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Glass Micromachining

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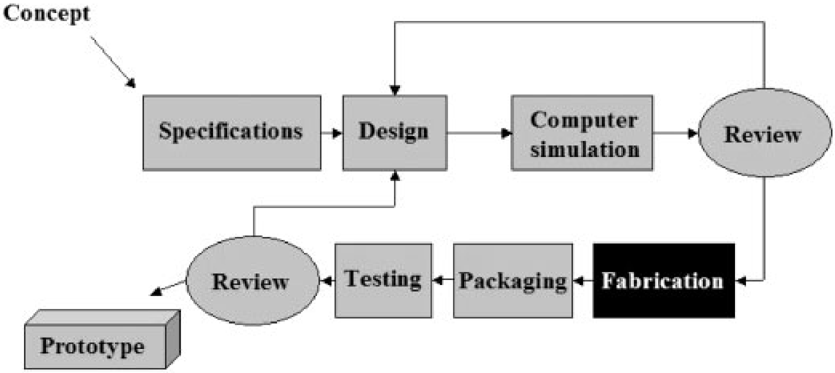

Glass can be characterized as a monolithic noncrystalline solid consisting mainly of silicon dioxide (SiO_2). Glass often contains additives or impurities that modify properties such as its mechanical stability and the glass transition temperature. An endless variety of glasses with different chemical compositions and physical properties are in use today. One can find optical glasses (filters and lenses), light sensitive and photochromic glasses, x-ray and gamma-ray absorbing glasses, glasses with coloring and discoloring agents, with luminescence and fluorescence effects, in applications like glass pH electrodes, glass lasers, optical fibers, and many others. The classification of glasses according to their optical properties is given in *Optical Properties of Glass* by Fanderlik [1], who gives attention to glasses exhibiting special optical properties and to the dependence of glass properties on its chemical composition, temperature, and thermal history.

The use of glass instead of silicon in μTAS applications is prompted by the unique properties of glass, e.g., glass is resistant to many chemicals, optically transparent (which allows for optical detection and visual inspection), and dielectric (and can therefore withstand the high voltages used in electrokinetically driven flows and separations). Other advantages of glass are its hardness, high thermal stability, and relative biocompatibility, which broadens its range of applications to DNA separations, enzyme reactors, immunoassays, and cell biology. For μTAS applications,

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Borofloat glass (and Pyrex®) and quartz wafers are mostly used, because they are compatible with many cleanroom processes. Quartz, the crystalline form of silicon dioxide, is an abundant mineral appearing in many forms and colors and occurring as grains (sand), in masses (chalcedony, carnelian, and jasper), and in hexagonal crystals as amethyst and rock crystal. Quartz is very hard, has a low thermal expansion coefficient, and transmits light from about 180 nm (UV range) to 4.5 μm (infrared). Being optically transparent to UV light, quartz can be employed for UV-absorption detection on microchips. However, crystalline quartz of optical quality is very expensive. Moreover, bonding of quartz to silicon or glass is difficult, because of the high melting point of quartz, 1713 °C. Quartz that has been melted and cooled to form amorphous glass, so-called fused silica, is easier to use in μTAS applications.

Borofloat glass shares many of the beneficial properties of quartz, i.e., Borofloat glass is chemically resistant, a dielectric, and optically transparent (although not down to the UV range like quartz and fused silica). Borofloat glass is significantly cheaper than quartz and can be bonded to silicon and glass rather easily. Borofloat glass is therefore extensively used in μTAS applications and is in the focus of this chapter.

Some traditional silicon microfabrication techniques, such as photolithography and wet chemical etching, have been adapted to glass processing. Nevertheless, micromachining of glass is less versatile than that of silicon, due to its noncrystalline structure and the limited experience with glass as a material for microsystems.

7.1
Wet Chemical Etching

Wet chemical etching for fabricating microfluidic networks in glass involves the use of traditional silicon-processing techniques such as photolithography and wet chemical etching. The glass substrate is spin coated with a 3–6-μm-thick film of photoresist. UV exposure through a mask and development of the photoresist provide the desired pattern of microfluidic channels. Because etch rates in glass are relatively low, etching times are typically fairly long. One problem in using photoresist as an etching mask in glass etching is its poor adhesion to glass. The photoresist layer tends to lift off during etching, allowing the etchant to etch the glass substrate indiscriminately. To prevent lift-off problems with photoresist, other masking materials are often used for glass etching, e.g., chromium, gold, aluminum, and polysilicon. The desired pattern is transferred to the mask layer by photolithography, as described in section 6.2.1.

Wet etching of glass is mostly done with hydrofluoric acid (HF) or buffered hydrofluoric acid (BHF). The chemical reaction involved in wet etching glass is

$$\mathrm{SiO_2 + 4\,HF \quad \rightarrow \quad SiF_4 + 2\,H_2O}$$

The etch rate of Pyrex® glass in 40% HF at room temperature (22 °C) is about 3.4 μm min^{-1}, and the etch rate of Pyrex® glass in BHF (5% HF) at room temperature is only about 0.04 μm min^{-1}. Adding 5–10% HCl to BHF (5% HF) increases the etch rate of Pyrex® glass to 0.23 μm min^{-1} at room temperature.

Because of the highly toxic nature of the HF used in glass etching, special safety precautions must be taken. Face shields and proper chemical-resistant gloves must be used at all times.

Glass is an amorphous material; therefore, the wet etching is always isotropic, meaning that curved geometries can be obtained. Sharp corners and high aspect ratios cannot be achieved by wet etching of glass. Inherent to isotropic etching is under-etching of the mask, resulting in channels wider than the pattern in the photoresist would predict. This should be taken into account in designing a mask. For example, if the desired channel dimensions are 100 μm wide and 25 μm deep, the channel width on the lithography mask should be only 50 μm, because the etchant removes glass equally in all directions. While etching to a 25-μm depth, the glass is also etched approximately 25 μm on each side, for a total channel width of 100 μm (50 μm + 2 × 25 μm = 100 μm). Under-etching tends to result in high surface roughness of the channel walls.

An exception to the rule that glass is always etched isotropically is a fabrication process that employs photostructurable glass [7]. The glass is masked by a photolithographic process and then chemically etched.

7.2
Reactive Ion Etching (RIE) of Glass

Dry chemical etching of glass is also possible. The etch rate depends on the RIE equipment, glass composition, and the process settings. For glass etching, a CF_4/O_2 plasma is typically used. For pure silicon dioxide, the RIE etch rates can be at least 200 nm min^{-1}, but probably higher if the equipment is optimized for this purpose. This is slow compared to the fast, inexpensive batch microfabrication that can be obtained with wet chemical etching.

7.3
Laser Patterning

Lasers can be used to apply large amounts of energy in small areas. With sufficient amounts of energy, material can be physically removed. Laser patterning of various glasses has been studied much recently. Laser micromachining can be used routinely to fabricate structures as small as 6 μm in glass, polymers, ceramics, and metals. Depending on the settings of the laser, the properties of glass can be modified without actually removing any material [2]. This technique can be used, for example, to change the refraction index of glass and thereby fabricate optical waveguides.

7.4
Powder Blasting

Powder blasting has recently been introduced as a bulk micromachining technique for brittle materials, such as glass, silicon, and ceramics. This technology is based on mechanical material removal from a substrate by a jet of particles. A mask containing the design covers the substrate, and then particles are accelerated towards the target by high-pressure airflow through a nozzle. Because of their high resistance to powder blasting, metals and elastomers may serve as mask materials, and therefore standard lithographic techniques can be used to define complex designs. The removal rate by powder blasting depends on the substrate materials properties, such as the Young's modulus, hardness, and fracture toughness, and on the kinetic energy of the powder particles. As reported by Wensink and Elwenspoek [3], removal rates of 25 $\mu m\ min^{-1}$ can be achieved for glass and silicon. The minimum attainable feature size with powder blasting is about 30 μm with aspect ratios up to 2.5 [4]. Like wet etching, powder blasting is not a selective fabrication method. Additionally, this technique creates rough surfaces, which makes powder blasting not particularly attractive for the fabrication of μTAS.

7.5
Glass Bonding

For sealing a glass substrate with an etched microfluidic channel network, another glass substrate is often preferred as the cover plate. This type of device has been the workhorse in capillary electrophoresis experiments for a decade (section 10.4). The three most frequently used glass-to-glass bonding methods are thermal fusion bonding, anodic bonding, and adhesion bonding. Among these methods, fusion bonding has been the most popular, because it is a direct bonding method, which means that no intermediate layers are necessary. An additional reason for its popularity is that the only equipment needed is a furnace and an etching bath for preparation of the wafer surfaces. This is fortunate, since laboratories that do not have cleanroom facilities also can work with chemical analysis on microfabricated devices.

Even though the mechanism of fusion bonding is not completely understood, it is believed to rely on a chemical reaction between hydroxide groups (OH–) present in the interface of the wafers (Fig. 7.1) according to the following reaction:

$$\mathrm{Si-OH + OH-Si} \quad \rightarrow \quad \mathrm{Si-O-Si + H_2O}$$

in which water (H_2O) is formed and released under heating, causing the hydrogen bonds between the silanol groups (Si–OH) to turn into covalent siloxane bonds (Si–O–Si).

It is clear from Figure 7.1 that the wafer surfaces have to have exposed hydroxide groups for bonding to be successful. This is typically done by hydrophilization

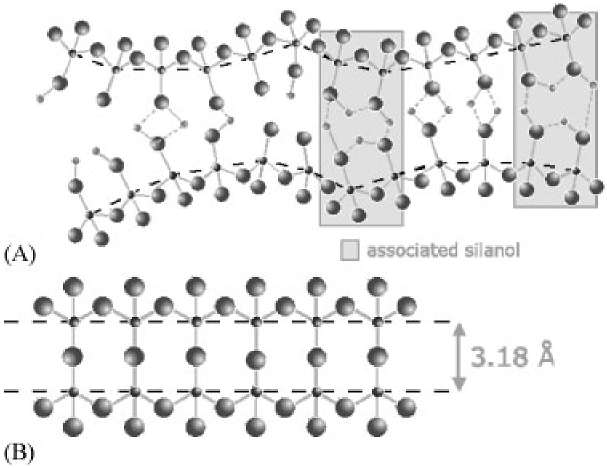

Fig. 7.1 Glass fusion bonding process. A: Two glass wafers face each other. In some places, the surface hydroxide groups (OH^-) form silanol bonds, which pull the glass wafer together. These initial forces facilitate the subsequent fusion bonding.
B: After the glass wafers have been heated under light pressure, silanol bonds between the glass surfaces form siloxane bonds (Si-O-Si) according to Equation 7.2 (figures courtesy Steen Weichel).

or hydration in a so-called Piranha solution, which is a mixture of H_2O_2 and H_2SO_4. This is advantageous, because a hydrophilic surface has many silanol groups. Treatment in an oxygen plasma can also be used to hydrophilize the surfaces. The wafers are typically dried and placed in a furnace after assembly. Ramping the temperature slowly to below the glass transition temperature (600–650 °C) results in bonding if the wafer surfaces are smooth enough. A load is also often placed on the wafer pair to facilitate bonding.

An alternative method that sometimes gives better results is to leave a thin film of water between the wafers. The temperature is ramped to below the boiling temperature, e.g., 80 °C, to let the water film evaporate slowly. The temperature is subsequently increased to below the glass transition temperature.

The smoothness of the wafers is critical, because sufficient contact area is necessary to achieve a successful bond, and the contact area is controlled mainly by the surface roughness. Commercially available glass substrates are polished to a roughness of about 1 nm, which is generally sufficient for fusion bonding.

Even though the bonding procedure seems straightforward, it is in fact almost black magic to get it to work, because it is so sensitive to the cleanliness and smoothness of the substrates. The quality of the bond also depends highly on the bonding area [5]; it is generally easier to bond small pieces of glass than whole wafers.

Fusion bonding of fused silica substrates is also possible; a temperature of about 1000 °C is typically needed, due to the higher glass transition temperature of this material.

Anodic (or electrostatic) bonding is a field-assisted thermal bonding technique typically used to bond a structured silicon substrate to a borosilicate glass cover plate (see Chapter 6). This bonding method generally has a higher yield than thermal fusion bonding, because the wafers are kept in contact by electrostatic forces, so the requirements concerning surface roughness and cleanliness are considerably relaxed. Two glass substrates can unfortunately not be anodically bonded without the use of at least one intermediate layer, such as polysilicon [6].

Adhesion bonding or gluing has also been widely used for assembling wafer pairs. The success of this packaging solution is determined by the adhesive surface tension (wetting), which depends on the surface energy of the material, the adhesive viscosity, and the surface cleanliness. The strength of this sealing depends on both adhesion forces and the internal strength (cohesion) of the adhesive itself. One can, for example, use polymeric adhesives that turn from the liquid to the solid state by various polymerization reactions (UV exposure, anionic reaction, in the absence of oxygen, thermal cure, etc.). A thin layer of adhesive is typically spun onto one of the wafers (e.g., the cover) in the same manner as spinning of photoresist (section 6.2.1). The wafers are pressed slightly together and the glue is hardened.

An advantage of this bonding method is that it can be done at room temperature, for example for polymerization upon UV exposure. A disadvantage is that the bonding process can affect the definition of the fluidic channels, possibly even clogging them, if they become filled with glue. Another disadvantage is that polymer adhesion layers generally have a much lower chemical resistance than glass and that they may be toxic, which is true for some UV-cured adhesives.

An alternative solution is to use liquid glasses as an adhesive material. Liquid water glasses are silicate materials (quartz sand and solid water glass crystals), dissolved in alkaline solutions (sodium or potassium), having glass characteristics. Due to their high alkaline properties, liquid glasses are soluble in water, mixing in all ratios.

7.6
A Microfabrication Example

The vast majority of microdevices for capillary electrophoresis are fabricated by isotropic etching and fusion bonding of borosilicate substrates. The fluidic layout typically consists of a channel cross (Fig. 7.2).

An often-used processing recipe is shown in Fig. 7.3 as a general example. (The optimal processing conditions usually differ among different laboratories.)

First, the bottom substrate has to be cleaned, which can be done chemically, mechanically, or by a combination of chemical and mechanical cleaning. It should at least be cleaned chemically, for example by immersion into a 1:3 mixture of H_2O_2 and H_2SO_4 for 10 min (Piranha solution). A chromium adhesion layer about 100 nm thick is deposited on the substrate (Fig. 7.3, step a), so the photoresist does not delaminate and fall off during etching. Photoresist is subsequently

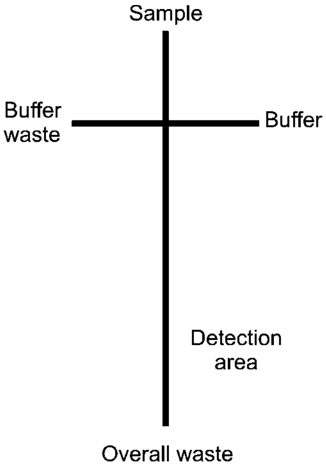

Fig. 7.2 Layout of a typical glass chip for electrophoretic separations. The channel lengths are in the centimeter range.

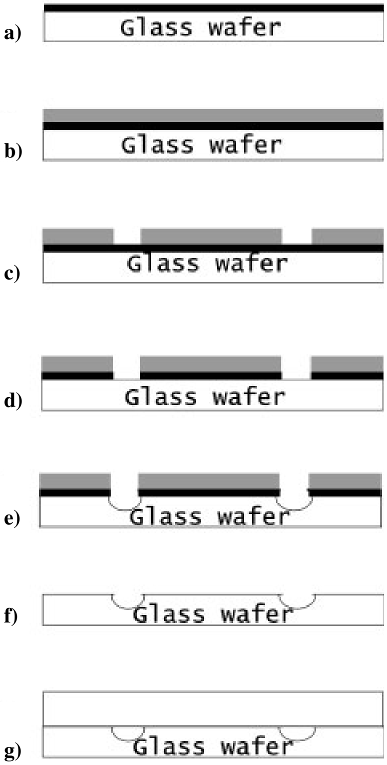

Fig. 7.3 Schematic processing sequence for fabricating microchannels on a bottom substrate. See text for detailed description.

spun onto the wafer (step b), and the mask pattern is transferred to the resist by standard UV photolithography (step c, see section 6.2.1). A resist thickness of about 4 μm should be enough to etch channels to a depth of 10–20 μm. In step d) the wafer is immersed in a chromium etchant to expose the areas of the channel network. The chromium is removed within a few minutes at an etching rate of about 60 nm min^{-1} when the following solution is used: 15 g cerium sulfate, 1215 mL H_2O, and 90 mL HNO_3. The channel network can be etched to a depth of 10–20 μm in 40% HF. The etching rate is about 3 μm min^{-1}, depending on the type of substrate (step e). The photoresist is stripped and the remaining chromium layer is removed by immersion for a couple of minutes in the chromium etchant (step f).

The inlet holes in the lid have to be fabricated before fusion bonding of the substrates (step g). A crude way of doing this is by drilling. It is, however, difficult to keep the substrate clean with this method, which is a disadvantage. The through-holes can alternatively be fabricated by etching, by the following procedure: The cover substrate is laminated with a HF-resistant polymer film. At the locations of the access holes, the polymer film is removed by, e.g., CO_2 laser ablation. Then the access holes are etched through the substrate with 40% HF, and the polymer film is removed.

The two substrates have to be rendered hydrophilic before fusion bonding. This can be done by immersion in a Piranha solution for 10–30 min (similar to the initial cleaning procedure before step a). The substrates are then pressed together and annealed in a furnace at 600–650 °C for a couple of hours to increase the bond strength. A more detailed description of fusion bonding can be found in section 7.5.

7.7
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