University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Chemical and Biomolecular Engineering -- All Faculty Papers

Chemical and Biomolecular Engineering, Department of

1989

REACTION MECHANISMS AND RATE LIMITATIONS IN DRY ETCHING OF SILICON DIOXIDE VITH ANHYDROUS HYDROGEN FLUORIDE

L. David Clements

James E. Busse

Jitesh Mehta

Follow this and additional works at: https://digitalcommons.unl.edu/chemengall

Clements, L. David; Busse, James E.; and Mehta, Jitesh, "REACTION MECHANISMS AND RATE LIMITATIONS IN DRY ETCHING OF SILICON DIOXIDE VITH ANHYDROUS HYDROGEN FLUORIDE" (1989). *Chemical and Biomolecular Engineering -- All Faculty Papers*. 69.
https://digitalcommons.unl.edu/chemengall/69

L. Davis Clements, James E. Busse and Jitesh Mehta

REACTION MECHANISMS AND RATE LIMITATIONS IN DRY ETCHING OF
SILICON DIOXIDE WITH ANHYDROUS HYDROGEN FLUORIDE

ABSTRACT: A novel dry etching process for silicon dioxide has
been developed.   This process, carried out at ambient
temperature and pressure, uses anhydrous hydrogen fluoride,
water vapor in a nitrogen carrier, and a unique processing
sequence to achieve etch rates of about 200A/second, with 5
percent or better uniformity.
        The overall reaction is a complicated sequence of surface
hydration and surface fluorination by adsorption, reaction, and
product desorption.   This paper   presents   two proposed
reaction mechanisms and describes how experimental data from a
laminar flow reactor were used to evaluate the mechanisms.

KEYWORDS: Silicon Dioxide Chemical Etching, Anhydrous Hydrogen
          Fluoride, Reaction Mechanisms

Introduction

Chemical etching takes place when products which are soluble
(wet) or volatile (dry) are produced by reaction of the surface
material with an etchant. Chemical etching occurs spontaneously with
xenon difluoride and silicon [1]. Beyer and Kastl [2] have described
a process for etching SiO_2 using HF/H_2O vapor. This work focuses on
a new process for chemical etching using anhydrous hydrogen fluoride
with silicon dioxide [3, 4].   This paper describes two proposed
mechanisms for anhydrous hydrogen fluoride dry etching and evaluation
of the apparent kinetics associated with each mechanism.

Dr. Clements is Professor and Chair and Mr. Busse is a Graduate
Research Assistant   at   the   Department   of   Chemical Engineering,
University of Nebraska - Lincoln, Lincoln, NE 68588-0126.   Mr Mehta
is the Japan Process Engineering Manager, FSI International, 322 Lake
Hazeltine Drive, Chaska, MN 55318-1096.

Used by permission.

Surface Preparation and SiO_2 Etching

The way in which the surface is prepared plays an important role in determining how the reaction of silicon dioxide with anhydrous hydrogen fluoride proceeds.   The surface of silicon resembles a diamond lattice.   The chemical and physical properties of an oxide grown on the silicon surface are dependent on its growing conditions. A SiO_2 surface can be grown with either oxygen (dry-oxidation) or steam (wet-oxidation) [5, 6].   The surface grown in oxygen is basically pure SiO_2.

The surface grown with steam will have many water and hydroxyl groups remaining absorbed on the SiO_2 surface once the oxidation is complete.   The hydroxyl group forms a silanol (Si-OH) group when absorbed on the surface.   The excess water and hydroxyls can be removed by heating the surface [7].   A pure SiO_2 surface remains after the removal.   The oxidation with steam is faster, so it is typically used to grow thick oxides [6].

Tyapkina and Guseva [8] found that a wet-oxide surface etches at a much faster rate than a dry-oxide surface.   A wet-oxide strip required 40 percent of the time of a dry-oxide strip, even though the wet-oxide was 10 times thicker.   They also found that pretreatment of the two surfaces with fluorine resulted in a marked increase in the etch rate of the wet-oxide surface.   The pretreatment did not effect the etch rate of the dry-oxide surface.

Arslambekov, et. al. [9] found that HF reacts with pure silicon, but at a much slower rate than with SiO_2.   An induction period that was dependent on the temperature was observed.   The activation energy for etching silicon was 13 to 17 kcal/mol.   According to the authors, this rather low activation energy indicates that an adsorption process occurs before the reaction actually begins.

White [10] found that the rate-limiting step for the reaction of anhydrous HF with chemically vapor-deposited (CVD) SiO_2 involves species other than just HF and that proton transfer plays a minor role in this step.   CVD SiO_2 resembles a dry-oxide surface.

Adsorption Mechanisms and Effects on SiO_2

The adsorption of both water and anhydrous hydrogen fluoride on the silicon dioxide surface is an important part of the overall anhydrous HF etching reaction mechanism.   Several groups have studied the adsorption process and how it alters the structure of the surface.

The adsorptive properties of silica and SiO_2 surfaces are very different.   The water and hydroxyl groups adsorbed on the silica surface promote the adsorption of hydrogen fluoride.   Voronin [7] found that the number of strongly adsorbed hydrogen fluoride molecules is equal to the number of silicon atoms present at the surface.   Since the oxide produced by dry-oxidation has no water or hydroxyls present, its ability to adsorb HF is limited.

Bersin [11] found that after a silicon dioxide surface was exposed to a CF_4-O_2 plasma, the surface was invulnerable to the

hydrogen fluoride reaction. He postulated that the silanol (Si-OH) groups had been turned into siloxane (Si-O-Si) bridges. The siloxane bridges do not hydrogen bond with hydrogen fluoride. The adsorption and reaction of HF onto this surface proceeds at a much slower rate than on the silica surface.

The HF is apparently attracted to the dipole produced by the surface hydroxyls. The HF molecule is polarized to form H^+ and F^-. Voronin [7] found that the greater the degree of hydration, the more that the hydrogen fluoride becomes like hydrofluoric acid. The fluorine ion reacts with the silanol to form a Si-F group and H_2O. The fluorine ion can also cleave the siloxane (Si-O-Si) bridges of the SiO_2 lattice [7, 12].

Once Si-F groups form, the structure of the surface changes. The fluorine is highly electronegative and imparts a large positive charge to the silicon atom. This positive charge decreases the 3d orbital energy. The silicon and neighboring oxygen undergo a p-d bond formation. This results in an increase in the bond angle and a change in the hybridization. Chukin [12] states that the fluorination of the surface leads to a transition of hybridization of an oxygen atom from sp^3 and sp^2 to sp. Consequently, the oxygen atom has been passivated. If the entire surface is fluorinated, the surface becomes very hydrophobic. This is due to the lack of active sites for adsorption.
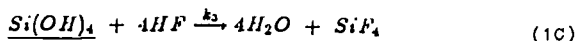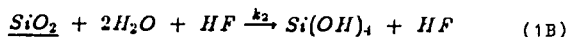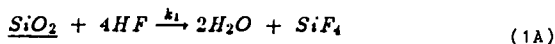
Voronin [7] found that extended contact of SiO_2 with HF gave rise to an infrared band at 935 cm^{-1}. This band indicates the presence of Si-F, showing that fluorination had taken place. He also found that when silica surfaces are pretreated by vacuum-conditioning at different temperatures, varying degrees of hydration at the surface resulted. For example, specimens that had been pretreated at 920, 720, and 570 K had an induction period of 30, 20, and 10 minutes respectively, before the surface reaction began. Voronin discovered that the degree of fluorination increased with the degree of surface hydration and with the time during which the adsorbed HF molecules were present on the surface. Prolonged exposure of the surface to hydrogen fluoride, 10 to 12 hours, resulted in almost complete replacement of the silanol groups. Five to seven percent of the groups could not be removed chemically. The silanol groups were only removed through vacuum-baking at 570-670 K.

Proposed Mechanism for Dry Etching of SiO_2 Using Anhydrous HF

The overall dry etching mechanism involves a number of steps. First, the reactants must diffuse to the SiO_2 surface. The reactants then adsorb onto the surface. Once the reactants are on the surface, the etching reaction occurs. This is the point where the proposed kinetic mechanisms are required. Once the reaction is complete, the products desorb from the surface and diffuse into the bulk gas phase.
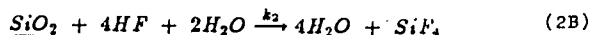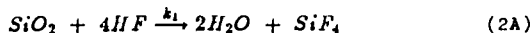
The diffusion of the reactants to and the products away from the surface has been described by Clements, et al [13] and Busse [14]. The adsorption, reaction, and desorption steps are all parts of the overall surface mechanism and will be described further here. The desorption of the products is assumed to be fast and is neglected in the surface mechanism.

Equation 1 describes a proposed etching mechanism consisting of three reactions.

$$SiO_2 + 4HF \xrightarrow{k_1} 2H_2O + SiF_4 \qquad \text{(1A)}$$

$$SiO_2 + 2H_2O + HF \xrightarrow{k_2} Si(OH)_4 + HF \qquad \text{(1B)}$$

$$Si(OH)_4 + 4HF \xrightarrow{k_3} 4H_2O + SiF_4 \qquad \text{(1C)}$$
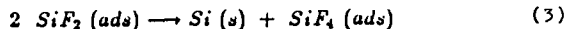
This mechanism has two distinct reaction paths. The first reaction is water-free. This reaction will occur if only hydrogen fluoride is used as a reacting species and no appreciable amount of water accumulates on the surface as a product of the reaction. The second and third reactions are coupled by the intermediate, $Si(OH)_4$. The formation of the $Si(OH)_4$ intermediate relies on the presence of water. Hydrogen fluoride is used as a catalyst in the hydrating reaction. Once $Si(OH)_4$ is formed, the reaction proceeds much like the first reaction.

A simplification of the three reaction mechanism was also tested. This mechanism involves the assumption that the intermediate in the three-reaction mechanism exists as an activated complex and, therefore, is short lived and does not accumulate. This assumption results in the overall number of reactions being reduced by one. The simplified mechanism is called the two-reaction mechanism shown in Equation 2.

$$SiO_2 + 4HF \xrightarrow{k_1} 2H_2O + SiF_4 \qquad \text{(2A)}$$

$$SiO_2 + 4HF + 2H_2O \xrightarrow{k_2} 4H_2O + SiF_4 \qquad \text{(2B)}$$

The reaction pathway

$$2\ SiF_2\ (ads) \longrightarrow Si\ (s) + SiF_4\ (ads) \qquad \text{(3)}$$

suggested by Chukin's work [12] was disregarded here. This mechanism may represent the steps involved in reaction 2-A, but based upon the data reported by Tyapkina and Guseva [8], this overall reaction is very slow at ambient conditions.

Experimental Results

A laminar flow reactor, shown schematically in Figure 1 and described in detail in reference [3], was constructed to take advantage
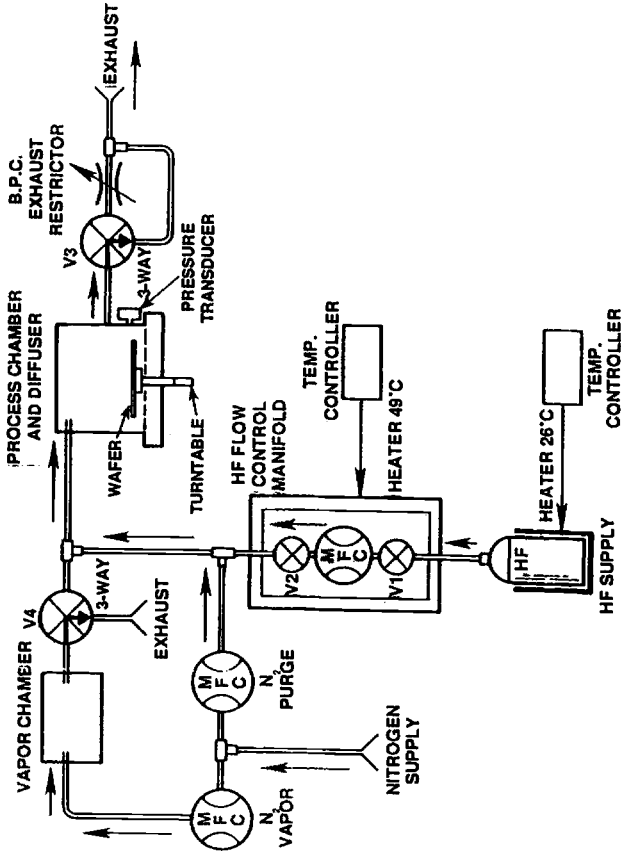
Figure 1. Schematic diagram of the laminar flow reactor

of the increased etch rate when using anhydrous hydrogen fluoride.
The reactor allows the wafer to be etched in a continuous flow
process.   The reactor is vented to the atmosphere to maintain near
atmospheric pressure inside the vessel.   The reactant gas is a
mixture of anhydrous hydrogen fluoride, dry nitrogen, and moist
nitrogen.   The amount of water and anhydrous hydrogen fluoride is
kept low in comparison to the nitrogen.   The reaction is terminated
by purging the vessel with pure, dry nitrogen.   Because of the very
rapid sequence of processing steps, high-speed pneumatic valves and
an automatic controller were used to operate the reactor system.
Novak [4] and Cleavelin and Duranko [15] have described the
operational performance of the commercial system.

   Table 1 gives the concentrations of reactants and products for
the nominal reaction case.   Table 2 shows the number of moles of
hydrogen fluoride at any given time in any unit volume (cm^3) of space
at the entrance of the reactor in relation to the hydrogen fluoride
flow rate.

Table 1. Mole Fractions of Typical
          Entrance and Exit Streams

Component	Entrance	Exit
Nitrogen	0.9690	0.9694
Water	0.0020	0.0028
Hydrogen Fluoride	0.0290	0.0276
Silicon Tetrafluoride	0.0000	0.0002

Table 2. Relationship Between the HF Concentration
          At The Inlet And The HF Flow Rate

HF Conc. ($gmol/cm^3$)	HF Flow Rate (1it/min)
0.00022	0.3
0.00037	0.5
0.00045	0.6
0.00052	0.7
0.00060	0.8

   The thickness of SiO_2 removed as a function of etch time is
shown in Figure 2.   The amounts removed are linear with etch time and
exhibit a definite time lag before reaction begins.   A similar lag
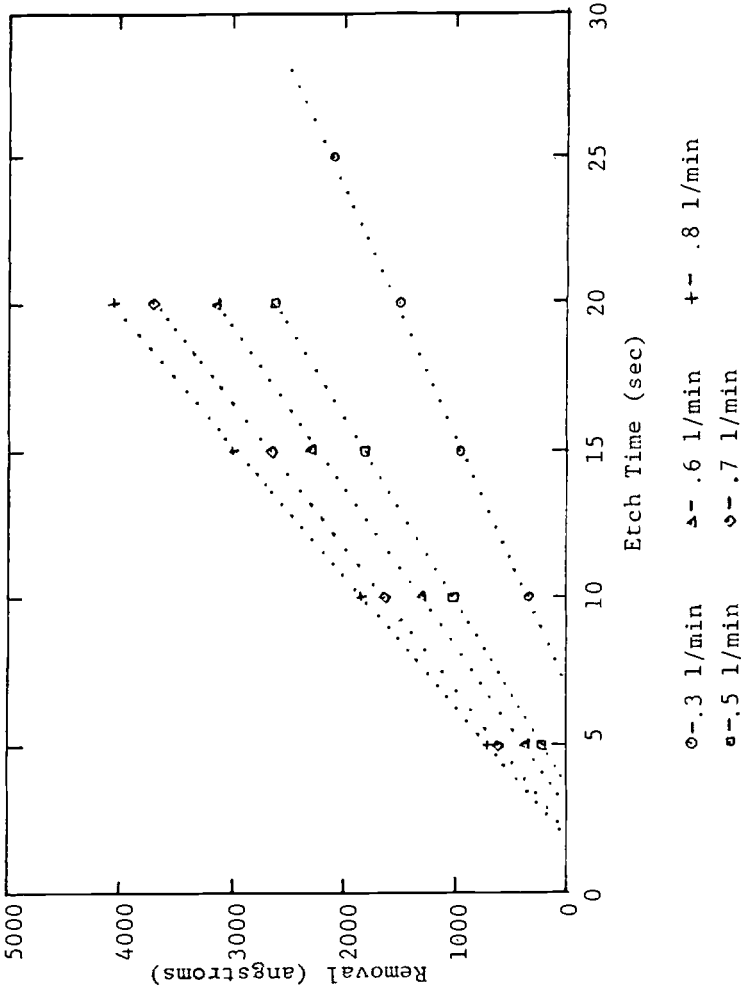time before etching was reported by Voronin [7].

Figure 2.   Removal of oxide at various HF flow rates
            in the laminar flow reactor

Voronin [7] found that there are 2.5×10^{-6} moles of silicon atoms for every square meter of surface area of a silicon dioxide surface. A 4.0 inch (10.16 cm) wafer that has been oxidized has 2×10^{-8} moles of silicon atoms at the surface. Since there are five active sites for the adsorption of water for each silicon atom, there are about 10^{-7} sites available for water to adsorb.

The lag time observed in etching a hydrated surface is accounted for by the time required for the adsorption of the hydrogen fluoride on the surface of the silicon dioxide. This phenomenon is called loading in the description to follow. The rate of adsorption of the hydrogen fluoride is related to the HF concentration over the surface, as illustrated by the data in Figure 2. The lag time appears to decrease as the amount of hydrogen fluoride increases.

The rate of loading of hydrogen fluoride on the surface can be estimated based upon a gas-phase model in the following manner. The gas phase acts as a high concentration source for hydrogen fluoride, while the reactions at the surface act as a sink for the adsorbed HF. The rate of transport of the HF to the surface can be assumed to be controlled by the diffusion rate of the HF from the gas bulk to the surface.

A certain fraction of the HF molecules that strike the surface actually bond to the surface. The diffusion expression, when multiplied by a coefficient that represents the fraction of molecules that stick, represents the rate of adsorption. If the coefficient is less than one, adsorption is the rate controlling mechanism, or if the coefficient is equal to one, then diffusion is the rate controlling mechanism for HF loading. The rate of accumulation of hydrogen fluoride on the surface can then be estimated using the diffusion equation shown in Equation 4.

$$Vr|_{Accum} = A(1 - \theta)\beta D_{HF,M}\frac{\partial n_{HF}}{\partial y}|_s$$ (4)

Here V and A are the characteristic volume and area, θ is the fraction of available sites for hydrogen fluoride adsorption, β is the sticking coefficient, and $D_{HF,M}$ is the rate of diffusion of hydrogen fluoride. The partial differential is the molar flux of HF evaluated at the surface, and θ is defined in Equation 5 as the number of sites where adsorption has occurred, n, divided by the total number of adsorption sites, n^*.

$$\theta = n_{NH,s}/n^*$$ (5)

Determination of β

An estimate of the sticking coefficient, β, is needed for a description of the lag phenomenon. This estimate is determined from data shown in Figure 2. For each of the five different flow rates of hydrogen fluoride, a least-squares curve fit was used to determine at what time the reaction began, based on the time axis intercept.

Table 3 shows that as the surface is subjected to a higher
concentration of hydrogen fluoride, the time before the reaction
commences decreases. This decrease is not linear with respect to the
concentration because it is dependent upon the diffusion rate, which,
in turn, depends upon the HF concentration gradient at the surface.

Table 3.   Observed Time Lag As A
           Function Of Concentration.

HF Conc. ($gmol/cm^3$)	Time Lag (sec)	r^2
0.00022	6.76	0.9952
0.00037	3.68	0.9973
0.00045	2.88	0.9991
0.00052	2.08	0.9990
0.00060	1.81	0.9967

Voronin [7] found that 90 to 95 percent of the sites available
for hydrogen fluoride adsorption must be filled before the reaction
begins. For the purpose of determining β , the percentage of
sites filled before the reaction begins is assumed to be 94 percent.
This assumption will be justified later.

Equation 5 is substituted into Equation 4 with the resulting
expression, Equation 6, used to determine β .

$$V \frac{dn_{HF}|_s}{dt} = A \left[1 - \frac{n_{HF}|_s}{n^*} \right] \beta D_{HF,M} \frac{\partial n_{HF}}{\partial y}\Big|_s \quad (6)$$

Here, V represents the volume where the reaction occurs. Since the
reaction occurs at a surface, an assumption must be made to give the
same basis to A and V. The volume chosen is an incremental volume
above the surface represented by $A(\Delta y)$. Then the diffusive flux is
discretized using a forward difference. This results in the
transformation of Δy into the step width, h. The accumulation of
hydrogen fluoride at the surface due to adsorption is given by

$$\frac{dn_{HF}|_s}{dt} = \left[1 - \frac{n_{HF}|_s}{n^*} \right] \beta D_{HF,M} \frac{n_{HF}|_h - n_{HF}|_s}{h^2} \quad (7)$$

where $n/_s$ is the number of moles at the surface and $n/_h$ is the number
of moles at a height h above the surface. This derivation results in
the assumption that the region of the reaction from the surface to
one step width above the surface is identical to a continuous stirred
tank reactor (CSTR). The properties in this region are considered
constant, with no convective or diffusive fluxes.

With the information in Table 3, β can be found for each
concentration. The resulting values for the sticking coefficient are
shown in Table 4.

Based on the   results shown in Table 4, the value of β
selected for the simulation is 6.3 x 10^{-6}. When β has this value
and the appropriate lag time is assigned at the various flow rates,
the percentage of surface covered by hydrogen fluoride as a function
of the concentration is within the range of 92 to 95 percent. This
is listed in Table 5.   The result   is in agreement with what was
observed by Voronin [7].   The assumption that the reaction begins
when 94 percent of the surface sites are filled at any flow rate
appears valid and is used in the simulation, since the largest error
in this determination is 2 percent.

Table 4. Sticking Coefficient At
          Varying HF Concentrations

HF Conc. (gmol/cm^3)

0.00022	6.0 x 10^{-7}
0.00037	6.0 x 10^{-7}
0.00045	6.2 x 10^{-7}
0.00052	7.0 x 10^{-7}
0.00060	6.9 x 10^{-7}

Table 5. Percentage Of Sites Filled At The
          Reaction Onset With β = 6.3 x 10^{-6}
          At Various HF Concentrations

HF Conc. (gmol/cm^3)	Percent of Sites	Percent Error
0.00022	94.5	+0.5
0.00037	95.0	+1.0
0.00045	94.5	+0.5
0.00052	92.0	-2.0
0.00060	92.5	-1.5

Two-Reaction Mechanism

The rate expressions for the two-reaction mechanism, Equation 8,
are determined from Equation 1.   The rate expressions describe the
rate of change of the apparent number of moles of each component at
the surface.

$$\frac{dn_{HF}|_s}{dt} = -4k_1 n_{HF}|_s - 4k_2 n_{HF}|_s n_{H_2O}|_s^2 \qquad \text{(8A)}$$

$$\frac{dn_{H_2O}|_s}{dt} = 2k_1 n_{HF}|_s + 2k_2 n_{HF}|_s n_{H_2O}|_s^2 \qquad \text{(3B)}$$

$$\frac{dn_{SiF_4}|_{\bullet}}{dt} = k_1 n_{HF}|_{\bullet} + k_2 n_{HF}|_{\bullet} h_{H_2O}|_{\bullet}^2 \qquad (8C)$$

The rate of accumulation at the surface is equal to the rate of adsorption plus the rate of reaction. The overall mechanism of reaction is different than the overall mechanism for adsorption. For the reaction mechanism, the rate of accumulation of any species in the flow regime is zero. Setting the rate of accumulation equal to zero in Equation 4 results in an expression that can be used to solve for the apparent number of moles of hydrogen fluoride at the surface. Similar expressions apply to the other components. Combining the assumption of no accumulation at the surface with the requirement that the rate of adsorption and reaction is matched by the rate of diffusion to the surface results in Equation 9. As before, the modelling is based on the gas phase, with the reactions at the surface entering as boundary conditions.

$$O = \chi D_M \frac{\partial n}{\partial y}\Big|_{\bullet} + r|_{React} \qquad (9)$$

Here χ is the sticking coefficient for the kinetic mechanism. The rate of adsorption during reaction is just the rate of diffusion multiplied by the constant, χ. If χ is less than 1.0, then the rate of adsorption controls this mechanism. However, if the coefficient is equal to 1.0, then the rate of diffusion is the controlling rate. The reaction sticking coefficient will only affect the rate expression of hydrogen fluoride, as was the case in the overall adsorption mechanism. χ is 1.0 for all other flow components.

Initially, only the rate constant for the first reaction is known. This value was determined from data taken by Tyapkina and Guseva [8]. A reaction on a wafer that was prepared by dry-oxidation showed an etch rate about 0.5 angstroms/sec. The value of the rate constant was backed out using the simulation described by Clements et al. [13]. The rate constant for the dry reaction, k_1, was varied until the etch rate matched the rate observed by Tyapkina and Guseva. The rate constant at this etch rate is approximately 2.5×10^{-4} sec^{-1}.

With k_1 known, the value for k_2 can be determined through a search technique. An approximate rate constant must be determined to find the time dependence of the reaction system. The value of is initially set equal to 1.0. The results with the adsorption coefficient at this value will show how the kinetics depend on the diffusion controlled system of equations and whether adsorption is important.

To find the rate constant, a reaction with known surface removal characteristics is chosen. For the results given here, the stream consists of 15 lit/min of nitrogen, 2 lit/min of water-saturated nitrogen, and 0.5 lit/min of hydrogen fluoride. This base case is used throughout as a basis for initial comparison of the simulation to the actual data. The simulation is run with this base case as the input with an etch time of 10 seconds. k_2 is varied to determine the sensitivity of the reaction system to the rate constant. The rate

constant that provides the greatest removal is chosen as a candidate
for the rate constant, since it corresponds to the diffusion
controlled system.

The sensitivity of the results for the mechanism as a function of
k_2 is shown in Figure 3. At values of $k_2 < 10^5$, the mechanism seems
to be dominated by the first reaction. The amount of surface removed
is around 3.0 angstroms. As k_2 is increased, the second reaction
begins to compete. When k_2 exceeds 10^7, the second reaction
dominates the kinetic mechanism. As k_2 is increased further, the
amount of surface removed dramatically increases. When k_2 reaches 7
x 10^{11}, a maximum removal of 6860 angstroms in 10 seconds occurs. As
k_2 is increased further, the amount of surface removal approaches
zero at values greater than 10^{14}.

The decrease in the amount of surface removal to zero is a result
of limits on the rate of adsorption. There exists a minimum surface
concentration of HF necessary for the reaction to be maintained. If
the reaction is very fast, a large portion of the adsorbed HF will
react. This results in a surface concentration well below the
minimum. The reaction cannot proceed until at least the minimum
amount is readsorbed. This requires a prolonged period of no
reaction, resulting in very little or no surface removal.

The value for k_2 used in the two-reaction kinetic mechanism is 7
x 10^{11}. This rate constant predicts that 6860 angstroms of surface
is removed in ten seconds. The actual amount removed was 1030
angstroms. Dividing these two numbers gives a value for X of 0.150.
Since this is less than 1.0, the rate of adsorption is assumed to be
the controlling rate in the kinetic mechanism.

The two-reaction simulation is run with the set of parameters
shown in Table 6. The results of the two-reaction mechanism are
shown in Figure 4.

Table 6. Parameters Used in the Two-Reaction Simulation

Parameter	Numerical Value
k_1	2.5×10^{-3}
k_2	7×10^{11}
F	2.0
β	6.3×10^{-6}
X	0.150

The results in Figure 4 indicate that the two-reaction kinetic
mechanism provides an acceptable correlation for the observed data
for all HF flow rates except the flow rate at 0.6 l/min at etch times
between 5 and 20 seconds. The predicted removals at 0.6 l/min are in
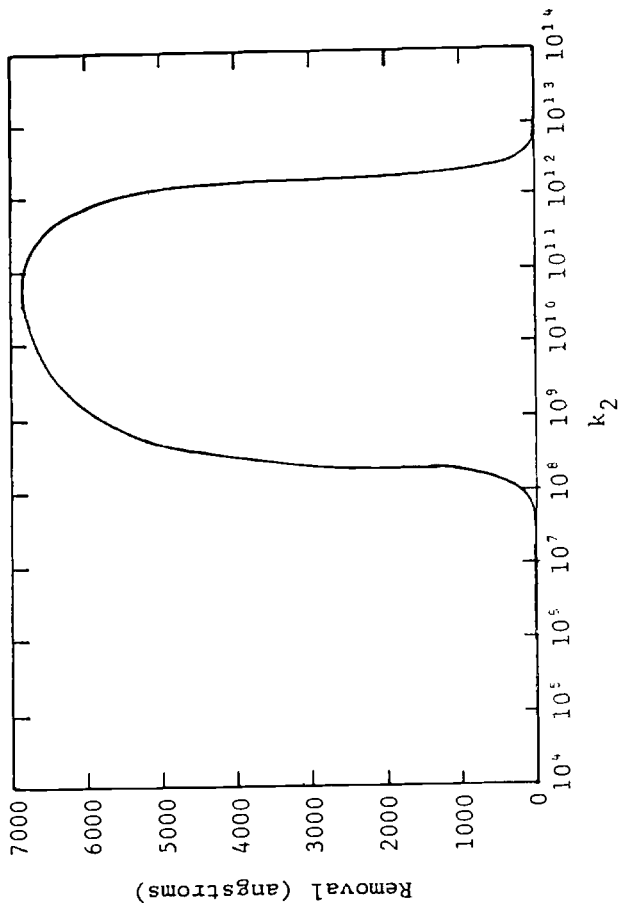excess of the observed removals by more than 100 angstroms.

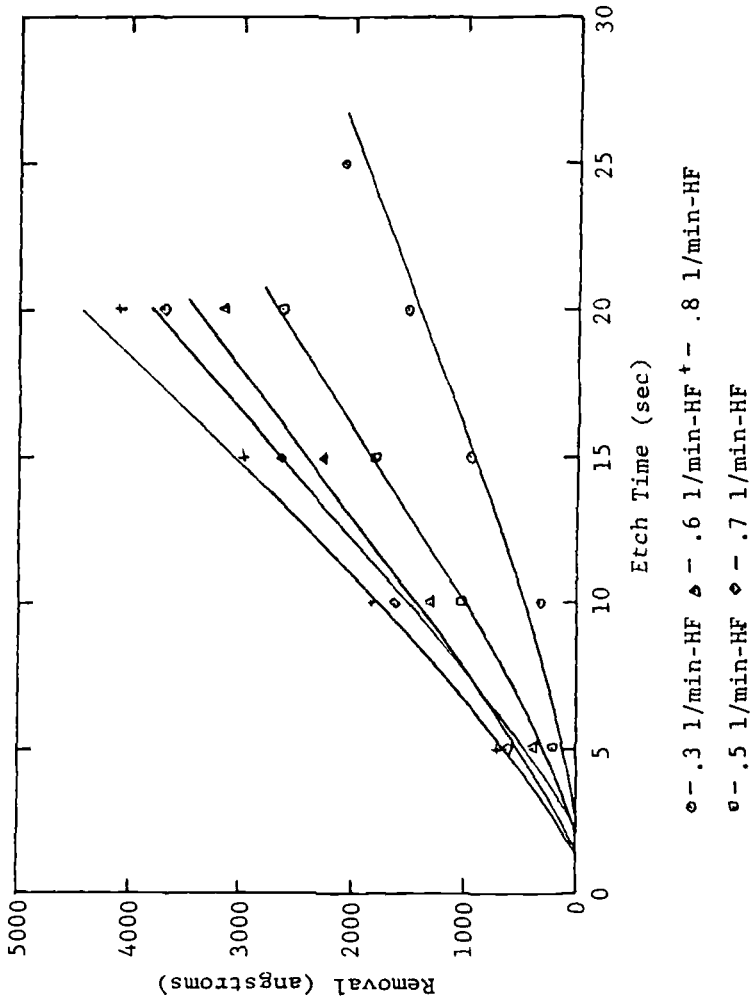Figure 3. Sensitivity of the two-reaction mechanism to k_2

Figure 4.   Comparison of removal data with the two-reaction
mechanism

The error seems to increase at etch times around 20 seconds for large HF flow rates. There is also an error at low etch times. However, even though the percent error is large for the 5 second runs, the difference in the values is no greater than 145 angstroms.

Three-Reaction Mechanism

The rate expressions, derived from Equation 1, for each component are shown in Equation 10.

$$\frac{dn_{HF}|s}{dt} = -4k_1 n_{HF}|_s - 4k_3 n_{HF}|_s n_{Si(OH)_4}|_s \qquad (10A)$$

$$\frac{dn_{H_2O}|_s}{dt} = 2k_1 n_{HF}|_s - 2k_2 n_{HF}|_s n_{H_2O}|_s^2 \qquad (10B)$$

$$+ 4k_3 n_{HF}|_s \, n_{Si(OH)_4}|_s$$

$$\frac{dn_{SiF_4}|_s}{dt} = k_1 n_{HF}|_s + k_3 n_{HF}|_s n_{Si(OH)_4}|_s \qquad (10C)$$

$$\frac{dn_{Si(OH)_4}|_s}{dt} = k_2 n_{HF}|_s n_{H_2O}|_s^2 - k_3 n_{HF}|_s n_{Si(OH)_4}|_s \qquad (10D)$$

where k_1, k_2, and k_3 are rate constants for each reaction, and n/s represents the number of moles of a component at the surface. As in the previous casethe number of moles at a surface cannot be physically determined, so an apparent quantity must be found.

As before, only the rate constant for the first reaction is known. The remaining two rate constants must be determined using a search technique. However, the value of the third rate constant is dependent upon the value assigned to the first and second. As a result, there exists a family of rate constants that will satisfy the problem.

A value of 10^{12} was assigned a priori to k_2. This can be substantiated by the following argument. Figure 5 shows the sensitivity of the three-reaction mechanism to changes in k_3 at two different values of k_2, 10^{12} and 10^{15}. The curves for both values of k_2 are so close that they are indistinguishable at the resolution that Figure 5 provides. The maximum value of removal occurs at slightly different k_3 values for each k_2. However, the magnitude of the removal for both cases is the same.

With two of the rate constants known, k_3 can be found in the same manner as the second rate constant was determined for the two-reaction mechanism. The value of X is set equal to 1.0 to determine the sensitivity of the diffusion controlled system and to determine if the rate of adsorption is important.

The sensitivity of the mechanism to changes in the rate constant is shown in Figure 5. When k_3 is below 1.0, the mechanism is solely
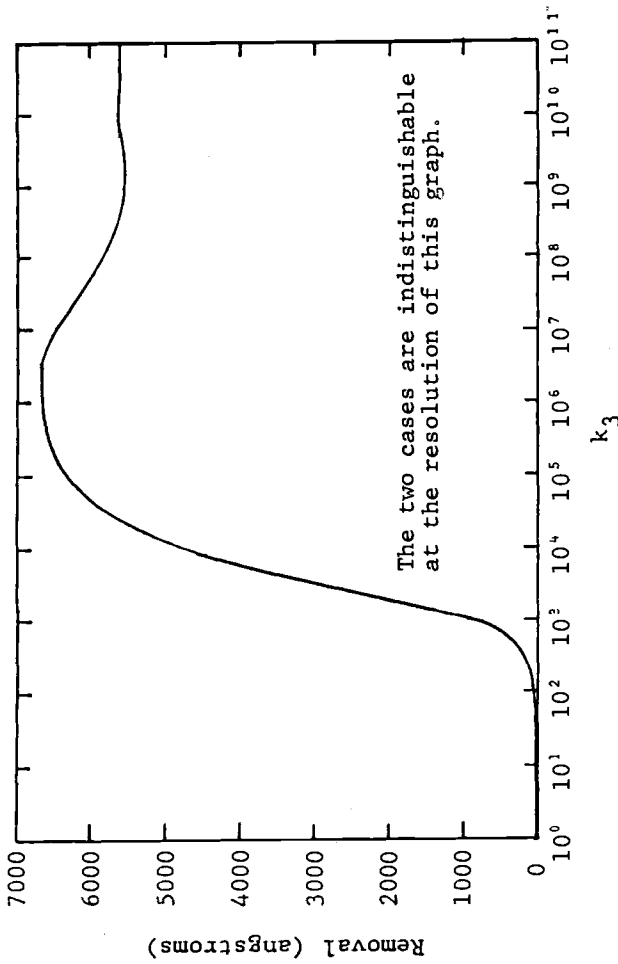
The two cases are indistinguishable at the resolution of this graph.

Figure 5.   Sensitivity of the three-reaction mechanism with k_2 held constant at 10^{12} and 10^{15}

dependent on the first reaction.   The amount of surface etched is about 3 angstroms. As k_3 exceeds 10^1, the overall mechanism becomes solely dependent on the water inclusive reaction.   As the rate constant increases, the amount of surface removed increases dramatically. When k_3 approaches 10^5, the removal reaches a plateau. The greatest amount of surface removal occurs when k_3 attains a value of 3×10^6, where 6660 angstroms is removed.   As the rate constant increases further, the amount of surface removed drops off to another plateau, with a value of 5670 angstroms removed.

The value for k_3 used in the three-reaction mechanism is 3×10^6. 6660 angstroms of the surface are removed when this rate constant is used.   The actual amount removed is 1030 angstroms.   Dividing the above two numbers provides a value for X of 0.155.

The three-reaction mechanism is implemented with the use of the parameters listed in Table 7.   The results are seen in Figure 6.

Table 7.   Parameters Used in the Three-Reaction Simulation

Parameter	Numerical Value
k_1	2.5×10^{-4}
k_2	10^{12}
k_3	3×10^6
F	2.0
β	6.3×10^{-6}
X	0.155

The three-reaction kinetic mechanism compares well with the actual data obtained at all HF flow rates.   The mechanism is most accurate generally at medium (10 to 15 second) etch times.   The three-reaction mechanism seems to be somewhat more inaccurate at high etch times for large HF flow rates, with errors as large as 17.5 percent.   However, at low etch times for all of the flow rates, the match appears to be very good.   Even though the percentage error is large, the absolute difference is not great.

The description of the surface reaction has two separate paths, a dry path and a wet path.   The dry path involves only hydrogen fluoride as a reacting species.   The hydrogen fluoride diffuses down to the surface and reacts on contact with the silicon atoms at the surface.   The wet path involves the formation of an intermediate. The intermediate is formed when the water diffuses to the surface. The hydrogen fluoride is used as a catalyst.   Hydrogen fluoride may prepare the surface in some way for the hydration to proceed or it may alter the characteristics of the water which leads to the hydration.   Once the intermediate is formed, the hydrogen fluoride replaces the hydroxyl groups to form silicon tetrafluoride.   It is apparent that the hydration reaction is many times faster than the dry reaction.
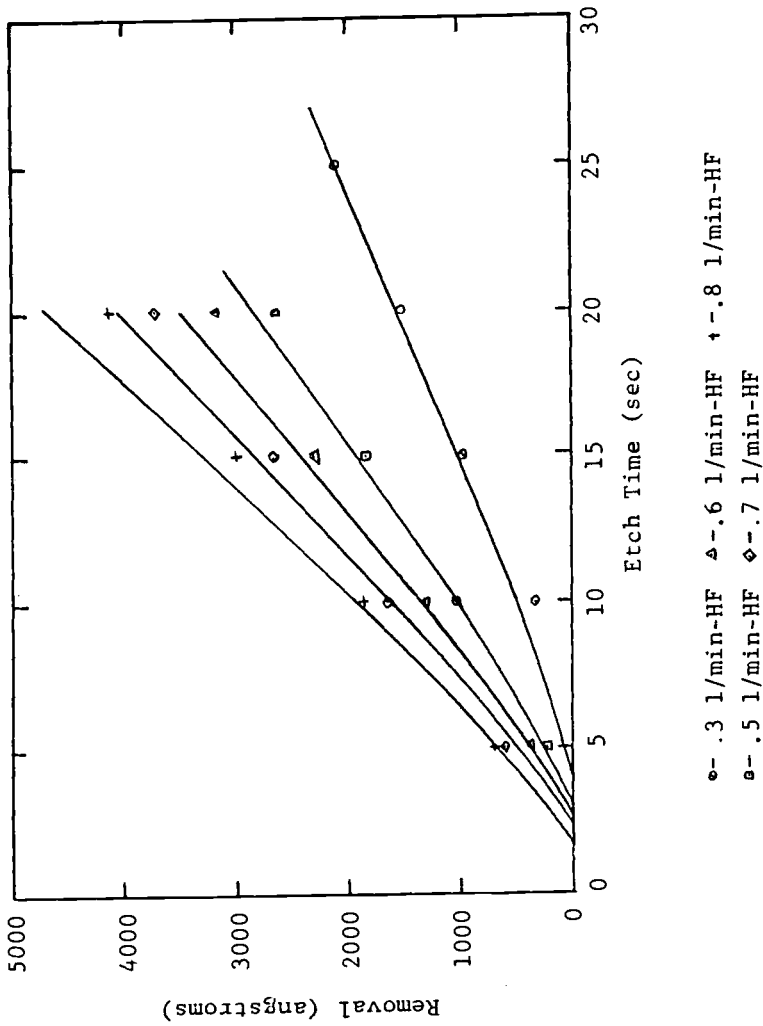
Figure 6. Comparison of removal data with the three-reaction mechanism.

Summary

The results for both kinetic mechanisms appear to give reasonable correlations of the data.   Considering both mechanisms together, 50 percent of the predictions were within 100 angstroms of the experimental result and 75 percent of the predictions were within 150 angstroms.

After etch times of 5 to 10 seconds, the etch rates for the simulated runs increase only slightly.   However, the experimental data show a constant rate once the reaction starts.

The fact that the two mechanisms give essentially identical results could be explained on the basis that the $Si(OH)_4$ intermediate proposed for the three reaction mechanism appears to have a high reaction rate and may serve as an activated complex.   It would be necessary to follow the surface reactions using an analytical tool such as FTIR to verify the presence of the silicon tetrahydroxide.

REFERENCES

(1) Winters, H. F. and Coburn, J. W., "The Etching of Silicon with XeF$_2$ Vapor," *Applied Physics Letters*, Vol. 34, No. 1, 1979, pp. 70-73.
(2) Beyer, K. D. and Kastl, R. H., "Impact of Deionized Water Rinses on Silicon Surface Clenaing," *J. Electrochem Soc.*, Vol. 129, No. 5, 1982, pp. 1027-1029.
(3) Blackwood, R. S., Biggerstaff, R. L., Clements, L. D., and Cleavelin C. R., "Gaseous Process and Apparatus for Removing Films from Substrates," U.S. Patent 4,749,440, June 7, 1988.
(4) Novak, R. E., "Anhydrous HF Etching of Native SiO$_2$: Applications to Device Fabrication," *Solid State Technology*, Vol. 31, No. 3, 1988, pp. 39-41.
(5) Sze, S. M., *VLSI Technology*, McGraw-Hill Book Company, New York, 1983.
(6) Ruska, W. S., *Microelectonic Processing, An Introduction to the Manufacture of Integrated Circuits*, McGraw-Hill Book Company, New York, 1987.
(7) Voronin, E. F., "Spectroscopic Investigation of Hydrogen Fluoride Chemisorption on the Surface of Aerosils with Various Degrees of Dehydration," *Zhurnal Prikladnoi Spektroscopii*, Vol.42, No. 6, 1985, pp. 954-959.
(8) Tyapkina, V. V. and Guseva, N. S., "Interaction of a Silicon Surface with Fluorine and Hydrogen Fluoride," *Russian Journal of Physical Chemistry*, Vol. 40, No. 5, 1966, pp. 573-576.
(9) Arslambekov, V. A., Corbunova, K. M., and Guseva, N. S., "Reaction of Si with Gaseous HF," *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, Vol. 12, 1976, pp. 2124-2126.
(10) White, L. K., "Etch Rates of SiO$_2$ Films in Deuterated Acidic Fluorides," *Thin Solid Films*, Vol. 79, 1981, pp. L73-L76.
(11) Bersin, R. L. and Reichelfelder, R. F.," The DryOx Process For Etching Silicon Dioxide," *Solid State Technology*, Vol. 20, No. 4, 1977, pp. 78-80.
(12) Chukin, G. D., "An IR Spectroscopic Study of the Surface Properties of Fluorinated Silica Gel," *Zhurnal Prikladnoi Spektroskopii*, Vol. 81, No.5, 1974, pp. 879-884.

(13) Clements, L. D., Busse, J. E., Smith, G. W., and Mehta, J.,
      "Hydrogen Fluoride Dry Etching of Silicon Dioxide: Process
      Modelling for a Laminar Flow Reactor," presented at 172nd
      Meeting of The Electrochemical Society, October 18-23, 1987,
      Honolulu, Hawaii.
(14) Busse, J. E., "The Reaction Modelling of a Vapor-Phase Semi-
      conductor Etching Process," M.S. Thesis, University of
      Nebraska-Lincoln, 1987.
(15) Cleavelin, C. R. and Duranko, G. T., "Silicon Dioxide Removal
      in Anhydrous HF Gas," Semiconductor International, Vol. 10,
      No. 12, 1987, pp 94-98.