



Chemical etching of glasses in hydrofluoric Acid: A brief review

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ABSTRACT

The removal of material, selectively or non-selectively, from the surface of glasses by using acidic, caustic, or abrasive chemicals is referred to as glass etching. Wet and dry etchings are extensively used for variety of applications, including flow channel designs in fuel cell electrodes. Since precise micro-level etching is challenging, optimization of the etching parameters is important. This paper reviews wet etching of glasses including fused quartz for formation of microchannels and microstructures for a variety of applications. The review also discusses different etch mechanisms including etch parameters and surface microstructure of the etched glass. It is found that HF concentration and etching time play a major role on the resulting surface microstructure of glass materials. The paper also describes the use of HF buffered with NH_4F solutions to improve the quality of the etched surface.

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1. Introduction

Glasses are frequently utilised in everyday life due to their distinctive characteristics. The most remarkable of their qualities are optical transparency and the capacity to endure a wide range of environmental effects. Due to their unusual viscosity-temperature relationship, glasses can be moulded into any required form with relative simplicity. Further, glasses are resistant to most gases and liquids. At room temperature, they can only be dissolved in hydrofluoric acid and other HF-containing aqueous solutions [1]. Hence, for a number of applications, controlled dissolution in HF-based etchants is used to etch away material from glass. In glass etching, three types of methods are used: mechanical, wet, and dry. Ultrasonic drilling, traditional drilling, and powder blasting, electrochemical discharge are all mechanical techniques. Smooth surfaces, on the other hand cannot be created using such techniques. Li et al discussed dry etching of glass in ICP reactors by using SF_6 plasma and Ni mask or bulk silicon as a masking layer and $\text{C}_4\text{F}_8/\text{He}$ plasma [2] or $\text{C}_4\text{F}_8/\text{CHF}_3$ plasma [3]. Because the process is slow (etch rate 0.5 nm/min [4]), it will only be

utilised for profiles with vertical walls. Aside from that, wet etching is a cost-effective option.

Etching solutions like concentrated HF (49%) [5,6], HF/HCl [7], or traditional HNA ($\text{HF}/\text{HNO}_3/\text{H}_2\text{O}$) [8] have widely been employed for etching glass. Despite its non-vertical profiles, wet etching of glass continues to interest micro fluidic researchers because of its benefits such as simplicity, cost effectiveness, outstanding etch selectivity and low surface roughness. Glass is primarily composed of SiO_2 , with small amounts of metals such as Ca, Mg, K, Na and related oxides, as well as modest additions of Al_2O_3 and B_2O_3 . Because different additives have different etch rates, the etched profile and etch rate for the glass substrate vary with different compositions [9].

Wet chemical etching of glasses in aqueous HF solutions is a subject that has studied for many years. Scheele et al. reported about the discovery of HF in 1771 [10] and then is being studied more extensively, Microfluidic components for a micro-peristaltic pump to be integrated in a tiny polymerase chain reaction (PCR) device are made via deep etching. Through holes for liquid access and electrical contacts, as well as a 200 m thick pump diaphragm, are among the components. This novel masking approach expands the options for fabricating microfluidic devices on glass surfaces. In various fuel cells, wet/dry etched glass surfaces with various patterns may be utilised as cathode and anode of fuel flow channels.

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In this paper, we present a brief review of the reaction mechanism, etch rate, under cut, surface morphology of etched glass surfaces and discuss the influence of glass kinds, etchant types, and hard mask layers on glass etching applications.

2. Wet etching mechanism and role of etch parameters

Only Hydrofluoric Acid or other HF-containing aqueous solutions are used to etch glasses. The fundamental chemical formula for HF dissolving silicon dioxide is shown in equation (1) [11].



The corrosive Hydrogen ion (H^+) and the poisonous fluoride (F^-) that makes up HF operate in two ways. The acid corrodes the surface of glass, allowing the harmful fluoride ion to pass through. Once within the glass, the fluoride ion bonds to calcium and therefore disrupts other chemical components of glass [12,13]. Glassy SiO_2 is made up of tetragonal SiO_4 units linked by covalent siloxane connections at all four corners to four other SiO_4 units [14]. These bridging oxygen connections must be disrupted in order to break down the network and free silicon from the glass. H^+ , F^- , and HF_2^- ions, as well as un-dissociated HF molecules, are present in HF solutions dissolved in water [15]. Glassy SiO_2 dissolution is a heterogeneous reaction, making the mechanism regulating the dissolving process challenging to analyse. However, breaking all of the chemical bonds, as shown in equation (1), will necessitate a number of reactions. Glass interacts with HF to produce silicon tetrafluoride and water, while SiF_4 combines with HF to produce H_2SiF_6 , which is insoluble in HF solutions. The concentration of the highly reactive HF ion in the etchant is reduced by adding buffer acid agents such as HCl, HNO_3 , NH_4F , H_3PO_4 and H_2SO_4 to HF solution. The etch rates are greater in etchants containing both HF and concentrated H_2SO_4 than in HF/HCl or HF/ HNO_3 etchants, a result that was attributed to the production of active fluorine-containing HSO_3F acid. The HF concentration is maintained as the sulfuric-acid concentration varies, and this is followed by an increase in activation energy. As a result, the addition of H_2SO_4 improves the surface roughness and etch rate. As mentioned above, the etch mechanism of HCl in HF is slightly different. Initially, the HF solution etches the glass and insoluble by product deposited on top of the glass surface. As time progresses, the size of insoluble by-products becomes larger and accumulates to interfere with etching of glass. However, HCl (other oxide series) releases impurities in HF-HCl mixed solutions [16]. The catalytic activity of H^+ ions on breaking siloxane links causes glasses to dissolve in acidic and mildly alkaline liquids [17]. After etching the glass, the depth of the deep etched zone is monitored to determine the etch rate. Rotation, stirring, or ultrasonic agitation of the etchant has a minor effect on it [18].

Most wet etching techniques are either isotropic (orientation independent) or anisotropic (orientation dependant). Isotropic procedures are suitable for geometries bigger than $3\text{ }\mu\text{m}$. Material is removed evenly from all directions by HF or buffered HF solutions in isotropic wet etching [19]. (NH_4F and HF mixture). Anisotropic etching methods, on the other hand, remove material evenly from a vertical direction (more control within vertical walls, fewer masks undercut). For a wet etch, it's critical to use a mask that doesn't dissolve in the etching solution, or at least dissolves at a slower pace than the layers to be etched.

2.1. Etch rate

The etch rate is an essential component in deep wet etching of glass. The selectivity of the etching is the desirable parameter of the procedure in various wet processes. Materials which are

employed as masking layers in wet etching of glass (mostly gold and silicon) are inert in HF-based etchants [2]. The etching process affected by defects in the masking layer and the etchant's ability to penetrate these flaws. As a result, a high glass etch rate will result in deeper etching yet defect formation will be high. For glass etching, the most common solution is HF based. Because of the various oxides and compositions employed during manufacturing, each variety of glass has a distinct etch rate. The concentration of HF in etchants determines the etch rate. A standard (maximum) concentration of 49% should be utilised to produce a high etch rate. By increasing HF concentration from 40% to 49%, the etch rate may be increased by 50–60% ($4.4\text{ }\mu\text{m}/\text{min}$ to $7.6\text{ }\mu\text{m}/\text{min}$ for non-annealed glass) [2]. Glass etch rates are significantly affected by the annealing process. Each variety of glass has a certain annealing temperature. When the HF concentration was raised from 40% to 49%, the etch rate rose from $9.1\text{ }\mu\text{m}/\text{min}$ to $14.3\text{ }\mu\text{m}/\text{min}$. For Corning 7740 glass wafers, Fig. 1 shows how the etch rate varies with the concentration of HF solution. When the concentration of HF is more than 32%, the etch rate dramatically increases. At the same time, the etching process is quite slow for low concentrations of the solution, with an etch rate of about $25\text{ nm}/\text{min}$, which is about 4 times slower than the thermal SiO_2 etching in buffered oxide etchant (BOE). We may conclude that annealing is a key parameter for both reducing internal stress and boosting etch rate [2]. There are several studies attempted to adjust various factors to optimise the etch rate. Baram et al. (2006) used conventional lithography methods to etch Pyrex glass using reactive ion etching (RIE) process with highest etch rate. They improved the etch process by using a design-of-experiment method to increase the etch rate, which led to the development of an analytical model to describe Pyrex etch rate [15,20]. In 2008, Queste et al. [21] developed high-aspect-ratio microstructures using high-speed directed etching of non-conventional materials. They used inductively coupled plasma reactive ion etching of quartz crystal, lithium niobate, and glass to examine the optimization of depth, etch rate, verticality of the walls, etch selectivity towards the etch mask, and surface smoothness using fluorine and fluorocarbon based plasma-chemical etching processes [13,21]. Kim et al. (2019) [22] created (3D) micro fluidic channels in glass using the selective laser-induced etching (SLE) technique. They looked into the process window of the SLE method, scan speed, including laser pulse intensity, pulse repetition rate, to get the best etching selectivity. A 3D micro fluidic channel branching to three multilayered channels was

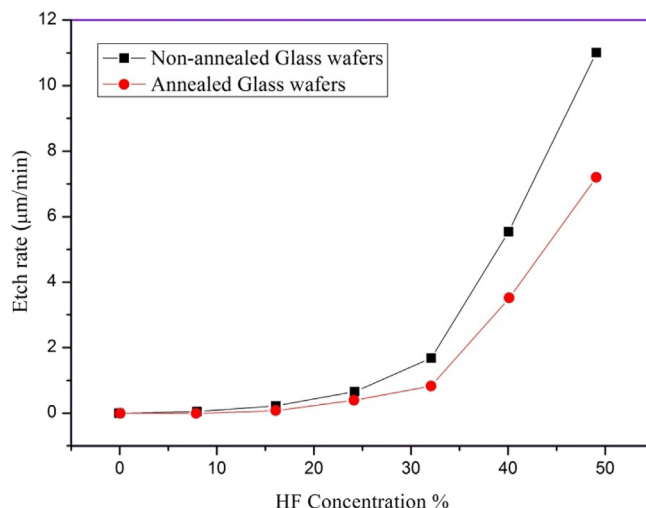


Fig. 1. Variation of the etching rate with HF concentration for annealed and non-annealed Corning 7740 glass wafers.

effectively made in a 4 mm wide glass using the optimal process window [15,22]. Utilising ultrasonic agitation and heating the solution to 40 °C –50 °C are two more ways utilised to increase the etch rate. The first approach was tested in a sealed Teflon container heated to the above-mentioned temperature using hot water. The rate of etching increased significantly. However, due to safety concerns, this approach is not suggested. We saw a rise in etch rate with ultrasonic agitation, although the resistance of the masking layer in the etchant was significantly lowered [2,5].

2.2. Masking Layer:

The material to be etched must be covered with an etch-resistant layer for the etching methods listed above. The mask must be designed in order to reveal the etched portions of the underlying material. The mask may be made of a metallic, ceramic, polymeric layer or a multi-layer mixture of various materials. However, a pattern of masking layer is commonly produced using a photoresist layer using the photolithography process. This acts as an etch-mask during the etching process [3,14,23].

Photoresist used as a masking layer for wet etching SiO₂ in BOE or HF. One main issue with photo resist masking layer is that the integrity of the masking photoresist layer decreases when exposed to high concentrations of HF. Before the photoresist mask starts to tear off, maximum etching durations in highly concentrated HF (49%) vary from 2 to 5 min [4,7,24]. This has been attempted to be overcome by lowering the concentration of the etchant with DI-water [4,25]. The etching durations could be increased to 120 min at best, although at the expense of the etch rate, which drops fast as the HF concentration is lowered [4,24]. Despite the lower etch rate, the maximum etched depths were found to be greater than in the non-diluted condition for glasses.

Metal masks, such as Cr/Au masks, have been found to protect borosilicate glasses against etch depths considerably above 90µm [7,17]. Different masks are compared in Table 1. The major issue with these masks is pinholes, which are flaws in the metal masks. Pinholes are tiny defects on the glass substrate that cause issues because they obstruct the etch pattern. Pinholes are most commonly caused by tensile tension and non-uniformity in the masking layer [2,26]. One may cover pinholes by performing a sequential deposition of the primary metal mask. The general idea is to finish one deposition cycle and then wait for it to cool before moving on to the next. The second layer will certainly not have defects in the same location as the first, preventing the etchant from entering the glass and producing pinholes [4]. The Al-glass adhesion was still too weak for long-term etch to prevent lateral HF penetration. The silicon-based thin film is another well-known HF-inert material; it has good adherence to the glass substrate and, more significantly, its surface is hydrophobic [8,9,27], which greatly reduces the development of surface pin holes and notching during the HF etch. Because of this characteristic, this masking material may be a suitable fit for deeply fused silica substrates.

2.3. Etching solutions

Standard glass etchants are made up of hydrofluoric acid and a buffering agent like ammonium fluoride (NH₄F). Concentrated HF (usually 49% HF in water) etches silicon dioxide too quickly for good process control and removes lithographic patterning photo resist. For more controlled etching, a buffered HF or buffered oxide etch is often used [6,28]. As mentioned earlier, in HF solutions, certain oxides form insoluble compounds. As a result, HCl is frequently added to BHF solutions to dissolve these insoluble compounds and provide a better etch [6,7]. The volume ratio of 40% NH₄F in water to 49% HF in water in a typical buffered oxide etch solution is 6:1. At 25 °C, this solution will etch thermally

formed oxide at a rate of around 2 nm/sec [29]. The etching rate may be enhanced by increasing the temperature. During the etching process, continuous stirring ensures a homogenous solution that may etch uniformly by removing etched material from the surface [16].

2.4. Influence of glass composition

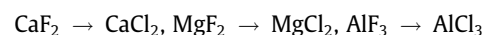
There are currently a great variety of glasses available, each with its own set of features and composition. The major qualities of the glass are determined by the composition and concentration of the oxides. As a result, characterising glass etching can only be done in general terms. The etching rate varies due to differences in composition. In HF solution, several oxides, such as CaO, MgO, or Al₂O₃, produce insoluble compounds [7,30]. These insoluble compounds are deposited as masking layers on the produced surfaces. As a result, the surface becomes rough, and the etching rate slows down with time. So extensive wet etching of glass is indicated for glasses with low oxide concentrations that produce insoluble compounds in HF. Fused silica is an especially attractive material among all forms of alternate transparent substrates because, In addition to all of the desirable features of borosilicate glass, it also has great thermal stability and high purity (100 percent silicon dioxide).

2.5. Undercut characterization

The etched structure always has a semi-circular wall due to the isotropic nature of the wet etch, and the undercut is defined as the geometric difference between the planned etching window and the resulting opening. In an ideal case, the undercut amount is equal to the etch depth, or the isotropy ratio (U/D) is 1. However, the quality of the masking material in terms of interface adhesion this ratio. The isotropy ratio for silicon-based compounds was close to 1, implying that these materials had outstanding adhesion to glass substrates during the HF etch. This ratio increased to 3 for the Au/Cr layer, indicating that the film delaminated during the HF etch and a tapering wall developed at the etching window's edge. This ratio is high as ten for a PR, implying that the glass-PR adhesion was significantly less than that of other masking materials.

3. Investigation of textured glass morphology

Depending on the etching solution, the glass etching procedure not only eliminates surface products but also changes the surface morphology of the glass. For processes like via holes, microchannels, wafer thinning, and through-hole etching, deep wet etching of glass requires a long processing time in a highly concentrated HF solution. The etched surface becomes rough after etching, and non-uniformities may be seen at the bottom of the etched holes [5]. Insoluble products might be the cause of the rough surface, just as they could be the cause of the slowing etching rate with time. These insoluble compounds are deposited as masking layers on the produced surfaces. We can make the insoluble products soluble by adding HCl to them:



Theoretically, adding HCl can improve the quality of the etching process. Iliescu (2005) reported the greatest value of the roughness of HF: HCl ratio 10:1 (for corning 7740). The roughness values, for all the compositions studied are in an acceptable range of 2 to 8 nm [2]. HingWah Lee (2012) developed Ag as masking material, as the thickness of mask increased a more continuous film with fewer grain boundaries was observed. The presence of plate-like

Table 1

Comparison of mask layers for different glasses, showing maximum attainable depth.

Glass Type	Etchant	Masking Layer	Etching Depth	Ref
Borofloat-33	49% HF	Si/Cr/Au	~106 μm	[9]
Borosilicate glass	49% HF	Silver (Ag) with photoresist	300 μm	[31]
Borofloat 33	49% HF	Cr/Au	90 μm	[35]
Fused silica	49% HF	HF-resistant photosensitive resist (HFPR)	600 μm	[36]
D263 glass substrate	25% concentrated HF	Molybdenum layers and positive photoresist (SPR220-7)	Up to 1.2 mm	[37]
Pyrex glass	49% HF	Cr/Au with photo resist (AZ7220)	500 μm	[17]
Pyrex glass	48 %HF	Cr/Au/Cr/Au with photoresist (SPR220-7)	300 μm	[6]
Aluminosilicate glass	48% HF	SU-8 photoresist and polished polycrystalline silicon	300 μm	[5]

structures was also observed on the 300 nm Ag film [31]. Shown in Fig. 2 is a typical scanning electron micrograph of a surface of a polished soda lime glass etched in a 2.5 wt% HF + 4.6 wt% HNO₃ solution [1,32].

The development of cusps on etched surfaces is linked to the presence of surface defects prior to etching. These defects range in size and depth from micro fractures that appear after polishing to big cracks caused by mechanical activities such as grinding or particle erosion [1,33,34]. As the etching progresses, a closed fault or micro crack is etched open, and this surface defect is eventually converted into a cusp. This mechanism demonstrates that fluorine species diffuse rapidly over the glass surface into the closed fracture, relative to the dissolving rate [1].

4. Applications of wet and dry etching

Big channels for micro fluidics, through holes for inlet and exit fluid in microfluidics and cavity for micro fabricated resonators are commonly used wet etching and dry etching procedures for glass patterning without needing extremely accurate structure. Thermal sensors employ etched glass structures to sense the heat of live cells in liquid. Glass has a low heat conductivity, which is one of the benefits that makes it useful in thermal sensors [38–40]. Thermal sensors are often manufactured using well-known methods such as photolithography, dry etching, and wet etching. The wet etching approach is used to create the vacuum chamber and microfluidics, while the dry etching method is used to shape the holes for intake and exit of liquids. Because glass and silicon have comparable thermal expansion coefficients, they may be readily bonded together using an anodic bonding technique [41] and utilised in hermetically packed capacitive silicon resonators. Silicon-glass bonding has emerged as a significant technique for device

integration in a variety of disciplines, including MEMS, microelectronics, and optoelectronics. The parasitic capacitance reduction [42,43] and hermetically packed device [44] both use anodic bonding between the glass substrate and silicon. As shown in [42], the resonator structures on silicon-on-insulator (SOI) are moved to the glass substrate to decrease parasitic capacitances from the underlying silicon layer. In various fuel cells, wet/dry etched glass surfaces with various patterns may be utilised as cathode and anode fuel flow channels [4,45,46]. Many PEM fuel cells employ rectangular and serpentine fuel flow configurations [47,48]. Many papers [44,49] have discussed capacitive silicon resonators, which are commonly used for sensing applications and timing references. The variation in capacitance between a sensing electrode and the resonant body is used to generate their output signal. Despite the fact that wet etching techniques for patterning glass are commonly utilised in microsystems, they have issues with tiny pattern structures and dimension repeatability. Dry etching, particularly the RIE process, may be used to precisely design tiny glass structures. Optical modulators, glass microfluidics combined with a thin silicon coat for biological sample monitoring, and other applications employ dry etching techniques. As previously stated [50–52], several optical systems based on micro-optical-electro-mechanical systems used the high transparency feature of glass. Optical devices allow light to be manipulated in terms of amplitude [53] and phase [54]. For functional image sensing applications optical modulator device that can integrate an image sensor are used. The optical window is controlled by a dynamic electrical control of liquid wetting behaviour on the micropillar surfaces [3,4,52,55,56]. Dry etching is also utilised in Microfluidics [38–40], which has a lot of potential for bio-applications. To avoid any negative impacts on biological samples, it is critical to use biocompatible microfluidic material. As a result, glass becomes the material of choice for biomedical applications [57]. Furthermore, studying cellular dynamics with high-resolution observation of living cells aids in a better understanding of biological processes. According to Nishiyama et al [58], the surface structure of cancer cells was studied at the nanoscale using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) [3]. Using TEM equipment and a micro fluidic chamber, a floating particle in the liquid was detected [59].

5. Conclusions

Etching of SiO₂ glass-based films is commonly used in semiconductor device and IC technology. The key elements that contribute to a good wet etching process of glass are glass composition, etching solution, etch rate, and masking layers which include photoresist and metals like Cr-Au, molybdenum and Ag. Important advantages of wet etching of glass based on HF solutions are its simplicity, low cost, and also resulting well-controlled surface structures. However, the main drawbacks of wet etching are its limitation in realizing micron-level structures and also the dimen-

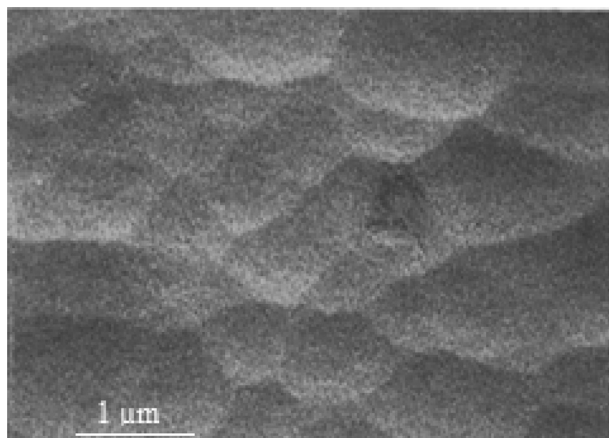


Fig. 2. Scanning electron micrograph showing the cusp-like surface roughness obtained after etching a polished soda lime silicate glass.

sional control at the micron level. The RIE process has the ability to accurately define tiny glass structures; however, due to a low etching rate and limited selectivity, creating very deep glass structures is difficult. Nevertheless, HF based glass etching has been successfully used to fabricate advanced devices in MEMS, biotechnology and solar cells. The approach described in this paper for improving the quality of the wet-etched glass surfaces using an HF/HCl solution has advantages for constructing a variety of glass structures, including fuel cell flow channels.

CRedit authorship contribution statement

A. Shubhava: Writing – original draft. **A. Jayarama:** Formal analysis, Investigation, Methodology. **Ganesh K. Kannarpady:** Conceptualization, Data curation. **Sangeeta Kale:** Supervision. **Shriganesh Prabhu:** Resources. **Richard Pinto:** Writing – review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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