Etching Mechanism of Vitreous Silicon Dioxide in HF-Based Solutions

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Received October 25, 1999

Abstract: A reaction mechanism is proposed for the dissolution process of silicon dioxide networks in aqueous HF-based solutions. Etch experiments with thermally grown silicon dioxide were used to create a model for the etch process. Literature data on the etching of other vitreous silicon dioxide materials were used to refine the model. A new method, using a quartz microbalance, is used to monitor the etch rate in situ and to establish the reactive species. The first reaction step determines the rate of the etch process. It is the substitution of a surface SiOH group, which is bonded to three bridging oxygen atoms, by an SiF group. Due to an acid/base equilibrium reaction of the silanol groups on the surface with its protonated and deprotonated forms, the substitution reaction rate is pH dependent. At low pH (<1.5) water is eliminated from the protonated silanol group and an HF_2^- ion or an H_2F_2 molecule supplies an F^- that binds to the positively charged silicon atom. At higher pH values (>1.5), the elimination of an OH^- group from the SiO_2 surface becomes the major reaction route. Once the OH^- group is eliminated, an HF_2^- molecule supplies an F^- ion. The pK_a value of the deprotonation reaction increases due to the buildup of surface charge at pH > 4. Consequently, the SiOH surface concentration and the etch rate are higher than expected from a simple acid/base equilibrium reaction. All subsequent reaction steps to remove the Si−F unit from the SiO_2 matrix are fast reaction steps (18−20 times faster) involving HF_2^- addition reactions on F_xSi−O bonds. Using this reaction model, published etch rate data of multicomponent glasses can be understood. Metal ions in glass break up the SiO_2 network and create Si atoms bonded to less than four bridging oxygen atoms. The nonbridging oxygen atoms are terminated by a metal ion, and the silicon bonded to these oxygen atoms etches as fast as the Si−F units in vitreous silicon dioxide. Therefore, the etch rates of multicomponent glasses are higher than that of vitreous silicon dioxide.

Introduction

In 1771, Scheele first prepared hydrofluoric acid and probably discovered that it etches silicate glasses, which was in his case his glassware.[1] More than 50 years later, Berzelius found the reaction products of the reaction between SiO_2 and HF to be tetrafluorosilane and water.[1,2] It was later found that a strong acid was formed which was hexafluorosilicic acid, the reaction product of tetrafluorosilane with HF.[1,3]

Today, etching of vitreous SiO_2 and other silicate glasses with HF is widely used in the glass industry,[4] in the flint industry, in oil recovery, in surface micromachining,[5] and in the production of integrated circuits on silicon wafers.[6] The latter is extremely critical, because silicon dioxide patterns, on silicon substrates, of less than 3 nm thick and 70−100 nm wide are processed. Due to the introduction of fast-etching silicon oxide layers, such as the new low-*k* dielectric material,[7] etch control is becoming increasingly important. Therefore, the etch rate of the HF-containing solutions has to be controlled very precisely.

The first step in controlling the etch rate is to understand the relationship between the HF concentration, the ionic composition of the solution, and the etch rate.[8] HF is a weak acid and is not fully dissociated in a water solution. Moreover, it can dimerize and the dimers can lose one proton. Equilibrium constants between the H^+, F^-, HF, HF_2^-, and H_2F_2 species are published and at 25 °C are[9,10]

$$[H^+][F^-]/[HF] = 6.85 \times 10^{-4} \text{ mol/L}$$

$$[HF_2^-]/[HF][F^-] = 3.963 \text{ L/mol}$$

$$[H_2F_2]/[HF]^2 = 2.7 \text{ L/mol}$$

The etch rate of glass or silica is not a simple function of the HF concentration. Judge found that the SiO_2 etch rate is linearly related to the HF and HF_2^- concentrations and is not related with the F^- concentration at any pH.[11] However, the linear relationships were valid only at low HF concentrations and at low pH (<2). The etch rate was not understood for the data

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that fall outside Judge's intervals. To serve integrated circuit (IC) engineers, etch data have been fitted into relationships which have no chemical meaning. Judge's model has been statistically extended to include H^+ and H_2F_2.[12]

Born and Prigogine studied the dissolution of glass with a more kinetic view and postulated a relationship between the etch rate, HF_2^-, and both HF and H^+ in a Langmuir isotherm.[13,14] The Langmuir isotherm was introduced to describe the concentration of reactive surface sites on the glass surface with which H^+ and HF interact. Unfortunately, these researchers did not include the HF dimerization reaction that results in H_2F_2, which is one of the reactive species.[12,36] Again, the etch rate model is valid only in the low pH (<2) range.

In present IC technology HF concentration monitors are used to control the etch rate. These concentration monitors use the resistivity of the solution or determine the concentration of the reactive species by using near-IR, Raman, or UV spectroscopy.[15] For etch rate control it is assumed that there is a well-defined relationship between the concentration and etch rate. To control the etch rate directly, a new method to directly measure the etch rate of an HF-based solution has been developed and is described in this paper. The etch rate of the SiO_2 which is used for this in situ monitor is compared to those of other SiO_2-based materials. More importantly, an etch mechanism will be proposed which is valid throughout the pH range of 7 and below.

Experimental Section

A patented in situ etch rate monitor was made in-house.[16] It consists of a quartz microbalance with a first resonance frequency of 5 MHz. The electrodes on the quartz are made of chromium. A 1-μm layer of SiO_2 is sputtered on top of the electrode. The quartz crystal is enclosed in a PE housing where only one side of the crystal is exposed to the process liquid. The etching of the sputtered SiO_2 layer is measured by the change in resonance frequency (d*f*) of the crystal. The change in frequency per time unit is related to the mass difference per time unit, i.e., the etch rate.[17]

Vitreous SiO_2 is prepared by the oxidation of silicon. In an oxygen atmosphere at 950 °C, an oxide layer of 100 nm is grown on a ⟨100⟩ silicon wafer (diameter 150 mm). For determining the etch rate on this oxidized silicon wafer, a semiautomated wet bench fabricated by Universal Plastics (Akrion) is used. The HF-based solution in the process bath is recirculated and filtered through a Millipore filter. The temperature of the liquid is controlled with a heat exchanger and is set to 25 °C (±0.2 °C). A robot arm immerses the wafer in the bath with a controlled speed and automatically transfers the wafer to a water rinse position at the end of the etch step. The oxide layer thickness gradient in the direction of the immersion direction is measured at 49 points using a Tencor UV1250 spectroscopic ellipsometer (difference between pre- and postmeasurement) and the least-squares method. The etch rate of silicon dioxide in HF can be determined from the relationship between the immersion speed and oxide thickness gradient on the wafer. Etch rates will be denoted in angstroms per second.

NH_4OH (25% w/w in water), HCl (37% w/w in water), and HF (50% w/w in water) have a purity grade which is standard for the ULSI industry. All concentrations mentioned between brackets are in moles per liter and do not imply ionic activity. For the calculation of the ionic concentrations of the relevant species in HF solutions, the equilibrium constants are used which are tabulated in the Introduction. Since it is not possible to analytically calculate the concentration, an iterative process is used until the laws of electroneutrality ($[H^+] + [NH_4^+] = [F^-] + [HF_2^-] + [Cl^-]$) and mass ($C_F = [F^-] + [HF] + 2[HF_2^-] + 2[H_2F_2]$) are obeyed. In the case HCl or NH_4OH is added, it is assumed that it is fully ionized into Cl^- or NH_4^+, respectively.

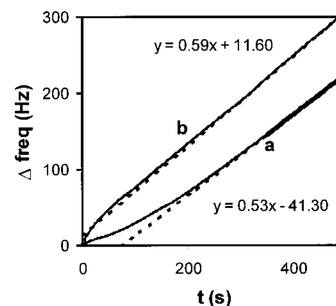

Figure 1. Examples of the results of the in situ etch rate monitor: (a) after the monitor is rinsed with DI water and placed in 0.1% HF and (b) after the monitor is rinsed in 37% HCl (5 min), short-rinsed (5 s) with water, and placed in 0.11% HF. The resonance frequency increases because the sputtered SiO_2 layer is etched.

Results

The etch rate (R) of sputtered silicon dioxide can be determined using a quartz microbalance. Figure 1 depicts typical results from such measurements. From this diagram it can be seen that the measured etch rate is not constant in time. In all the measurements, where the etch monitor is rinsed with DI water prior to the measurement, the etch rate increases as a function of time and stabilizes after about 5 min. When the etch rate monitor is rinsed with concentrated HCl prior to the immersion into the HF solution, the etch rate seems to decrease a little before it stabilizes. Furthermore, the etch rate becomes stable in a shorter period. This indicates that the previous observed increase in etch rate is not a systematic error of the measuring device, but is a surface conditioning phenomenon of sputtered silicon dioxide.

The etch rates of specific etch HF solutions can be extracted from the slope, d*f*/d*t*, of the line obtained after stabilization of the etch rate. This d*f*/d*t* is multiplied by an equipment-specific calibration constant of 0.089 Å s, which results in the etch rate in angstroms per second. The in situ etch rate monitor can measure the etch rates for thermally grown oxides down to 0.001 Å/s; it can be measured that low because the silicon oxide layer used on the monitor has a higher etch rate than the thermally grown silicon dioxide to which it has been calibrated. Furthermore, the sensitivity can be altered by changing the measuring time.

In Figure 2, the etch rate results of a series of experiments at constant pH are plotted as a function of the total fluoride concentration.[18] The etch rate increases gradually with the total fluoride concentration. In the same plot, the concentrations of two potential nucleophiles are plotted. The observation that the concentration of HF_2^- increases in the same way as the etch rate and the F^- increases differently strongly suggests that the etch rate at constant pH is related to the HF_2^- concentration. In fact, using the proper scaling factor, the curve of the HF_2^- fits the measured data point of the etch rates. Table 1 shows the scaling factors $[HF_2^-]/R$ at different pH values. Since the HF

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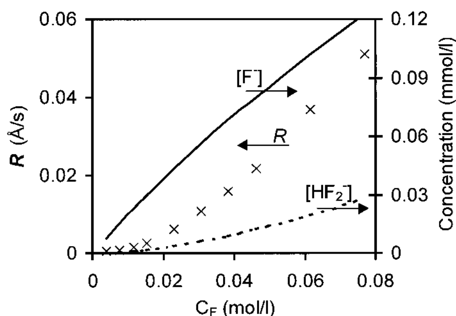

Figure 2. In situ etch rate monitor. Measured SiO_2 etch rate (×) as a function of the total fluoride (C_F) concentration in 0.326 M HCl. The lines represent the HF_2^- and F^- concentrations.

concentration follows the same trend as F^- as a function of C_F, HF can also be excluded as a reactive nucleophile in this reaction. However, H_2F_2 follows the same trend as HF_2^- and therefore cannot be excluded as a reactive nucleophile at this point.

From the results obtained with the in situ etch rate monitor it can be concluded that for etching silicon dioxide, both $[H^+]$ and the concentration of the nucleophile HF_2^- or H_2F_2 are key parameters. Without knowing much about the etching mechanism of vitreous SiO_2, it is safe to say that silicon−oxygen bonds have to be broken and replaced by silicon−fluorine bonds. One possible mechanism is a nucleophilic substitution reaction (or an elimination reaction followed by addition of a nucleophile). Nucleophilic substitution reactions are enhanced by Lewis acids, such as H^+. Let us assume that the reaction of HF with a silicon dioxide surface is a two-step reaction. The first step is the protonation of a surface oxygen atom bond to the silicon atom: $Si-O-X + H^+ \rightarrow Si-O(H)^+-X$ (X = Si or H).[36] The second step is the nucleophilic attack of HF_2^- (or H_2F_2) on the electrophilic silicon atom: $Si-O(H)^+-X + HF_2^- \rightarrow Si-F + HO-X + HF$. The HO−X group is a stable leaving group.

On the basis of the proposed reaction scheme described above, reaction rates can be expressed as a function of reactant concentrations. The reaction rate depends on the concentration of activated surface sites and the concentration of the nucleophile (eq 1):

$$\frac{dSiO_2}{dt} = k_d[SiO(H)^+X][HF_2^-] \quad (1)$$

The concentration of activated surface sites depends on the pH and the maximum number of available sites (Si_{active}). Equations 2 (acid/base equilibrium of surface sites) and 3 (total number of active surface sites, $[Si_{active}]$, is constant) result in a Langmuir eq 4:

$$\frac{[SiO(H)^+X]}{[SiOX][H^+]} = K_{act} \quad (2)$$

$$[SiO(H)^+X] + [SiOX] = [Si_{active}] \quad (3)$$

$$[SiO(H)^+X] = \frac{K_{act}[H^+][Si_{active}]}{1 + K_{act}[H^+]} \quad (4)$$

This Langmuir equation describes the adsorption of protons on the SiO_2 surface, which is different from the approach of HF (or HF_2^-) adsorption on SiO_2 surfaces.[13,14] The active surface sites are these oxygen atoms on the SiO_2 surface that can be protonated and react with a nucleophile HF_2^- (or H_2F_2), resulting

Table 1. Etch Rate Monitor Results: $[HF_2^-] = S_f R_{pH=constant}$

$[H^+]$ (mmol l^{-1})	scaling factor, S_f (mmol s L^{-1} Å^{-1})
1630	0.094 (±0.004)
326	0.58 (±0.05)
33	3.6 (±0.2)
7.9	13[a]

[a] One measurement, because pH is not constant with different C_F.

in etching. Substituting the Langmuir eq 4 into eq 1 results in eq 5:

$$\frac{dSiO_2}{dt} = k_d\frac{K_{act}[H^+][Si_{active}]}{1 + K_{act}[H^+]}[HF_2^-] \quad (5)$$

Using experimental etch rates, it is not possible to determine the number of active surface sites and the k_d independently. Therefore, k_d and $[Si_{active}]$ can be summarized with one constant, which will come out of the experiment (k_{exp}):

$$R = \frac{dSiO_2}{dt} = k_{exp}\frac{K_{act}[H^+][HF_2^-]}{1 + K_{act}[H^+]} \quad (6)$$

This formula can be transformed into eq 7:

$$\frac{[HF_2^-]}{R} = \frac{1}{K_{act}k_{exp}}\frac{1}{[H^+]} + \frac{1}{k_{exp}} \quad (7)$$

By plotting $[HF_2^-]/R$ as a function of the reciprocal proton concentration, one can isolate the two constants from the curve-fitting parameters.

Etch experiments to verify this simple etch model (eq 7) were carried out on vitreous SiO_2 layers thermally grown on silicon wafers. To eliminate unwanted time effects (see results with the in situ etch rate monitor), the wafers are immersed in the etch solution with a constant, low speed (0.03−0.36 mm/s). The silicon dioxide layer thickness variation after the full immersion is used to determine the etch rate. Etch solutions were made up of HF (variation from 0.054 to 1.22 M) to which HCl (variation from 0.025 to 2.04 M) or NH_4OH (variation from 0.051 to 0.823 M) was added.

In Figure 3, the experimental $[HF_2^-]/R$ data are plotted as a function of the reciprocal proton concentration. The experimental error in the data points at low pH ($1/[H^+] < 10\,000$) are relatively small (3−8%). Closer to the point of equivalency (pH 6.9 for the titration of HF with NH_4OH), errors in volumetric determination of HF and NH_4OH have a significant impact on the calculated $[HF_2^-]$ and $[H^+]$. Therefore, the experimental error at higher pH ($1/[H^+] > 10\,000$) becomes significant (10−40%). Nevertheless, the relationship between $[HF_2^-]/R$ and $1/[H^+]$ shows a smooth trend. It is not just one straight line, however, and the reaction of vitreous SiO_2 with HF appears not to be one simple reaction. On first examination of the curve, it looks like there is a reciprocal summation of two reactions with two linear intervals. For $1/[H^+] < 10$ the reaction rate constants are different than for $500 < 1/[H^+] < 10\,000$, which indicates that there are at least two reactions paths.

Linear curve fits in the two pH ranges are included in Figure 3, and they are both corrected for the contribution of the other reaction. This correction is done by extrapolating the etch rate contribution of the other reaction and subtracting it from the experimental value. Both curves show a good linear relationship between the reciprocal proton concentration and the normalized reciprocal etch rate. The equilibrium constants (K_{act}) are 8100

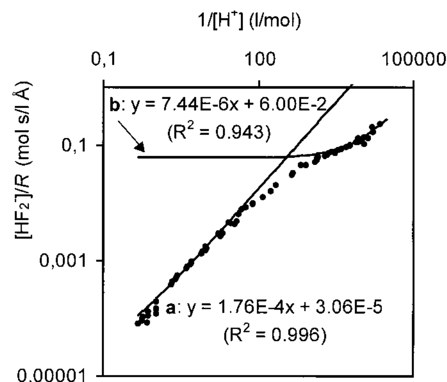

Figure 3. Product of the reciprocal etch rate of vitreous silicon dioxide (R) and $[HF_2^-]$ as a function of the reciprocal proton concentration ($[H^+]$). (a) A linear fit of selected SiO_2 etch rate data with $1/[H^+] < 10$ (L/mol). (b) A linear fit of selected SiO_2 etch rate data with $500 < 1/[H^+] < 30\,000$ (L/mol). The error in the data point strongly depends on the pH. Data points with $1/[H^+] < 100$ have an error bar smaller than the depicted dots. For $100 < 1/[H^+] < 10\,000$, the error compares with the dot size, while for $1/[H^+] > 10\,000$ it is approximately double the dot size (mind log scale).

and 0.17 L/mol, and the reaction rate constants (k_{exp}) are 17 and 33 000 Å L mol^{-1} s^{-1} for the high- and low-pH ranges, respectively.

At the extreme low end ($1/[H^+] < 1$) of the etch rate curves of $1/[H^+] < 10$ (Figure 3), a systematic deviation from the linear relationship is noticed, i.e., the etch rate is higher than expected from the linear extrapolation. It indicates that in this pH range a third reaction is proceeding, and it might be a reaction between $[Si-O(H)^+-X]$ and a nucleophile other than HF_2^-. In Figure 4, the deviation from the expected etch rate is plotted against the product of the $[Si-O(H)^+-X]$ ($K_{act} = 0.17$ L/mol; X = H) and the H_2F_2 concentration (see eq 1 for similar relation with $[HF_2^-]$). A linear correlation is found with a k_{exp} of 7 Å L mol^{-1} s^{-1}. No linear correlation was found when the residual etch rate was plotted as a function of the product of $[Si-O(H)^+-X]$ and the monomeric HF concentration.

The results discussed above indicate that the reaction of HF with SiO_2 is not a single substitution reaction. There are at least two different equilibrium reactions with a proton on the surface. One has a pK_a value of −0.7, and another one has a pK_a value of 3.9. On the surface of vitreous SiO_2 it is likely to be the equilibrium between SiO^-, SiOH, and $SiOH_2^+$. If this is the case, then, according to these data, vitreous silicon dioxide should have an isoelectric point (iep) or point of zero charge (pzc) at the pH of (3.9 − 0.7)/2 = 1.6, which is close to the value of 1.8 found by others.[19] The concentrations of SiOH and $SiOH_2^+$ will be interrelated and result in eqs 8 and 9.

$$[SiOH_2^+] = \frac{K_3K_4[H^+]^2[Si_{active}]}{K_3K_4[H^+]^2 + K_4[H^+] + 1} = \frac{K_3[H^+][Si_{active}]}{K_3[H^+] + 1 + 1/K_4[H^+]} \quad (8)$$

$$[SiOH] = \frac{K_4[H^+][Si_{active}]}{K_3K_4[H^+]^2 + K_4[H^+] + 1} \quad (9)$$

The reaction rate of the dissolution of vitreous SiO_2 in HF is the summation of at least three reactions (eq 10), each with a different pH range in which they become dominant:

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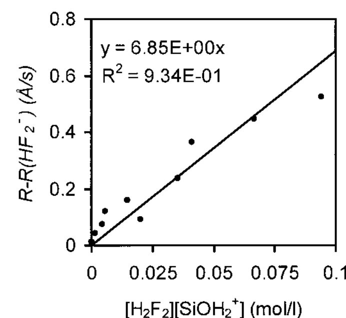

Figure 4. Selected SiO_2 etch rate data at extreme low pH ($1/[H^+] < 1$ (L/mol)).

Table 2. Fit Data from Figure 5

	model I	model II
k_0 (Å L mol^{-1} s^{-1})	8 (1)	7 (1)
k_1 (Å L mol^{-1} s^{-1})	21 000 (4000)	18 000 (4000)
k_2 (Å L mol^{-1} s^{-1})	12.7 (0.4)	12.6 (0.5)
K_3 (L mol^{-1})	0.27 (0.06)	0.28 (0.06)
K_4 (L mol^{-1})	15 000 (2000)	13 000 (2000)
α	na	0.85 (0.06)

(1) In the reaction that occurs at pH < 1, the concentration of HF_2^- is very low and the concentrations of $SiOH_2^+$ and H_2F_2 are high.

(2) At pH between −1 and 3, a large component of the etch rate is due to the second term consisting of $SiOH_2^+$ and HF_2^-.

(3) Above pH 2, the term which is built up of SiOH and HF_2^- becomes the major reaction route.

If the concentrations of SiOH and $SiOH_2^+$ are inserted into eq 10, the overall relationship between the solution composition and etch rate can be described (eq 11). It is referred to as Model I.

$$R = k_0''[SiOH_2^+][H_2F_2] + k_1''[SiOH_2^+][HF_2^-] + k_2''[SiOH][HF_2^-] \quad (10)$$

$$R = (k_0[H_2F_2] + k_1[HF_2^-])\frac{K_3[H^+]}{1 + K_3[H^+] + 1/K_4[H^+]} + k_2[HF_2^-]\frac{K_4[H^+]}{1 + K_4[H^+] + K_3K_4[H^+]^2} \quad (11)$$

Statistical analysis was performed on the data published here and the data published by Kikyuama.[20] A Golub−Pereyra algorithm was used to calculate the k,K values from eq 11.[21] To obtain a convergent solution, the relationship between K_3 and K_4 was fixed: $K_3K_4 = 10^{(2(iep))} = 10^{(2(1.8))} = 3981$. Furthermore, the data for a pH larger than 4 were left out of the analysis and will be handled in the Discussion, because it needs an additional explanation. The k and K values can be extracted more precisely from this analysis and, using the five new parameters (see Table 2), all the data below pH 4 can be fitted in one curve using eq 11 (see Figure 5, model I).

Discussion

The current data show that the rate-determining reaction step of the dissolution of vitreous SiO_2 in HF solutions involves protonation and deprotonation of the reactive surface sites. Since

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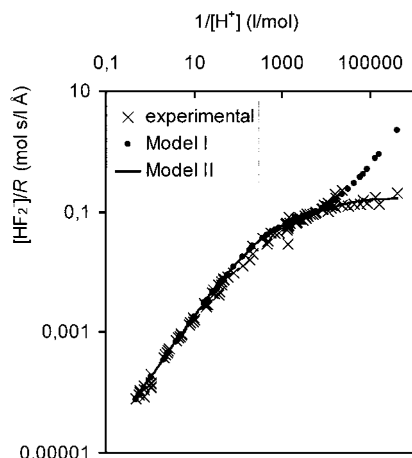
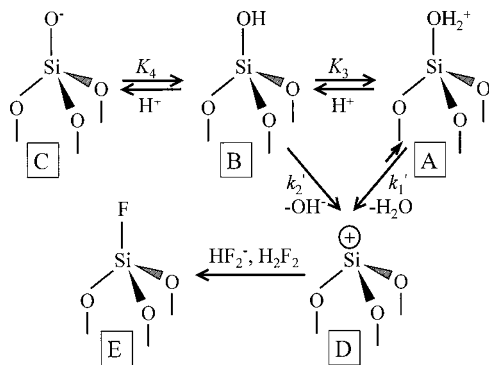


Figure 5. Data fit through experimental values published here and by Kikyuama using eq 11 (model I, $1/[H^+] < 10\,000$) and with a correction on K_4 (model II, eq 13) using all 105 data points.[20] Fit parameters are given in Table 2.

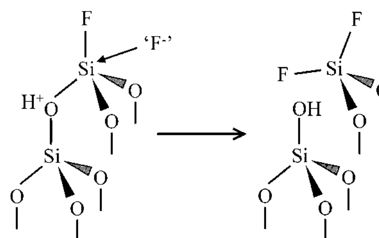
Scheme 1. Proposed Reaction Mechanism of the Rate-Determining Reaction Step of the Dissolution of SiO_2 in HF Solutions: Replacement of the SiOH Unit by an SiF Unit



this can only be a silanol and not an Si−O−Si unit, the rate-determining step is the substitution of an SiOH group by an SiF group. For a nucleophilic substitution reaction, a nucleophile has to approach the electrophile from the opposite side from that of the leaving group. An SiOH group is bound to three oxygen atoms from the SiO_2 matrix, and an approach from the rear side is impossible. Therefore, it can be concluded that the first reaction step is the elimination of OH^- or H_2O from the surface to form the reactive intermediate D (see Scheme 1). After the elimination of both OH^- or H_2O, D can react with three different nucleophiles. With the addition of H_2O, no etching will be measured, and since the $[H_2O]$ is nearly constant in all experiments, this reaction cannot be monitored. In vapor-phase etching,[22] however, which is out of the scope of this report, this reaction may become measurable. The reaction of D with H_2F_2 and HF_2^- will result in the reaction product E, the SiF unit. The measured reaction rate will be the product of the elimination and the addition reactions.

Once the SiF unit is formed, the reaction can proceed very quickly. Three subsequent nucleophilic substitution reactions (see Scheme 2) will break the SiF unit out of the SiO_2 matrix and will bring the surface back into its initial form, where an SiOH unit has to be replaced by an SiF unit to continue the etching process. The reaction rates of nucleophilic substitution reactions are in general faster than those of elimination/addition

Scheme 2. One of the Nucleophilic Substitution Reactions on an SiF_x ($x = 1$, 2, or 3) Unit, Which Will Result in the Removal of the SiF Unit from the SiO_2 Matrix



reactions, because they do not have to form a high-energy intermediate, such as D. It is, therefore, obvious that less dense silicon oxide layers, such as chemical vapor deposited (CVD) layers, etch faster.[23] Since these layers contain silicon atoms to which less than four bridging oxygen atoms are bonded, not all Si−OH that emerges to the surface will be a silanol unit. For example, due to relatively high oxygen content, not all oxygen atoms in an SiO_2 layer will be bonded to two silicon atoms, and these oxygen atoms will generate a certain amount of silan-diol groups during the etching process. The silan-diols that reach the surface do not have to undergo the slow elimination reaction but can immediately undergo the nucleophilic substitution reactions. All silicon atoms that are bonded to four oxygen bonds that are, in turn, bonded to other silicon atoms limit the rate of the SiO_2 etch process. Indeed, the apparent energy of activation of the etching of SiO_2 layers with different Si/O ratios are not much different,[24] which suggests that the rate-determining step remains the same.

During etching of very thin SiO_2 layers on silicon, passivation phenomena have been observed where the etch rate drops to 0.[25] Nielsen and Hackleman found that the SiO_2 etch can be stopped by applying a current, either with a potentiostat or by illumination of $n+$ doped silicon under the SiO_2 layer. It was proposed that a site reaction, elimination of F from an SiF unit, could result in an Si^+ unit (like in D) on the surface. If the electric field was strong enough, the Si^+ unit could be reduced by electron donation from the silicon substrate to form $Si^\bullet$ or Si^-. This passivation mechanism would fit the reaction mechanism presented here, because Si^+ formation would now be part of the reaction path. Deactivating the reactive intermediate, D, will stop the etching process.

The formation of long-living Si^+ intermediates as in D is not very likely. Moreover, if such an intermediate will form, F^- would be a good candidate to bind to this site, while it is found not to be reactive. Finally, OH^- groups are very poor leaving groups, which means there should be some kind of assistance to eliminate them. Therefore, it is proposed that the elimination and addition reactions take place in a "closed" system. H_2F_2 and HF_2^- can assist the elimination of OH by coordination with the FH part parallel to the HO side of the silanol group (see Scheme 3). This action brings the second F atom of H_2F_2 or HF_2^- close to the silicon atom. The elimination and addition can take place consecutively. Monofluorides, such as HF and F^-, are not able to do this. Furthermore, this also explains why HF_2^- reacts faster than H_2F_2: the angle F−H−F is probably larger in the HF_2^- ion than in the square-shaped H_2F_2 molecule. The larger angle brings the F^- ion, which has to be transferred, closer to the reactive center.

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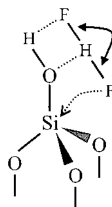
Scheme 3. HF_2^--Assisted OH^- Elimination Reaction with a Consecutive F^- Addition



The surface condition and the pH have a significant impact on the etch rate and the initial etch rate. Protonation of the surface enhances the etch rate, which was observed by the in situ etch rate monitor. The pK_a values found in these experiments differ from those published in the literature for silica surfaces. The lowest and most often cited value for the deprotonation equilibrium of the silanol group is that of Schindler and Kamber: 6.8 ± 0.2.[26] It was reported that the pK_a value of the silanol group of silicic acid ($Si(OH)_4$, p$K_a = 9.8$) decreases with the degree of polymerization down to 6.5.[27] Apparently, the pK_a value of silanol groups can decrease even further to 4.1 when silicic acid is polymerized to a quartz-like structure as in thermally grown silicon dioxide. Furthermore, thermally grown silicon dioxide is like perfectly polymerized silicic acid, with only silanol groups on the surface silicon atoms and not more than one per silicon atom.

The HF solutions used in the work described in this publication were diluted and prepared from HF and NH_4OH mixtures. Due to small volumetric errors, the calculated $[H^+]$ is not well established at higher pH values, because it roughly depends on the added amount of HF minus that of NH_4OH. However, in the literature, there are a number of publications which give silicon dioxide etch rates as a function of solution composition at higher pH values. Kikyuama reported etch rates of HF/NH_4OH mixtures at high concentrations and pH varying from 1.5 to 5.5.[20] In Figure 5, it can be seen that the measured data fit the calculated data below the pH of 4 ($1/[H^+] < 10\,000$). Above the pH of 4, the experimental etch rates are higher than the calculated ones. A similar change in reaction rate was observed for etching with HF as a function of NH_4F addition.[24] In what the authors call "region 1", the pH is smaller than 4, and in what they call "region 2", the pH is above 4.

The reason for the deviations of the etch rate from model I might be the variation of the pK_a value of the silanol group as a function of surface charge.[26,28,29,36] Others have noticed that the surface charge of silica starts to increase from pH 4 upward.[30] The relationship between the pK_a and pH is understandable, as it will be more difficult to remove a proton from a more negatively charged surface. The implication for SiO_2 etching is that the concentration of SiOH groups on the surface above the pH of 4 is higher than anticipated from the simple acid−base equilibrium, as denoted in eq 2. Higher concentrations of SiOH imply a higher etch rate. In addition, a surface that is negatively charged will eliminate an OH^- group more easily than a less negatively charged surface. Therefore, surface charging will also increase the reaction rate constant (k_2). The combined effect results in increased etch rates above the pH of 4.

It is impossible to establish the relationship between the pK_a value and the pH from the current data, because the k_2 might also be affected by the pH changes. Moreover, different studies are dedicated to the laborious relationship between the pK_a and the surface charge (which is a function of pH and pK_a) and electrolyte concentration.[28,29,31,32] Most of the approaches describe the relationship as an intrinsic pK_a value plus a part that is a function of ionization level. It is, therefore, proposed to approach the K_4 (the K_a value for the $SiOH/SiO^-$ equilibrium) value by taking an intrinsic K_4^0 value (the K_4 value from the curve fit below pH 4) and to add the reciprocal proton concentration multiplied by a factor α to it (eq 12).

$$K_4 = K_4^0 + \alpha/[H^+] \qquad (12)$$

In the statistical analysis of all the data using the Golub−Pereyra algorithm and the modified K_4 value, a fit is obtained with a residual quadratic error of 0.36 (Table 2). Moreover, no systematic deviations occur in the residual plot other than a randomly larger error at pH > 4, which is probably caused by an error in the determination of the pH. These new theoretical values (eq 13, model II) are plotted with the experimental ones in Figure 5. The validity of this model II is limited to certain pH values. Since the function in eq 12 increases continuously with an increasing pH while the pK_a should level off at a certain pH, this approach is valid only for a small pH range (4−7). The pH where the K_4 levels off depends, among other things, on the electrolyte concentration: the higher the concentration, the lower the level. If the K_4 value levels off, the etch rate will drop very quickly to zero. Therefore, eq 13 describes the etch rate in the pH range from −1 to 6−7.

$$R = (k_0[H_2F_2] + k_1[HF_2^-])\frac{K_3[H^+]}{1 + K_3[H^+] + 1/(K_4[H^+] + \alpha)} + k_2[HF_2^-]\frac{K_4[H^+] + \alpha}{1 + \alpha + \alpha K_3[H^+] + K_4[H^+] + K_3K_4[H^+]^2} \qquad (13)$$

There is an implication in using the approximation of the new K_4 (eq 12). Since, at pH above 4, the reaction rate is mainly going through the substitution of SiOH by HF_2^-, the reaction rate can be approximated by

$$R = k_2\frac{K_4[H^+] + \alpha}{1 + \alpha + K_4[H^+]}[HF_2^-] \qquad (14)$$

At higher pH values, the $K_4[H^+]$ will become much smaller than α, which means that, within this limit, both $K_4[H^+]$ increments of eq 14 can be ignored. Consequently, the etch rate will become independent of the pH. However, it is valid in a certain pH range, and the $[HF_2^-]$ remains dependent on the pH.

Etching of multicomponent silicate glasses is not much different from etching of vitreous SiO_2. The diffusion of the alkali and earth alkali metals out of the SiO_2 network is much faster than the etching of the SiO_2 network.[33] Therefore, the first few nanometers of glass is a metal-free $SiO_2{}^{+}{}_xH_x$ layer.

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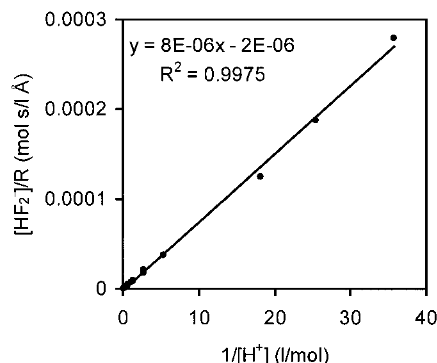

Figure 6. Etch rate data from Spierings and van Dijk of $Na_2O-MgO-CaO-SiO_2$ glass in HF with HNO_3, HCl, or H_2SO_4 added.[34]

The $Na_2O-MgO-CaO-SiO_2$ glass etch data of Spierings and van Dijk have been plotted in Figure 6 in the $1/[H^+]$ to $[HF_2^-]/R$ format.[34] The published HF_2^- and H^+ concentrations were used but did not result in a linear curve. Recalculated values using the HF dimerization reaction, which were omitted by the authors of ref 34, were used (Figure 6). In contrast to the published $R/[H^+]$ over $[HF_2^-]$ plot, all the data fall on one line when the dimerization reaction is included. Due to the large error in the intercept value, the *y*-intercept is not positive, which means that both the k_1 and K_3 values should be negative. If the same K_3 value is assumed as in the vitreous silicon dioxide case, a reaction rate $k_1 = 1.31 \times 10^5$ Å L mol^{-1} s^{-1} follows from the slope ($1/k_1K_3$). The etch rate of the glass is about 20 times higher than that of vitreous silicon dioxide. Also visible at larger magnification is the systematic deviation at low pH due to the reaction of H_2F_2.

With this glass etch data it is possible to estimate the etch rate of silicon fluoride or silanol groups that are bonded to less than three bridging oxygen atoms. Assume a network model where the dissolution rate of silicates with the composition of SiO_xM_y ($x \geq 2$, M is one or more types of metal ions) is composed of a slow reaction (R_a) due to etching of silicon atoms bonded to four bridging oxygen atoms and a fast reaction (R_b) due to the etching of silicon atoms which were bonded to less than four bridging oxygen atoms. Equation 15 should be valid in the range from $2 < x < 2.5$:

$$R(x) = R_a\frac{2.5 - x}{0.5} + R_b\frac{x - 2}{0.5} \tag{15}$$

For $x > 2.5$ and a homogeneous distribution of M, every silicon atom in the SiO_2 network will have one or more nonbridging oxygen atoms, and the reaction rate will be constant and equal to R_b. The R_b/R_a ratio would follow from a plot of $R(x)/R_a$ as a function of x:

$$\frac{R(x)}{R_a} = 2\left(\frac{R_b}{R_a} - 1\right)x + \left(5 - 4\frac{R_b}{R_a}\right) \tag{16}$$

The slope and intercept of a least-squares fit in the range $2 < x < 2.5$ (see eq 16) and the final level at $x > 2.5$ all yield the R_b/R_a ratio. Figure 7 depicts a plot and fit of published etch rate data of glasses (note that etch rates are corrected for density of glass) with known composition relative to the measured etch rate of vitreous SiO_2 (R_a).[33] With the exclusion of some data points it can be concluded that, at 20 °C in 2.9 M HF, R_b is about 18 times R_a.

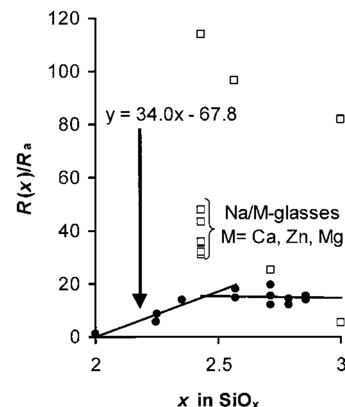

Figure 7. Normalized etch rate of silicate glasses as a function of oxygen content. R_a is the etch rate of thermally grown SiO_2 and $R(x)$ is the etch rate of glass with composition SiO_xM.

The exceptions to the above-described network model of glass etching might be due to the difference in the diffusion rates of metal ions that have to diffuse out of the glass while H_3O^+ and H_2O diffuse into the glass.[35]

Conclusions

Dissolution of vitreous silicon dioxide and (multicomponent) silicate glasses in HF-based solutions depends on three parameters:

1. The first is the number of silicon atoms bonded to four bridging oxygen atoms. The replacement of the first oxygen by a fluorine ion is a slow and rate-determining reaction step. The subsequent reaction steps, to remove the SiF unit from the SiO_2 network, are 18–20 times faster.

2. The pH influences the equilibrium reaction of surface silanol groups with its protonated and deprotonated forms. The elimination of H_2O that occurs at low pH is much faster than OH^-. Deprotonation of the silanol inhibits the etching process.

3. The nucleophile HF_2^- (and H_2F_2 at very low pH) reacts with the silicon center that just lost an H_2O or OH^- group and probably facilitate the elimination of the H_2O or OH^- groups. The concentration of HF_2^- will decrease at low pH values, which works counterproductive to the enhanced elimination of H_2O.

The effects of superstoichiometric amounts of oxygen in SiO_2 on the etch rate can be studied with glasses. This is difficult with silicon dioxide layers applied by chemical vapor deposition methods or wet chemical methods followed by a furnace treatment, because the composition is not reproducible.

The relationship between the SiO_2 etch rate and the solution composition is not straightforward. Furthermore, pretreatment of the surface with strong acids or bases can influence the initial etch rates of the SiO_2. Therefore, for proper etch rate control, it is best to monitor the etch rate directly with an identical pretreatment. A high sensitivity can be obtained with an in situ etch rate monitor assuming the two oxide surfaces react identically.

Acknowledgment. The author thanks T. J. J. (Dee) Denteneer for performing the statistical analysis with the Golub–Pereyra algorithm. F. C. (Eric) van de Heuvel and F. J. Touwslager are also acknowledged for the preparation of the quartz crystal and assistance during the measurements with the crystal, respectively. The discussions with G. A. C. M. Spierings on the etching of glass were appreciated.

JA993803Z

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