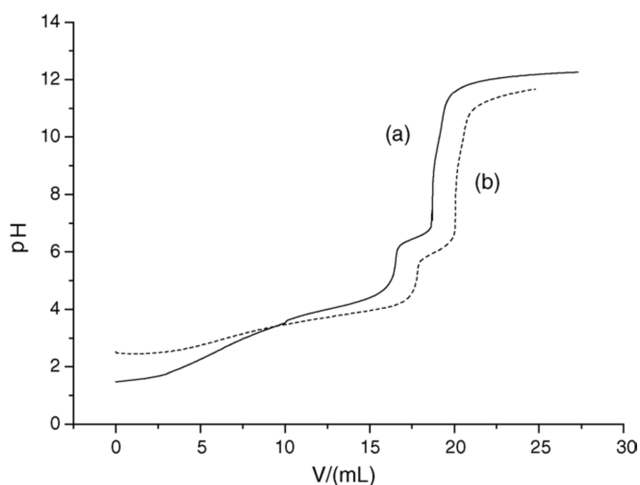


Fig. 6. Titration curves of 1 mL synthetic etching solution (0.7073 g silicon dissolved in an acid mixture of initially 35 mL 40% (w/w) HF and 15 mL 65% (w/w) HNO_3) with 1.0 mol L^{-1} NaOH: (a) immediately after preparation and thermostating and (b) 3 days after preparation and storage at room temperature.

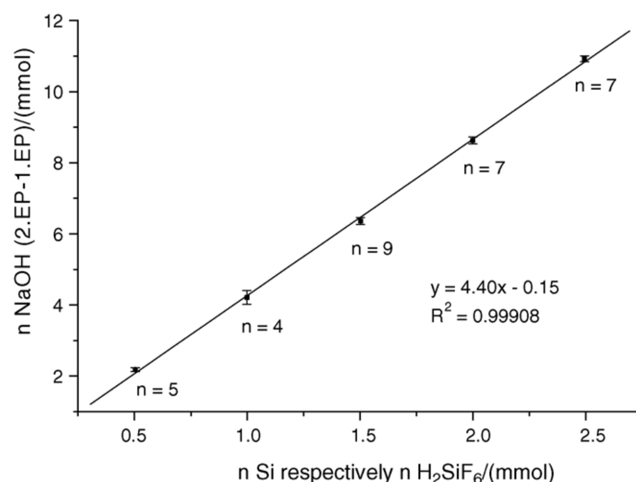


Fig. 7. Plot of the molar amount of silicon dissolved in the HF–HNO_3 acid mixture vs. the titrated molar amount of NaOH derived from the difference between the equivalence points (EP: equivalence point). The molar amounts are referred to 1 mL etching solution.

stoichiometry of Eq. (5) is caused by increasing densities of the etching solution as function of the amount of dissolved silicon (Fig. 5). Pipetting a constant volume of etching solutions with increasing silicon content results a rising deviation in the expected stoichiometry.

The effect of density on the analytical results is avoided by comparing the results between titration and ICP-OES, in which the influence of the density is cancelled out (Fig. 8). Then, the slope of 3.97 ± 0.02 agrees with the expected stoichiometry of 4 according to Eq. (5) and proves therefore the applied procedure of titrimetric silicon determination.

The slope of 4.40 ± 0.03 can be considered as an applicable calibration curve for etching solutions with unknown acid contents (Fig. 7). This curve was used to determine the silicon content of other synthetic silicon-acid mixtures of different HF–HNO_3 ratios and known silicon content. Table 2

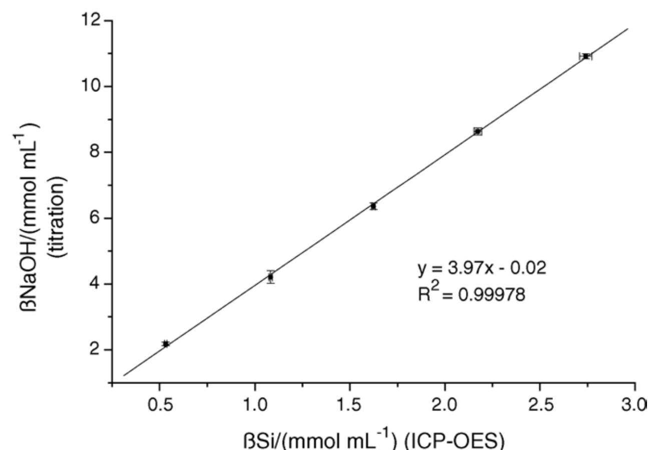


Fig. 8. Plot of the molar amount of titrated NaOH vs. the molar concentration of Si determined by ICP-OES. The confidence intervals ($P = 0.95$) of the titration with NaOH are taken from Fig. 7 for the ICP-OES measurements calculated for $n = 8$.

Table 2
Recovery of the silicon content by the titration method for synthetic etching mixtures of varying HF–HNO_3 ratios and known silicon content

β-Si ($g\,L^{-1}$) given	HF_c (initial mixture) (%, v/v)	HNO_{3c} (initial mixture) (%, v/v)	β-Si ($g\,L^{-1}$) calculated	Recovery (%)
53.9	70	30	53.2	98.7
16.3	30	70	16.0	98.2
32.2	60	40	32.7	101.6
21.4	40	60	21.4	100.0
27.0	50	50	26.5	98.2

shows that a sufficient silicon recovery for these solutions is yielded even for varying HF–HNO_3 ratios and therefore varying densities.

As a consequence, the calibration is independent on ageing and sufficiently independent on the density of all studied silicon–acid mixtures solution.

By weighting sample aliquots results independent of density were obtained. In this case, the plot of molar amount Si versus molar amount NaOH shows a slope of 4.06 ± 0.03 (linear fit equation $y = 4.06x + 0.06$, $R^2 = 0.99954$; cf. Fig. 7). In practice, the time-saving volume sampling was preferred.

4. Conclusions

A potentiometric titration method for the determination of total silicon content in HF–HNO_3-etching solutions is presented. After establishing a calibration curve, the silicon content can be determined independently on the HF–HNO_3 mixing ratio, i.e. independently on the density, and on the state of aging of the mixture. The method is applicable only at silicon contents equal or below the theoretical maximum solubility according to Eq. (1). This method provides a fast analysis of unknown etching solutions within 30 min.

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