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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 $K_1 = 6.7 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ and $K_2 = 0.26\,\mathrm{mol\,l^{-1}}$ [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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determine the reaction rate. The specific property of 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 $\equiv$Si–F and $\equiv$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. Θ 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 reported by Judge [6], who obtained for thin film SiO_2 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 rate of silicate glasses is kinetically controlled, it is only 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 etched in a 2.5 wt % HF + 4.6 wt % HNO_3 solution [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

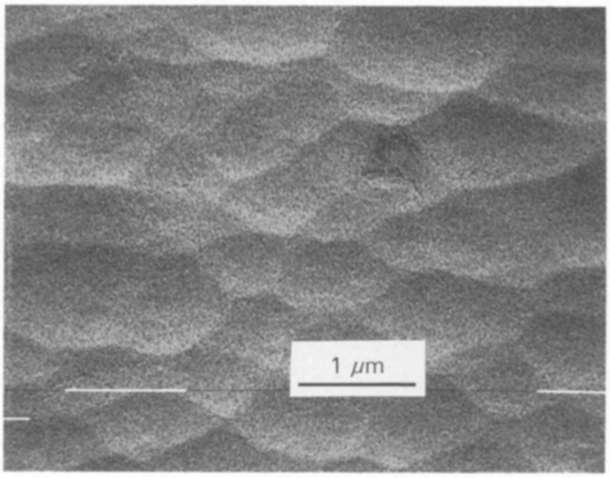

Figure 1 SEM micrograph showing the cusp-like surface obtained after etching a polished soda lime silicate glass surface [14].

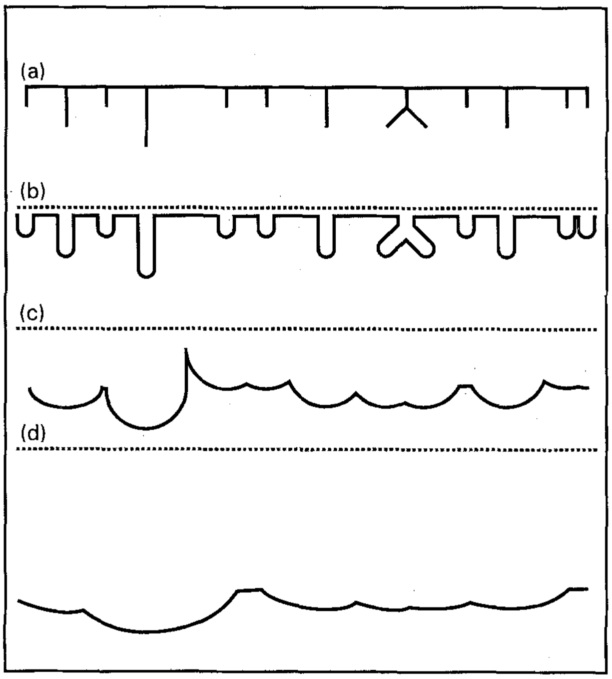

Figure 2 Transformation of a surface with closed microcracks or flaws into a cusp-like glass surface by wet chemical etching. (a) Initial surface. (b) After etching 0.2 time units. The dashed line indicates the initial glass surface. (c) After etching 1 time unit. (d) After etching 3 time units.

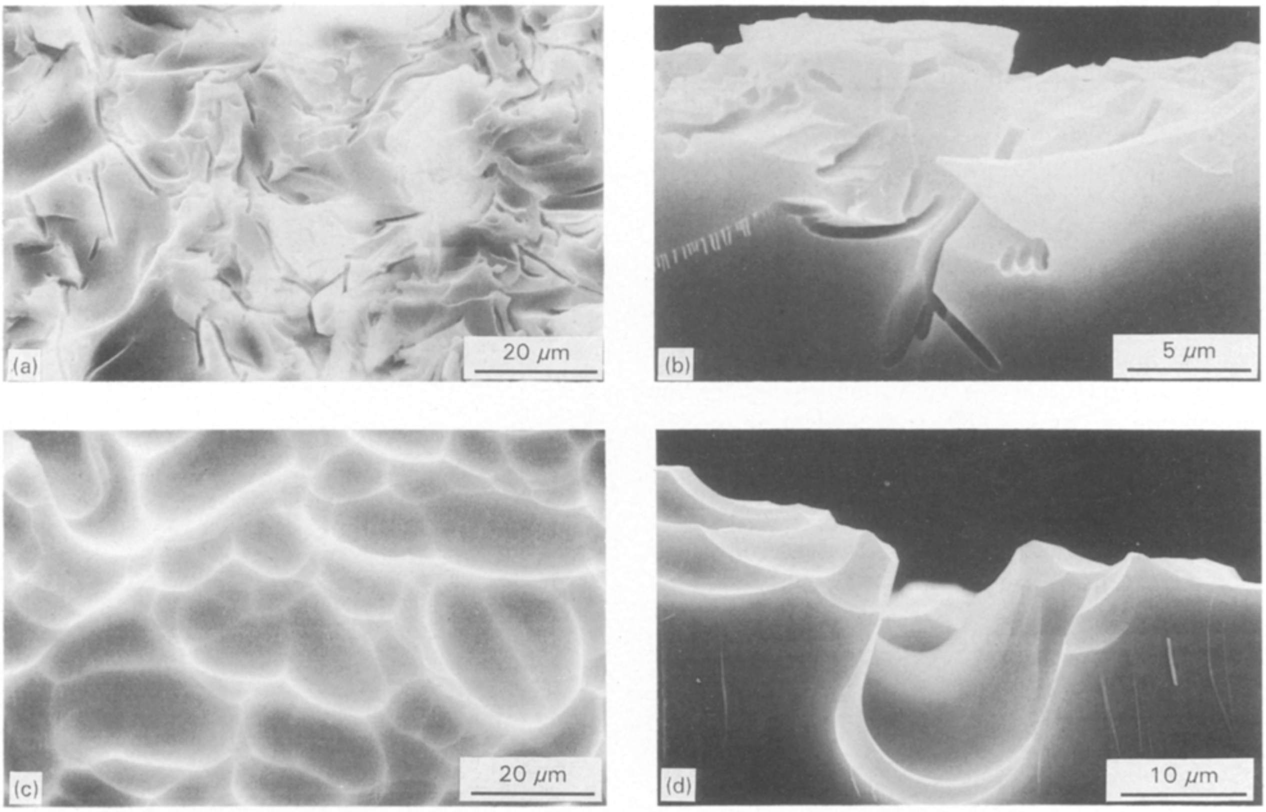

Figure 3 SEM micrographs of the surface of a soda lime silicate glass after particle erosion and etching in 2 wt % HF. (a) After 2 min, surface view showing the opened microcracks. (b) After 2 min, cross section. (c) After 30 min, surface view showing the cusp-structure. (d) After 30 min, cross section.

present after polishing to large cracks formed by 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

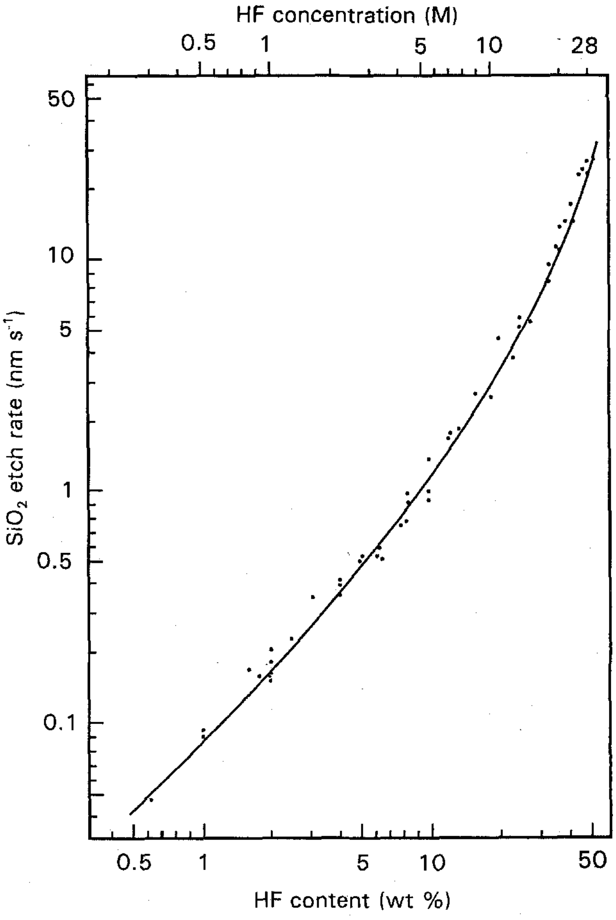

Figure 4 Collected etch rate data of SiO_2 in HF aqueous solutions at 23 ± 2 °C as a function of the HF content of the etchant [6, 16, 32, 39–45].

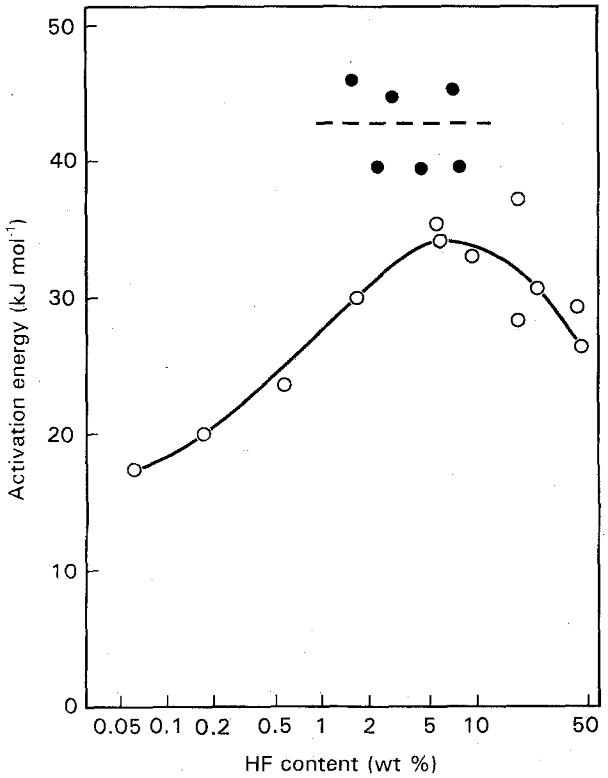

Figure 5 Activation energy of the dissolution reaction of SiO_2 as a function of the HF content in: ○ HF etchant [6, 8, 17, 40, 45, 46]; ● BOE etchant [6, 47, 48].

reactive HF_2^- ion in the etchant is lowered, following 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 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 %.

TABLE I Solubility (g per 100 g solvent) of the most relevant bifluorides and hexafluorsilicates 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

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

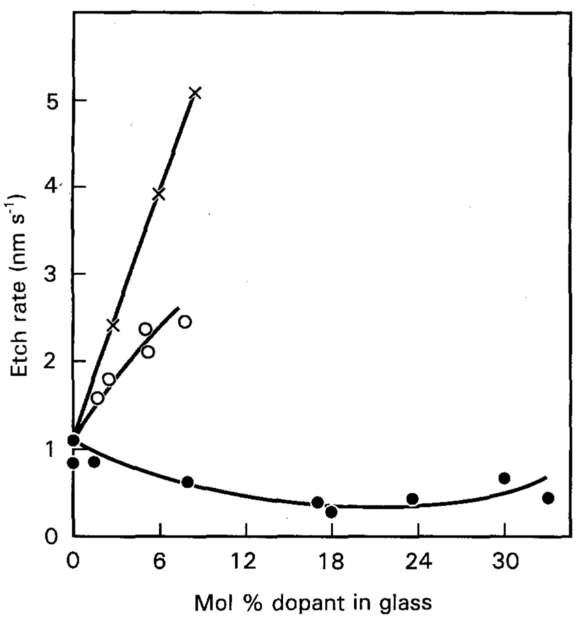

Figure 6 Effect of B_2O_3 (●) [33, 54], P_2O_5 (×) [33] and As_2O_3 (○) [29] content on the etch rate (at 23 ± 2 °C) of annealed doped SiO_2 films in BOE (10:1).

Si–O bond. To a first approximation the etch rate is determined by the SiO_2 content of the glass. The etch rate for SiO_2 doped with B_2O_3 in a buffered oxide etch (10:1) first decreases significantly with the B_2O_3 content (Fig. 6), indicating that the etch rate in buffered HF is primarily controlled by the breakage of $=B{-}O{-}Si\equiv$ bonds [34, 54]. At high B_2O_3 contents the $=B{-}O{-}B=$ bonds become more abundant [51] and these bonds are readily attacked by water, as indicated by the increased hygroscopicity.

The effect of B_2O_3 on the etch rate is found to depend on the type of etchant. In contrast to buffered oxide etches, in HF- or HF-strong acid-based etchants with low pHs the etch rate increases with B_2O_3 content [25, 34]. In these etchants the dissolution rate is limited by the SiO_2 content of the glass, because the $=B{-}O{-}Si\equiv$ and $=B{-}O{-}B=$ bonds are more rapidly attacked by H^+ ions, which are almost absent in the buffered oxide etch.

Three component all-network-forming oxide glasses, such as B_2O_3–P_2O_5–SiO_2 [55, 56] and Al_2O_3–B_2O_3–SiO_2 [34] glasses, have also been studied. The former glasses, known as BPSG glasses, are used widely in IC technology. At the relatively low temperature of 800 °C these materials have a low viscosity compared to SiO_2, so they will flow over sharp topography steps, smoothing the surface of a processed silicon wafer [30, 56]. The etch rate of BPSG glasses is determined by the boron and phosphor content. In BOE B_2O_3 has a decreasing effect, while P_2O_5 enhances the etch rate [55, 56].

Implantation of ions (Ar^+, P^+, N^+ and B^+) into a vitreous SiO_2 partially destroys the network structure. Consequently, the etch rate is enhanced, increasingly so with higher implantation doses [57]. This property has been used to determine implantation profiles of B^+ [27] and P^+ ions [27, 57]. SiO_2 prepared by implantation of large doses of O^+ ions into Si and subsequent annealing has an etch rate slightly lower than that for thermal SiO_2 [44], which is thought to be due to the presence of small concentrations of $\equiv Si{-}Si\equiv$ bonds in this material.

4.2. Effect of network-modifying oxides

Network modifiers such as Na_2O, K_2O, CaO and BaO are incorporated by breaking a siloxane bond, forming non-bridging oxygens by the reaction:

$$Na_2O + \equiv Si{-}O{-}Si\equiv \;\rightarrow\; 2 \equiv SiO^- \cdot Na^+$$

In this way the three-dimensional silicate network structure is partially broken down. The presence of already broken bonds will strongly increase the etch rate for the glass, as is clearly observed in Fig. 7, which shows the increase in etch rate as Na_2O is introduced into SiO_2.

Cations from the network-modifying oxides are bonded ionically to the silicate network and therefore they are relatively mobile. In aqueous solutions (such as HF etchants) these mobile monovalent and bivalent ions (such as Na^+ and Ca^{2+}) are leached out of the glass and are replaced by ion-exchanged H_3O^+ ions, which form $\equiv SiOH$ groups [19, 58]. The formation of this hydrated silica film preceeds the dissolution of the material in the HF etchant [21, 59]. Due to its open structure and the presence of already broken siloxane bonds it will dissolve more rapidly than vitreous SiO_2 and increasingly so as the network modifier content is larger. Furthermore, there are indications [21] that fluorine species also diffuse into this hydrated material attacking Si–O–Si bonds positioned within the hydrated material. The small effect on the etch rate by partially replacing Na_2O by CaO in a sodium calcium silicate glass [21] is an indirect proof for this mechanism. The formation of such a hydrated film is also supported by microhardness measurement data of etched sodium calcium glass surfaces. This data indicates the existence of a relatively soft surface layer extending to a depth of approximately 1 μm [60].

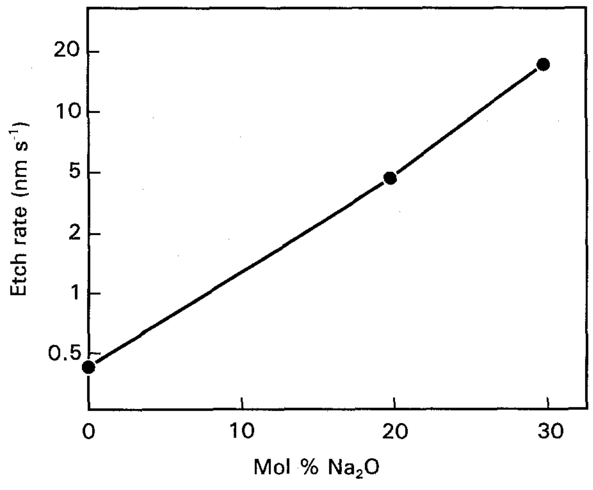

Figure 7 Effect of Na_2O content on the etch rate of $xNa_2O.(1-x)$ SiO_2 glass at 25 °C in 5 wt % HF [21].

4.3. Siliconoxynitrides

With chemical vapour deposition (CVD) techniques it is possible to prepare thin films of vitreous siliconoxynitrides. The incorporation of nitrogen considerably lowers the etch rate for these materials [61, 62], because the Si–N bonds are not attacked by HF solutions. For example, in a 48 wt % HF solution the etch rate for a SiO_2 film prepared by high-temperature CVD is 70 nm s^{-1}, for Si_2ON_2 it is 8 nm s^{-1} and for Si_3N_4 it is reduced to 0.2 nm s^{-1} [62].

4.4. Multicomponent silicate glasses

In multicomponent glass systems the compositional dependence of the etch rate becomes more complex as the number of components increases. In these glasses different network-forming and network-modifying oxides can be present, resulting in complex glass network structures. The etching rate of technologically important multicomponent glasses has been systematically studied by Honigmann [50], Molchanov [63] and Spierings [21]. The etching of lead silicate glasses was studied by Hasegawa [64]. From these papers the following picture arises.

(i) The etching rate of the glass increases as the SiO_2 content of the glass is lowered, because less 'silicate' network structure has to be broken by the reaction with HF.

(ii) Replacement of monovalent alkali ions by bivalent alkaline earth ions has a insignificant effect on the etch rate and this is in keeping with the view that the 3D network structure is unchanged. This also supports the view that a hydrated silica film is formed by ion exchange.

(iii) Introduction of other network-forming oxides (B_2O_3, Al_2O_3) at small concentrations lowers the etch rate. At larger concentrations the etch rate increases again [63].

The etch rate has been linked to the degree of linkage of the network structure and the concentration of SiO_2 [21, 64]. Ostaf'ev *et al.* [65] linked the etch rate of multicomponent optical glasses to their annealing temperatures and the expansion coefficients, however, both of these properties are also related to the network structure and the SiO_2 content of the glass. Phase separation, as occurs, for instance, in sodium borosilicate glasses, modifies the network structure and consequently changes the etch rate [66].

5. Applications

Applications of silicate glass etching are found in many areas of technology, as well as in daily life. In this section the most important applications are discussed.

5.1. Etch technology

The most simple and widely applied way to etch glass objects is by immersion into the HF-containing solution. Although the glass etch rate is not limited by the diffusion from and to the glass surface, the homogeneity and effectiveness of etching can be increased by stirring, bubbling and moving the object or by applying ultrasonic agitation of the etchant. For planar substrates such as glass wafers the homogeneity of etching can be increased by rotating the substrate and spraying the etchant onto the rotating wafer [67]. This process has some advantages as compared to immersion etching. Fresh etchant is supplied and reaction products are continuously removed, which results in better process control and uniformity. Aerosol jet etching with HF solutions has also been reported and is used to increase the anisotropy of etching [68].

When a glass object has to be etched locally, the glass is partially protected by covering it with a material which is resistant to the etchant. This can be a wax applied manually, but when dimensions of patterns in the submillimetre or even submicrometre range have to be realized, photolithographic techniques have to be applied which are more appropriate to planar substrates.

In IC technology, etching of SiO_2 glass-based films is predominantly used to pattern the film, e.g. for contact hole etching [69, 70], in order to make contact with the underlying silicon. The glass film is partly masked, before etching, with a photoresist which is patterned using lithographic techniques. After etching the photoresist mask is removed, e.g. by dissolution in acetone. Due to the small dimensions, it is necessary to work in clean rooms using specially developed particle-free chemicals. In pure HF solutions delamination of the photoresist occurs due to attack at the glass–photoresist interface. This can be avoided by using HF solutions which are buffered with NH_4F to increase the pH to about 5–6 [26, 71].

In ultra large scale integration (ULSI) of ICs the size of the contact holes is reduced into the submicrometre range. Consequently, the requirements for wet etching become very stringent [15]. In order to apply the buffered oxide etch (BOE), the etchant has to be optimized with respect to the NH_4F concentration in order to avoid the precipitation of $(NH_4)_2SiF_6$ at the SiO_2 surface [15, 72]. Furthermore, surfactants have to be added, such as aliphatic amines and aliphatic alcohols [15].

The photoresist delamination is a problem which occurs when long etching times or concentrated HF solutions are used. In such cases, a second HF-resistant film, such as chromium, can be applied as the HF etch mask. The chromium film is patterned with a photolithographic procedure and the patterned chromium film is, in turn, used as the etch mask for the glass [14]. This technique can be used to etch deep grooves into a borosilicate glass such as Pyrex (Fig. 8).

5.2. Silicate glass etching in IC technology

The deposition of SiO_2 and doped SiO_2 thin films on silicon wafers is widely applied in IC technology [69, 70]. Their most important use is for the intermetallic dielectric isolation barrier between electrically conducting parts of the IC. Many methods have been developed to prepare such thin films. With the high temperature (800–1200 °C) oxidation of mono-crystal-

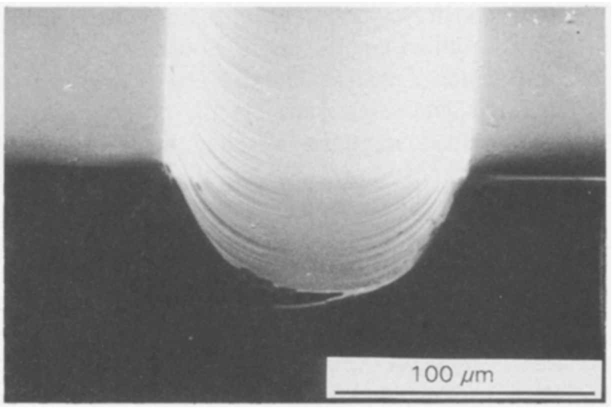

Figure 8 Semicircular groove etched into Pyrex glass using a chromium mask which was structured using photolithographic means.

line silicon in O_2 or H_2O, a SiO_2 film is formed on the surface of the silicon [73]. The etch rate of this so-called thermal oxide film is very similar to that of fused silica [74], which indicates a large similarity in structure. The thermal oxide layer serves as an etch rate standard for thin films prepared by other methods.

Techniques for the preparation of SiO_2 and doped SiO_2 films include various chemical vapour deposition (CVD) methods. When the process is performed at atmospheric pressure it is referred to as APCVD, similarly at reduced or low pressure it is known as LPCVD and when deposition is enhanced using a plasma the process is referred to as PECVD. For all these CVD methods many variant processes have been developed with respect to starting materials, pressures, additives, temperatures and equipment design. Other methods for SiO_2 film deposition include sol–gel processing [75], sputtering [74, 76], E-beam evaporation [74] and anodic oxidation [77]. Overviews of these deposition processes are given in IC technology handbooks [69, 70].

It has to be mentioned at this point that in present-day IC technology with sub-micrometre dimensions, plasma etching processes have largely replaced wet-etching with HF-containing solutions. However, wet-chemical etching still remains a simple and cheap method to etch SiO_2-based films in this field.

5.2.1. *Etching of as-deposited films*

Prior to annealing, as-deposited SiO_2 films are structurally and compositionally imperfect compared to fused silica or thermal SiO_2 films. These imperfections, which include non-stoichiometry, porosity and impurities, are related to the type of deposition technique and post-deposition processing [67, 68, 74, 78]. As-deposited SiO_2 films prepared by APCVD using $SiH_4 + O_2$ or via sol–gel routes are stoichiometric, but are also porous and incorporate $\equiv$SiOH groups and adsorbed H_2O [74]. PECVD films can contain Si–H groups [79, 86], while reactively sputtered films can be oxygen deficient [80]. The etch rate is found to be sensitive to all these imperfections. In general they lead to a higher etch rate for an as-deposited film compared to thermal SiO_2 films [17, 74]. In many papers dealing with deposition techniques of SiO_2 glass and related films the etch rate in HF solutions is used to monitor the quality of the films [67, 71]. For instance, higher deposition temperatures yield denser films with lower etch rates, as has been reported for PECVD [81] and APCVD [78, 82] films. Furthermore, storage of (PSG) films in a dry ambient environment at a relatively low temperature (450 °C), leads to a decrease in etch rate due to a compaction process [83].

Etch rate results for as-deposited and heat-treated films have been reported for APCVD [58], LPCVD [84], PECVD [58, 79, 85–87], sputtering [76, 88], sol–gel [75] and anodic SiO_2 [77]. Reviews of the early work in IC technology were published in 1977 [74] and 1986 [72]. To illustrate the variations in etch rate for the different SiO_2 films, Table II gives the etch rates for SiO_2 films prepared by different methods in the author's laboratory.

The porosity of the as-deposited stoichiometric SiO_2 films is manifested by a lower density and a lower refractive index. Fig. 9 shows the etch rate versus the refractive index (as a measure of porosity) for stoichiometric SiO_2 films prepared by APCVD [89] and sol–gel [75]. The difference in behaviour between the two films probably reflects the difference in pore

TABLE II Etch rate in buffered oxide etch (20:1) of some important types of SiO_2 thin films applied in IC technology

Thermal oxide	0.28 nm s^{-1}
LPCVD (TEOS + O_2)	0.53 nm s^{-1}
APCVD ($SiH_4 + O_2$)	0.95 nm s^{-1}
APCVD + anneal 500 °C	0.74 nm s^{-1}
APCVD + anneal 600 °C	0.71 nm s^{-1}
PECVD ($SiH_4 + N_2O$)	0.41 nm s^{-1}

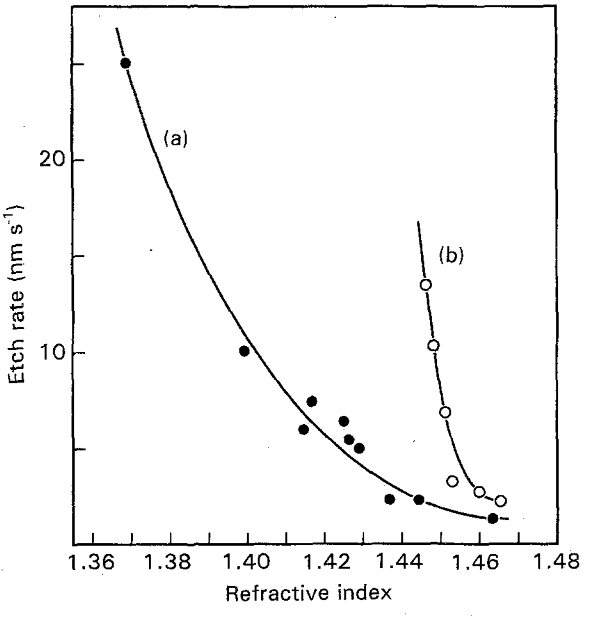

Figure 9 Dependence of the etch rate at 23 ± 2 °C on the refractive index for SiO_2 films, reflecting the influence of the porosity of the films for: (a) Sol–gel films prepared from solutions with different water/silicon alkoxide ratios, etchant BOE [75]; (b) APCVD films prepared with different anneal temperatures, etchant P-etch [89].

structure. When the porosity is sufficiently large to allow the etchant to penetrate throughout the complete film, etching takes place throughout the film volume and a very high etch rate is obtained [90].

Non-stoichiometric SiO_2 films with an Si/O ratio > 0.5 can be prepared by PECVD with excess SiH_4 [79] or by reactive sputtering at too low O_2 pressures [80, 91]. The etch rate of these SiO_x ($x < 2$) films is lower than that of stoichiometric SiO_2 due to the presence of $\equiv$Si–Si$\equiv$ bonds.

5.2.2. Etching of annealed films

Annealing as-deposited films densifies the material. This densification process consists of the removal of adsorbed H_2O and H_2O from the condensation reaction $\equiv SiOH + HOSi\equiv \rightarrow \equiv Si\text{–}O\text{–}Si\equiv + H_2O$ followed by molecular compaction [92]. Densification leads to a lower etch rate for the films [55, 56, 75, 77, 79, 83, 92, 93]. Fig. 10 shows this effect for an APCVD [92], a PECVD [56] and a sol–gel film [75]. After densification of a film by annealing at sufficiently high temperatures, the etch rate becomes comparable to that of a thermal SiO_2 film.

5.2.3. Etching dopant glass films

Doping monocrystalline silicon with boron or phosphor is an essential step in IC processing [69, 70]. Presently, this is commonly achieved using ion implantation, but earlier B or P doped SiO_2 films deposited by CVD methods were used for this aim. During an annealing step B and P atoms diffuse into the underlying silicon, thus doping the material. Afterwards these films are removed by etching in a fast etching solution such as the so-called P etch, with composition 2 HNO_3(70 wt %) : 3 HF (49 wt %) : 60 H_2O (by volume) [52, 89].

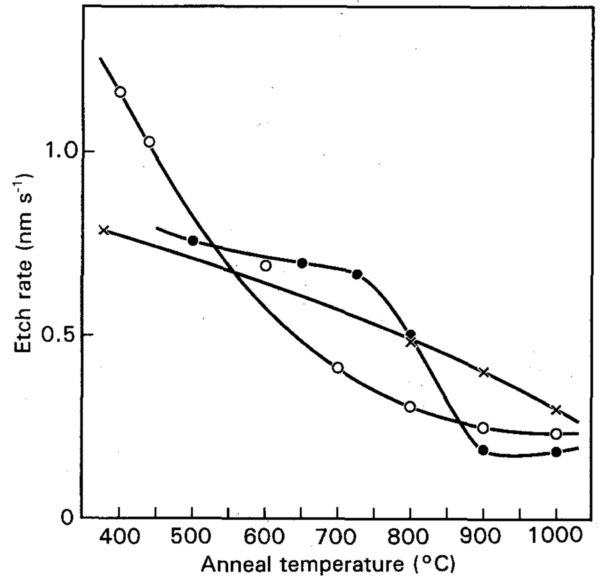

Figure 10 Effect of annealing as-deposited SiO_2 films on the etch rate at 23 ± 2 °C of: ○ APCVD films, P-etch [92]; ● sol–gel films, etchant BOE [75]; × PECVD films, P-etch [56].

5.2.4. Slope etching

Aqueous HF solutions etch glasses isotropically. When a glass is etched through a window in a masking film such as a photoresist or chromium film, a wall is formed at the edge of the window. When the masking film has a good adhesion on the glass, a semi-circular wall is formed (Fig. 11a). Controlled delamination of the photoresist during etching at a fixed rate results in a tapered wall structure at the edge of the window [94, 95]. A similar tapering is obtained in a more controlled way by applying an extra film between the glass and the masking material which has a higher etch rate than the glass [96]. Figure 11b shows this effect. The ratio between the etch rate of this extra film and the glass determines the slope of the edge.

5.2.5. Cleaning silicon wafers

In the standard cleaning processes for silicon wafers a short (10–20 s) dip in a diluted (1 wt %) aqueous HF solution is applied to remove the 1–2 nm thick natural SiO_2 film, which is present at ambient conditions on mono-crystalline silicon [97, 98]. Dipping in the aqueous acid changes the surface of the wafer from exhibiting hydrophilic to hydrophobic behaviour.

5.3. Glass surface modification

Etching can be used to modify the constitution or morphology of a glass surface. In this section the most important applications are discussed.

5.3.1. Glass surface cleaning

Processing silicate glasses for many purposes requires a clean surface. For instance, the etching processes discussed here can only be applied satisfactorily when the glass surface is free from contaminants. The methods necessary to clean a glass surface depend strongly on the type of contamination [99]. Consequently, for each cleaning problem a dedicated process has to be designed, also taking the glass composition into account [100]. In general, cleaning methods are preferred which do not etch or otherwise chemically attack the glass object, such as for instance organic solvents, aqueous detergent solutions or

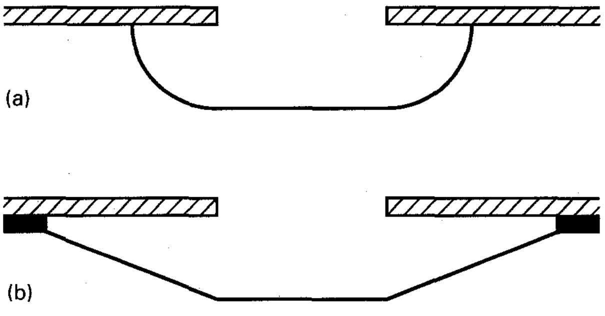

Figure 11 The contour of the wall at the edge of a window etched in an HF solution. (a) Good adhesion of the masking material. (b) Controlled etchant penetration between masking material and glass either by controlled delamination or the addition of an extra fast dissolving film.

strong acids. However, for some contaminants which are not attacked by these liquids, it is necessary to use a process which dissolves the glass surface and thus frees the contaminant from the surface by using the lift-off principle [100]. Aqueous HF etching is used in that case. The formation of insoluble fluorides can be avoided by adding a strong acid.

5.3.2. *Glass strengthening*

The strength of a glass object is determined by the quality of the surface with respect to the presence of surface flaws. These flaws serve as concentration points for stresses applied on the glass. Removing the surface flaws by dissolution of the damaged surface layer is an effective way to increase the strength of a glass body, even by a few orders of magnitude [37]. The strength of a soda lime silicate glass which was not protected during handling was found to increase from about 100 to about 3000 $\mathrm{MN\,m^{-2}}$ after removing a layer of 400 μm from its surface. For a polished aluminosilicate glass a layer of 30 μm has to be removed to increase its strength four-fold [101].

5.3.3. *Frosting, polishing*

Etching can be used for frosting a glass surface. This occurs when reaction products are formed at the surface during etching and which for some period prevent the dissolution of the underlying material. In this way, pyramidal elevations are formed at the surface, which cause the light scattering necessary for obtaining the frosting effect [50]. To achieve this, HF solutions are used with large concentrations of NH_4F, so $(NH_4)_2SiF_6$ can form easily. Frosting also occurs when large concentrations of alkali fluorides are added [102]. Pastes can be used for locally frosting the glass surface. These consist of an HF solution with insoluble particles such as $BaSO_4$ added. This frosting process is widely applied to the inside of incadescent light bulbs to realize diffuse light scattering [103].

By alternating short etch and washing steps of the glass object, etching can be used to polish a glass surface chemically [104, 105]. This process is mostly used for lead silicate glasses using concentrated $HF–H_2SO_4$ mixtures, e.g. $1\,H_2O:1\,HF(49\ \mathrm{wt}\,\%):3\,H_2SO_4(96\ \mathrm{wt}\,\%)$ (by volume). Although these surfaces are less smooth than mechanically polished ones, it is possible to transform ground surfaces into optically transparent surfaces.

5.4. Micromachining

The increasing trend towards miniaturization in present day electronic and optical device technology has caused a drive towards new fabrication technologies. These technologies are referred to as micromachining. It is well established that chemical processes play an important role in micromachining [106, 107]. In this field silicate glasses are also used.

5.4.1. *Photosensitive glasses*

In the early fifties Stookey (Corning) developed glasses which are photosensitive [108, 109]. These glasses, with Li_2O and SiO_2 as main components [109, 110], contain easily reducible ions and so-called sensitizer polyvalent ions. Usually these are Ag^+ and Ce^{3+} ions. When the glass is exposed to u.v. light (310 nm), the reaction

$$Ce^{3+} + Ag^+ + h\nu \rightarrow Ce^{4+} + Ag^0$$

takes place. On baking the glass at 400 °C, the silver atoms coagulate and form small particles (~ 8 nm). At 600 °C these particles serve as nucleation sites for the crystallization of lithium silicate crystals in the glass matrix. The etch rate for the crystallized glass is about 50 times larger than that of the glass, so the crystallized glass can be etched preferentially [109]. Three-dimensional structures can be obtained from glass plates when masking techniques are used during u.v. exposure, so the glass is only locally exposed. Fig. 12 shows a micrograph of an etched glass plate with a hexagonal honeycomb structure obtained in this way.

5.4.2. *Etching optical fibres and other optical devices*

Optical fibres consist of a light-conducting core glass and a cladding glass. The higher refractive index core glass is prepared from SiO_2 doped with, for example, GeO_2 or P_2O_5, while the cladding can be doped with B_2O_3 or F. The etch rate of these materials is determined by the type and level of the dopant and the differences can be used to etch a profiled structure at the end of the fibre which correlates with the dopant profile, which in turn corresponds with the refractive index profile [46]. In this way it is possible to make microlenses at these fibre-ends which are used for efficient coupling of light from laser diodes into the optical fibre [111–113]. Etching can also be used to decrease the diameter of an optical fibre, e.g. for making tapered points at the end of the fibre [114]. To obtain this taper the fibre is dipped into the etchant which is covered with a thin non-mixable liquid, e.g. oil, which controls the miniscus of the etchant at the fibre surface [115]. The immersed part is slowly withdrawn from the etchant producing a tapered point at

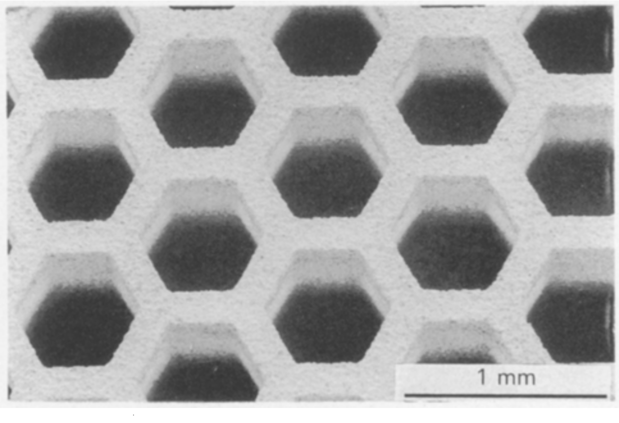

Figure 12 SEM micrograph of a hexagonal honeycomb structure etched into photosensitive glass.

the end of the fibre. By melting the tapered point a small lens for laser diode coupling is formed.

Other applications in guided optics are:

(i) Removal of refractive index dip in the centre of the optical fibre preform tube [116];
(ii) Etching circular grooves which can be filled with higher refractive index material to prepare planar optical waveguides [117].

Etching such grooves as shown in Fig. 8 can also be used in the fabrication of printer heads for use in ink jet printers, of which many examples can be found in the patent literature [118]. The complex groove structure necessary to transport ink to an array of nozzles is etched in the glass substrate using photolithographic techniques. After bonding a flat plate to the etched substrate, the transport canals for the ink are formed.

5.4.3. *Sacrificial film technology*

Sacrificial etching is an effective method developed for fabricating miniaturized mechanical components on planar substrates (e.g. silicon wafers) using IC fabrication technologies. These micrometre sized objects are fabricated using polycrystalline silicon (polysilicon) as the construction material. Polysilicon and BPSG films are subsequently deposited and intermediately structured using photolithographic techniques. In this way complex three-dimensional polysilicon structures can be built which are embedded in the BPSG. After 'sacrifying' the BPSG by etching in aqueous HF solutions, the polysilicon object is released and becomes free-standing. Using this technology many miniaturized microdevices have been fabricated in recent years, including micromotors [119], hinges [120] and cranks [121].

5.5. Miscellaneous applications

5.5.1. *Fusion tracks etching*

High energy heavy ions and fission fragments damage the material when travelling through an insulating material such as glass [122]. These damaged regions have a larger etching rate than the surrounding undamaged material. The track of a particle can be observed by etching the bombarded glass in HF-containing solutions [123, 124]. At the surface the position where a particle enters the material can be observed as a well-defined circular etch pit with a diameter determined by the type and by the energy of the particle. Usually $HF-H_2SO_4$ solutions are used for this purpose.

5.5.2. *Pretreatment of silica sand*

Etching is used to remove impurities from the surface of the quartz sand used for the production of fused silica [49]. The thickness of the layer to be removed is about 30 μm.

6. Concluding remarks

Etching of silicate glasses in HF-containing solutions is used in many areas. Although the mechanism of the reaction is not well understood at a molecular level, sufficient experimental work is available for the satisfactory use of these processes on an industrial scale.

Hydrofluoric acid and other HF-containing solutions, together with the waste reaction products, are considered to be hazardous and poisonous. The disposal of these materials can be difficult. In the semiconductor industry in the USA, for instance, these materials account for 72% of all hazardous waste [125]. It is therefore of prime importance to minimize the quantity of etchant used during processing and to develop methods to regenerate HF-containing solutions [126].

In IC technology the trend to replace wet chemical etching by dry plasma etching processes will help to reduce the quantity of HF-containing wastes. Other large volume application can be found in frosting processes for incadescent lamp bulbs (Section 5.3.3). This process could be replaced by the application of light-scattering coatings to the inside glass surface of the bulb. It will be interesting to see how this conflict between the negative environmental aspects and the relative simplicity of the wet chemical glass etch technology will be resolved.

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