# Review
# Wet chemical etching of silicate glasses in hydrofluoric acid based solutions

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The etching of silicate glasses in aqueous hydrofluoric acid solutions is applied in many technological fields. In this review most of the aspects of the wet chemical etching process of silicate glasses are discussed. The mechanism of the dissolution reaction is governed by the adsorption of the two reactive species: HF and $HF_2^-$ and the catalytic action of $H^+$ ions, resulting in the breakage of the siloxane bonds in the silicate network. The etch rate is determined by the composition of the etchant as well as by the glass, although the mechanism of dissolution is not influenced. In the second part of this review, diverse applications of etching glass objects in technology are described. Etching of $SiO_2$ and doped $SiO_2$ thin films, studied extensively for integrated circuit technology, is discussed separately.

## 1. Introduction
Silicate glasses, because of their unique properties, are widely used in everyday life. The optical transparancy and the ability to withstand many environmental influences can be considered as the most striking properties in this respect. This is combined with the relative ease with which the material can be given the desired shape, due to its unique viscosity–temperature relation. Silicate glasses are resistant to most gases and liquids. At room temperature they are only readily dissolved by hydrofluoric acid or other HF containing aqueous solutions [1]. Controlled dissolution in HF-based etchants can be applied to remove material from glass objects for a variety of applications.

Wet chemical etching of silicate glasses in aqueous HF solutions is a subject which has been studied over many years. The first report originates from the discovery of HF by Scheele in 1771 [2]. However, this subject has never been studied intensively and publications on this subject are wide apart in time and scattered over a range of technical journals. In integrated circuit (IC) technology wet chemical etching of $SiO_2$ and doped $SiO_2$ thin films was and is being studied more extensively, because these films are widely applied as the dielectric isolation material in IC devices.

In this paper the etching of vitreous $SiO_2$ and multicomponent silicate glasses, in bulk as well as thin films, is reviewed and an attempt is made to combine the results from the fields of glass technology and IC fabrication. First, the etching mechanism is described. This is followed by a description of the effect of etchant and glass composition. Then the etching of thin $SiO_2$-based films is discussed. Finally, most of the important applications are reviewed.

## 2. The etching process
### 2.1. Reaction mechanism
The dissolution of vitreous $SiO_2$, chemically the most simple silicate glass, into an aqueous HF solution can be described by the overall reaction

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \qquad (1)$$

This equation is a simplification of the reactions occurring during the heterogeneous $SiO_2$ dissolution. Vitreous (as well as crystalline) $SiO_2$ consists of tetragonal $SiO_4$ units connected at all four corners with four other $SiO_4$ units by covalent ≡Si–O–Si≡ (siloxane) bonds. In this way a covalently interconnected three-dimensional silicate network structure is formed. It is necessary to break all four siloxane bonds in order to break down the network and release a silicon from the glass.

HF, dissolved in water, is a weak acid and its solutions contain $H^+$, $F^-$ and $HF_2^-$ ions and undissociated HF molecules. Their concentrations are related by Equations 2a and b:

$$K_1 = [H^+]\cdot[F^-]/[HF] \qquad (2a)$$

$$K_2 = [HF]\cdot[F^-]/[HF_2^-] \qquad (2b)$$

At 25 °C $K_1 = 6.7 \times 10^{-4}$ mol l$^{-1}$ and $K_2 = 0.26$ mol l$^{-1}$ [3]. Values for $K_1$ and $K_2$ at other temperatures are summarized in [4]. In concentrated solutions higher $H_nF_{n+1}^-$ polymeric species have been observed [5].

The dissolution of vitreous $SiO_2$ is a heterogeneous reaction, which makes it difficult to study the mechanism(s) governing the dissolution process. The breaking of all the chemical bonds which results in Equation 1 will require several reaction steps. One of these steps will be the slowest and its rate constant will

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HF-containing solutions to attack the glass is related to the presence in solution of the fluorine-containing species: $F^-$, HF and $HF_2^-$. As it is well established that solutions of, for example, NaF or $NH_4F$ do not attack $SiO_2$, so the reactivity of $F^-$ ions can be considered to be negligible [6, 7].

The insensitivity of the etch rate to agitation of the solution [8] and the activation energy $E_a$, which is in the 25–40 kJ $mol^{-1}$ range, (to be discussed in Section 3) both indicate that the dissolution reaction is kinetically controlled. Consequently, the adsorption or chemisorption of the reactive species and the effect of this adsorption on the siloxane bonds at the glass surface dominate the dissolution process.

The dissolution mechanism, in particular the role of the various fluorine-containing species, has been studied in more detail by Judge [6], Prokopowicz-Prigogine [9–11], Kline and Fogler [12, 13], Spierings [14], Kikuyama *et al.* [15, 16] and Proksche *et al.* [17]. The most detailed model has been presented by Prokopowicz-Prigogine [11], in which the adsorption processes of HF molecules, $HF_2^-$ and $H^+$ ions determine the reaction rate. The $HF_2^-$ ions are adsorbed on surface silanol groups, the HF molecules on vicinal silanol groups and $H^+$ ions on surface bridging oxygens in siloxane units. Fluorine adsorption complexes have been observed at hydrated $SiO_2$ surfaces in gaseous HF by infrared spectroscopy. These are transformed into surface groups such as ≡Si–F and ≡Si–O–$SiF_3$ [18]. The adsorption of HF and $HF_2^-$ increases the electronic density on the bridging oxygen in the siloxane unit. This in turn makes these oxygens more basic, so more $H^+$ ions are adsorbed, which leads to more siloxane bonds being broken per time unit, i.e. a kind of catalytic effect. The rate-determining step is then the breakage of the siloxane bond by the combined action of the adsorbed species. The catalytic action of $H^+$ ions on breaking siloxane bonds also occurs in the dissolution of glasses in acidic and weakly alkaline solutions [19]. This effect had already been observed in early HF etching studies by Palmer [20]. The above model results in a complex Equation 3 in which the etch rate $V_E$ is determined by the concentration of $H^+$, $HF_2^-$ and HF [11]:

$$V_E = k_1 \cdot \Theta(H^+) \cdot \{k_2 \cdot \Theta(HF_2^-) + k_3 \cdot \Theta(HF)\} + k_4 \cdot \Theta(H^+) \quad (3)$$

where $k_i$ are constants which contain the reaction rate and adsorption equilibrium constants as well as the number of adsorption sites per unit surface area. $\Theta$ expresses the degree of coverage of active adsorption sites, which can be assumed to follow Langmuir's isotherm, e.g.

$$\Theta(HF) = b \cdot [HF]/(1 + b \cdot [HF]) \quad (4)$$

where $b$ is the ratio between the rate constants of adsorption and desorption, respectively.

Etch rate data in solutions with varying HF and $HF_2^-$ concentrations show a substantially higher reactivity of the $HF_2^-$ compared to that of HF [11]. Previously this higher reactivity of the $HF_2^-$ ion was etched in HF–$NH_4F$-containing solutions

$$V_E = a \cdot [HF] + b \cdot [HF_2^-] + c \quad (5)$$

At 25 °C $a = 0.250$, $b = 0.966$ and $c = -0.014$ with $V_E$ in nm $s^{-1}$. Recent studies of the etching in HF solutions buffered with $NH_4F$ [16, 17] also report the relation in Equation 5 at low $NH_4F$ concentrations.

Although the above investigations all report that $HF_2^-$ ions have a higher reactivity than HF molecules, Kline and Fogler [12, 13] came to the opposite conclusion, that only HF molecules are reactive. The catalytic role of $H^+$ ions was also observed by these authors, which results in the etch rate equation

$$V_E = k_1 \cdot \Theta(HF) \cdot \{1 + k_2 \cdot \Theta(H^+)\} \quad (6)$$

An etch rate versus concentration (Equation 7) relation was proposed recently which follows the theoretical treatment of Kline and Fogler [12, 13] but with the difference in reactivity between HF and $HF_2^-$ and the catalytic effect of $H^+$ all taken into account:

$$V_E = k_1 \cdot (k_2[HF_2^-] + k_3 \cdot [HF]) \cdot (1 + k_4 \cdot [H^+]) \quad (7)$$

This relation gives a satisfactory explanation of the observed etch rate of a multicomponent silicate glass in HF–strong acid mixtures [14].

It is clear from the above discussion that the exact reaction mechanism at the molecular level, and particularly the rate determining step, is not completely understood. The discrepancy, particularly in the reactivity of the HF and $HF_2^-$, has to be investigated in more detail.

The mechanism(s) proposed for the dissolution of vitreous $SiO_2$ described above can also be applied to the dissolution of glasses with more complex compositions [21] and for compositionally related crystalline silicates such as α-quartz [22] and feldspars [12, 13, 23]. However, the etch rate varies widely.

## 2.2. Determination of the etch rate

Different methods have been developed to determine the etch or dissolution rate of glasses. The weight loss of dispersed powders with known surface areas was particularly used in early studies [24], and more recently using a slurry reactor [12]. A second group of methods is based on partially masking the surface of a glass body, e.g. a disk, by photoresist or wax [8, 14, 25–27]. The glass is locally dissolved and the quantity of material which has dissolved can be determined either by measuring the weight loss [8] or the depth of the recessed etched region [14, 26, 27].

The etch rate for thin glass films deposited on a substrate material can be measured by monitoring the decrease in film thickness during etching by ellipsometry [28–31] or other optical interference methods [6, 31, 32], such as colour evaluation [33]. Kern developed a method for thin glass films on silicon wafers, which makes use of the hydrophobic/hydrophilic transition occurring when the glass film is completely removed [34, 35]. Since the dissolution

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slightly affected by agitation of the etchant by rotation, stirring or ultrasound [8, 32, 35].

## 2.3. Surface morphology

The etching process of a glass not only removes surface material, but it also changes the surface morphology of the glass. When a smooth, e.g. polished, surface is etched the surface roughens slightly and cusp-like structures are formed [7, 21, 36]. A SEM micrograph (Fig. 1) of the surface of a polished soda lime glass [14] shows this structure. Its formation is related to the presence of flaws in the surface before etching. The size or depth of these flaws varies from microcracks

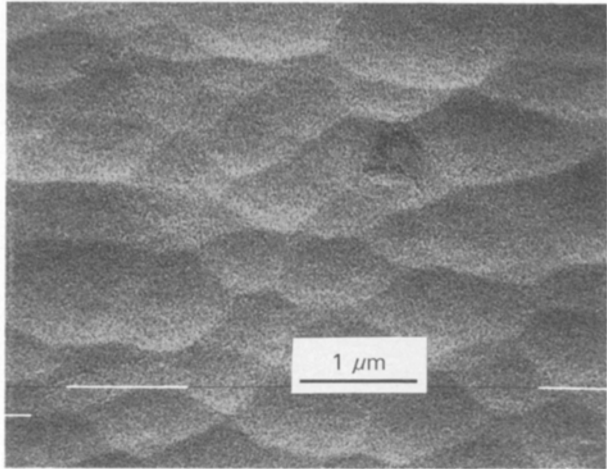



*Figure 1* SEM micrograph showing the cusp-like surface obtained after etching a polished soda lime silicate glass surface [14].

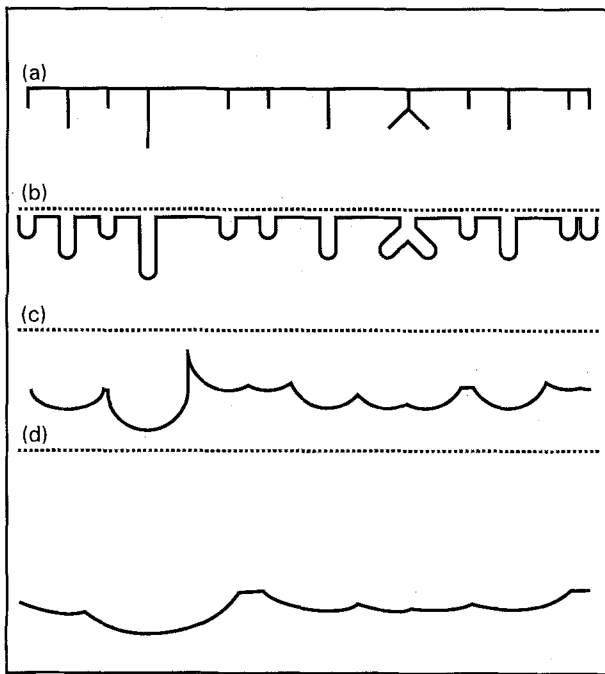
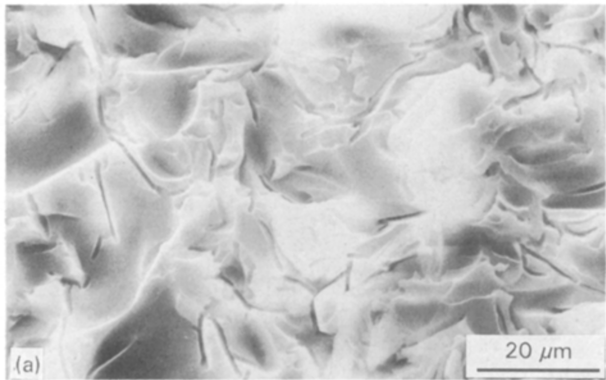
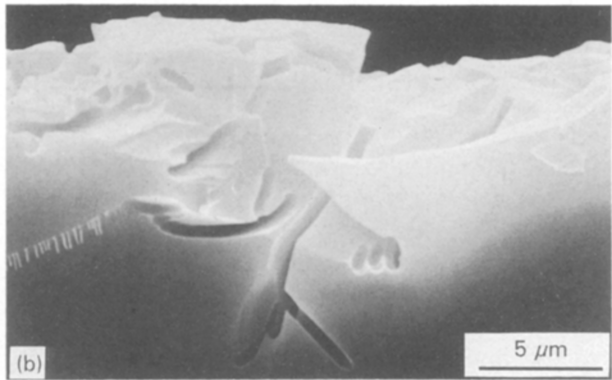
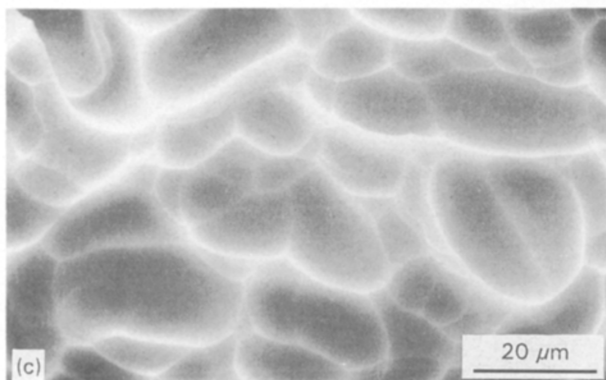



*Figure 2* Transformation of a surface with closed microcracks or flaws into a cusp-like glass surface by wet chemical etching. (a) Initial surface. (b) After etching 0.2 time units. The dashed line indicates the initial glass surface. (c) After etching 1 time unit. (d) After etching 3 time units.



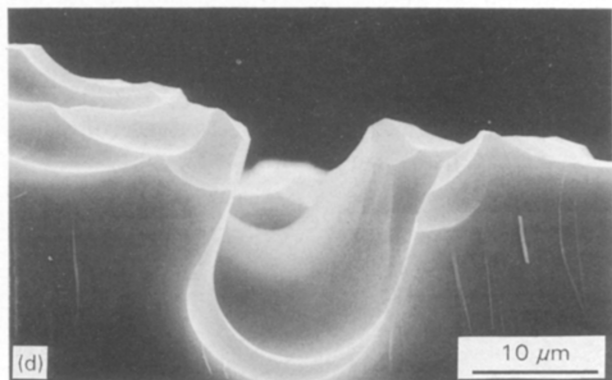




*Figure 3* SEM micrographs of the surface of a soda lime silicate glass after particle erosion and etching in 2 wt % HF. (a) After 2 min, surface view showing the opened microcracks. (b) After 2 min, cross section. (c) After 30 min, surface view showing the cusp-structure. (d) After 30 min, cross section.

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mechanical actions such as grinding or particle erosion [36, 37]. Fig. 2 shows how a closed flaw or microcrack is etched open and this surface defect is gradually transformed into a cusp as etching proceeds. This process indicates a diffusion of fluorine species over the glass surface into the closed crack, which is fast compared to the dissolution rate. When inhomogeneities are present in the bulk of the glass, e.g. in fused silica prepared by melting quartz sand, these will also give rise to a cusp-like surface structure on etching [38].

Etching glass surfaces with very small microflaws results in a surface containing very small cusps (~ 1 μm), as are shown in Fig. 1. When a glass surface severely damaged by particle erosion is etched, the surface reaction process opens all cracks which are present in large numbers at the surface. Initially this leads to the formation of a three-dimensional labyrinthian surface (Fig. 3a and c). This is also gradually transformed into a cusp-like structure (Fig. 3b and d), but with much larger cusps (~ 10 μm) than those shown in Fig. 1.

## 3. Effect of etchant composition

The reaction mechanisms discussed in Section 2.1 all indicate a difference in reactivity between the HF molecule and the $HF_2^-$ ion and a catalytic effect of $H^+$ ions. The concentration of these species which can be modified by adding, for example, fluorides or strong acids will determine the dissolution rate of a glass. These effects will be discussed in this section.

### 3.1. HF concentration

Fig. 4 shows the etch rate $V_E$ of vitreous $SiO_2$ in HF solutions versus concentration of HF, compiled from a large number of literature sources. The curve shows that in the middle concentration range (1–10 wt % HF) the etch rate is approximately linearly dependent on the HF concentration. At higher HF contents the etch rate increases more rapidly, an effect which can be explained by assuming that higher polymeric $H_nF_{n+1}^-$ ions are present in the etchant [5], which are more reactive towards the siloxane bonds [6, 24].

Fig. 5 shows that the activation energy for the dissolution of vitreous $SiO_2$ is dependent on the HF content. At low concentrations $E_a$ increases significantly with HF content, to the level of 30–35 kJ mol$^{-1}$ at about 10 wt % HF, with a tendency to decrease again in concentrated HF solutions. This concentration-dependent $E_a$ can be explained by assuming the presence of more than one reactive species [39]. At higher HF contents this could be caused by the assumed presence of $H_nF_{n+1}^-$ ($n > 1$) ions. The cause for the more drastic increase at small HF contents is not clear.

### 3.2. Addition of strong acids

By adding strong acids such as HCl, $HNO_3$ and $H_2SO_4$ to HF solutions, the concentration of the more

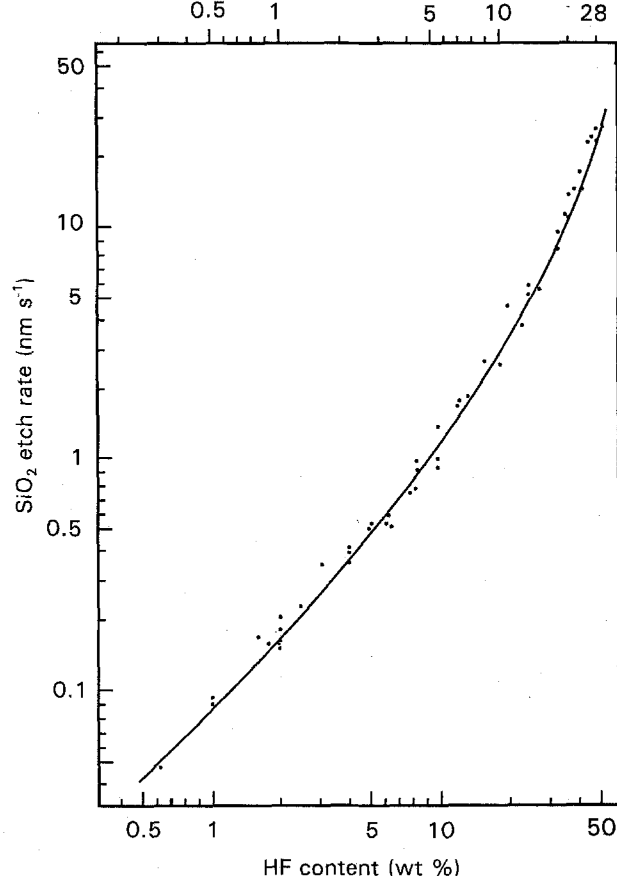


*Figure 4* Collected etch rate data of $SiO_2$ in HF aqueous solutions at 23 ± 2 °C as a function of the HF content of the etchant [6, 16, 32, 39–45].

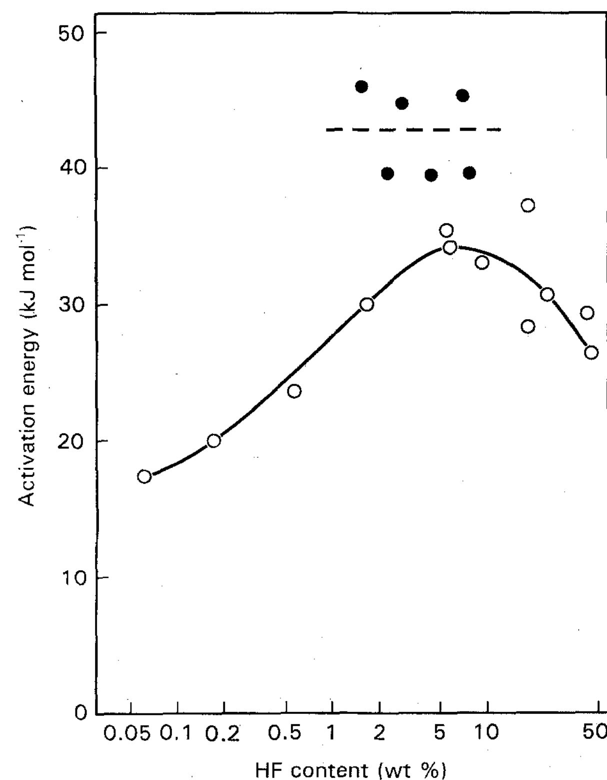


*Figure 5* Activation energy of the dissolution reaction of $SiO_2$ as a function of the HF content in: ○ HF etchant [6, 8, 17, 40, 45, 46]; ● BOE etchant [6, 47, 48].

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Equations 2a and b. At $H^+$ concentrations larger than 1–2M the etch rate is enhanced [8, 9]. This is due to the catalytic role of the $H_3O^+$ ions in the dissolution process [13–15], which more than compensates for the reduction in the $HF_2^-$ concentration which is already low in these etchants. For alkali calcium silicate glasses no difference in etch rate enhancement was observed between the three acids mentioned above [14]. Only in etchants containing both HF and concentrated $H_2SO_4$ were the etch rates higher than for the HF/HCl or $HF/HNO_3$ etchants, an effect which can be ascribed to the formation of the strong fluorine-containing $HSO_3F$ acid.

### 3.3. Addition of $NH_4F$

The addition of $NH_4F$ to an HF solution shifts Equilibria 2a and b, resulting in an increase in the $HF_2^-$ concentration as well as in the pH. Etching solutions prepared by mixing a concentrated 40 wt % $NH_4F$ solution with a concentrated 49 wt % HF solution in various ratios (usually from 6:1 to 10:1) are used extensively for etching $SiO_2$ and doped $SiO_2$ thin films in IC processing (see Section 5.2) [15–17]. They are often referred to as buffered oxide etches (BOEs) or buffered HF (BHFs).

Due to the dependence of the etch rate on the HF and $HF_2^-$ concentrations, the addition of $NH_4F$ affects the etching behaviour significantly [17]. Adding $NH_4F$ to a 6 wt % HF solution first increases the etch rate $V_E$ up to about 10–15 wt % $NH_4F$, where a maximum in $V_E$ is observed. At larger $NH_4F$ contents $V_E$ is found to decrease again. It is thought that at low $NH_4F$ contents the etch rate is enhanced because the concentration of the more reactive $HF_2^-$ ions increases. Furthermore, cations such as $NH_4^+$ (as well as $Li^+$ and $Na^+$) also have a catalytic effect on the dissolution reaction of $SiO_2$ [13]. At higher $NH_4F$ contents the reaction with HF becomes increasingly more important, because the $HF_2^-$ ions are inactivated by complexation with $NH_4^+$ ions [17].

The activation energy for $SiO_2$ dissolution in BOEs is significantly higher than for HF etchants with the same HF content (Fig. 5). This could be caused by the higher activation energy for the reaction involving $HF_2^-$ ions which predominate in BOEs as compared to that of HF [6], which are mostly present in the HF solutions.

At high $NH_4F$ concentrations the danger of $(NH_4)_2SiF_6$ precipitation, particularly at the glass surface, increases, due to its limited solubility [15, 50] (see also Table I). Its solubility is lowered from 20 wt % in a 6 wt % HF solution to about 1 wt % in a 40 wt % $NH_4F$ + 6 wt % HF solution [15].

### 3.4. Solubility of fluorides and hexafluorosilicates

An overview of the solubility of the most relevant bifluorides and hexafluorosilicates in a 30% HF solution [50] is presented in Table I. The low solubility of alkaline earth and lead hexafluorosilicates can cause the precipitation of these compounds particularly

bifluorides and hexafluorosilicates in 30 wt % HF solutions at 25 ± 2 °C [50]

| | $HF_2^-$ | $SiF_6^{2-}$ |
|---|---|---|
| $NH_4^+$ | 75.8 | 14.4 |
| $Na^+$ | 3.7 | 1.2 |
| $K^+$ | 32.8 | 0.6 |
| $Mg^{2+}$ | 0.0072 | Not formed |
| $Ca^{2+}$ | 0.0056 | Not formed |
| $Ba^{2+}$ | 0.084 | Not formed |
| $Zn^{2+}$ | 11.44 | 5.8 |
| $Pb^{2+}$ | 0.022 | Not formed |
| $Al^{3+}$ | 18.02 | 6.07 |

when multicomponent glasses incorporating these bivalent cations are etched in concentrated HF solutions. For instance, precipitations are observed when a soda lime silicate glass (with about 15 wt % $Na_2O$ and 10 wt % CaO) is etched in HF solutions with contents larger than 30 wt %.

### 3.5. Other additives

Factors such as wetting of the glass and foam formation on the etch solution become of prime importance when an extreme control of the wet chemical etching process has to be realized. This is the case for etching holes in $SiO_2$ film with submicrometre dimensions, as is required in the VLSI and ULSI IC technologies. It then becomes necessary to add HF-resistant additives, such as surfactants [15]. The effect of many surfactants on the etch behaviour has been reported [40].

## 4. Effect of glass composition

The incorporation of other oxides in vitreous $SiO_2$ modifies its interconnected three-dimensional siloxane structure. In this respect two types of oxides can be distinguished: network modifiers and network-forming oxides. The effect of the incorporation of both oxide types is discussed in this section.

### 4.1. Effect of network-forming oxides

$SiO_2$ films doped with the network-forming oxides $P_2O_5$, $B_2O_3$ and $As_2O_3$ are widely applied in the IC industry, and therefore they have been studied extensively. These network-forming oxides are incorporated into the silicate network structure or they form a separate network which is intimately mixed with the silicate network.

When a network-forming oxide $A_xO_y$ is added to $SiO_2$, ≡Si–O–A– and –A–O–A– bonds are formed [51], which also have to be broken in order to dissolve the material. The chemistry of the breakage of these bonds is not necessarily the same as for the siloxane bonds and the etch rate will be affected. Fig. 6 shows the effect of the incorporation of $P_2O_5$, $B_2O_3$ and $As_2O_3$ into $SiO_2$ thin films on the etch rate in 10:1 buffered oxide etch (10 $NH_4F$ (40 wt %):1 HF (49 wt %)). For $P_2O_5$ [26, 52] and $As_2O_3$ [53] the etch rate increases, indicating that the rate of breakage of P–O and As–O bonds is high compared to that of the

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