Comparing fusion bonding methods for glass substrates

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Comparing Fusion Bonding Methods for Glass Substrates

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Abstract

Glass bonding is often necessary in microfluidic, nanofluidic and MEMS applications. Fusion bonding is a popular method in which glass substrates are permanently bonded using chemical treatment, low pressure and annealing. This project investigates a range of bonding methods and measures the bond strength. Float glass substrates were chemically cleaned and prepared using four different methods (Ethanol Rub, Ethanol Rub + NH_4OH, piranha + NH_4OH, and piranha + HCl + NH_4OH), pressed together by hand, and placed in the oven at 400°C for 10 hours. Bond strength was assessed using compressive shear stress. It was determined that the piranha + HCl +NH4OH produced the strongest bond. All methods produced satisfactory bonds and the simplicity and safety of a simple Ethanol rub means it should be considered whenever possible.

1 Introduction

Bonding of glass to glass or glass to silicon is commonly used to lid micro and nanofluidic devices, and can be achieved in many different ways. Anodic bonding is a process of bonding that involves placing the substrates between two electrodes, while applying compressive force and an elevated temperature. The electrodes provide a DC potential difference up to 1kV and this potential difference causes sodium ions to clean the surface of the glass and cause the silicon's surface to react with the glass surface, forming a bond. While it is a popular method of bonding silicon to glass, it is also possible to use this process to create a glass-glass bond [1]. Fusion bonding may be performed when anodic bonding equipment is not readily available, or when the substrates are too thick to achieve a sufficient electric field. Plasma bonding uses a plasma to treat a surface with various ions. This may remove organic contaminants, and sterilise the surface and generate high density hydroxyl groups on the surfaces to be bonded [2]. Fusion bonding can do all these without the need for a plasma asher/etcher.

Bonding using adhesives is the simplest and quickest method of bonding glass substrates. While the adhesive layer is particularly useful for bonding non-flat surfaces, it introduces a foreign chemical with different chemical, mechanical, and electrical properies. Adhesive bonding is not an option for many chemically sensitive micro and nanofluidic applications.

Fusion Bonding is an inexpensive and versatile way of irreversibly bonding silica glass surfaces. In addition to bonding entire wafers [3], bonds can be localised using a microheater [4]. Applications for fusion bonding include silicon on insulater material fabrication, power electronics, light emitting diodes with high brightness, micromechanical devices, MEMS (Microelectromechanical Systems), microfluidics and nanofluidics.

Previously, experiments have been carried out to determine bond strengths of certain materials for specific applications (such as those in [5], [6], [7], [8], [9] and [10]). However, the influence of cleaning procedures on bond strength for glass substrates has not been studied, despite its use. The aim of this work is to compare and quantify methods described in the micro and nanofluidics literature.

Liao et al. "Sub-60 nm Nanofluidic Channels Fabricated by Glass-Glass Bonding" bonded glass to glass by cleaning their samples using an acetone solution, followed by a piranha bath, and subsequently rinsing in deionised water. The samples were then blown with nitrogen gas, bonded by hand, and placed in the oven [5]. Lin et al. "Fabrication of sub-40 nm nanofluidic channels using thin glass-glass bonding" used the same technique to clean their glass [6].

Plößl et al. "Wafer direct bonding: tailoring adhesion between brittle materials" suggests the hydrochlric hcid solution at a ratio of 1:1:6 ($HCl:H_2O_2:H_2O$) and an ammonium hydroxide solution at a ratio of 1:1:5 ($NH_4OH:H_2O_2:H_2O$) [7]. It also suggests piranha at ratios of 1:4 or 1:2 (H_2O_2:sulphuric acid) as well as a mixture of hydrogen peroxide and nitric acid [7].

Han et al."Nanofluidic device for continuous multiparameter quality assurance of biologics", used a piranha solution, rinsed with deionised water, and subseqeuntly used 29% NH_4OH for 30 minutes at room temperature prior to bonding and annealing [8].

Wang et al. "Capillary kinetics of ferrofluid in hydrophilic microscope slide nanochannels", used Acetone in order to remove any remaining photoresist following the etching process. Subsequently, a 1M HCl solution was used in order to remove precipitated particles and also, interestingly, to "enhance surface flatness" [10]. After this, the authors used piranha solution as the final cleaning step prior to preheating the samples in the oven at 400°C, with the bonding step occuring after, at 580°C.

The papers cited above show that there are many uses of fusion bonding, and many procedures used, and that they do not draw on literature or best practice. There is clearly a need for a more evidence-based approach to the fusion bonding methods. In this work we fix the substrate material and the annealing process, and only vary the chemical cleaning step.

2 Theory

Unless the hydroxyl groups are purposely removed, the surface of silicon dioxide, and hence glass, contains silanol groups. The surface chemistry of glass is highly dependent on the density of these $Si-O-H$ (silanol) groups on the surface. In an ideal world, glass surfaces are flat and clean. In reality the surface becomes contaminated with different substances, hence cleaning and surface preparation are critical steps for fusion bonding. This surface contamination is typically particle contamination, organic contamination, and ionic contamination [7]. Particle contamination involves physical particles such as dust or fibres on the surface, while organic contamination refers to substances like hydrocarbons from the environment (eg. human skin). Ionic contamination refers to metal ions contaminating the surface, originating from eg. metal tweezers or salts.

The most problematic of these for bonding is particle contamination. Particles can be difficult to remove and a particle inside the bond will prevent substrates from coming into contact. The non-contact area depends on the height of the particle and the thickness of the parts to be bonded. A thin (100μm thick) wafer can deform around a particle reducing the unbonded area, whereas a 5 mm thick optical flat will flex very little, causing a large unbonded area.

Organic contamination is typically less problematic as it has little influence on surface roughness and is readily removed with chemical cleans [7]. It can however, limit adhesion between the two surfaces during annealing due to the 'nucleation of interface bubbles' [7]. Piranha and HCl solutions are commonly used to minimise organic contamination, the

latter also helping to remove metal ions. NH_4OH is used in order to increase the density of silanol groups and hence improve hydrophilicity of the surface [11].

Ionic contamination is perhaps the least problematic of the three, as it neither affects the bond at room temperature or during annealing. It may be a concern if the bonded part is used for electronic applications as the properties of materials may be altered through metallic ions.

After cleaning the surfaces and ensuring a high density of silanol groups, the bond can be initiated by lightly pressing the two surfaces together. At this stage the water molecules on the one hydrophilic surface will mix with those from the other hydrophilic surface, creating a very thin layer of water between the two surfaces. This layer contains some liquid water and some hydrogen bonded structures [12].

Since the substrates are not perfectly flat, the thickness of the water gap between the substrates will vary [13]. Where the two glass slides are sufficiently close together, the annealing process diffuses the water molecules away and subsequently creates a Si-O-Si covalent bond structure between the two glass pieces [14]. During the annealing process (exposing substrates to high temperatures), the papers cited in the introduction used temperatures ranging from 550 to 1050°C at durations ranging from 6 to 12h. Where this happens, there will no longer be a water layer or any sort of boundary between the layers, and the glass pieces will become one piece. Ideally, the bond will be undetectable.

Perfect fusion does not typically occur everywhere (only where the glass pieces are sufficiently close together). In the places where it doesn't there may still be water (and possibly some contaminants) but the bond will remain reversible, held together only by hydrogen bonds and dipole-to-dipole forces, and the shear strength of the bonded substrate.

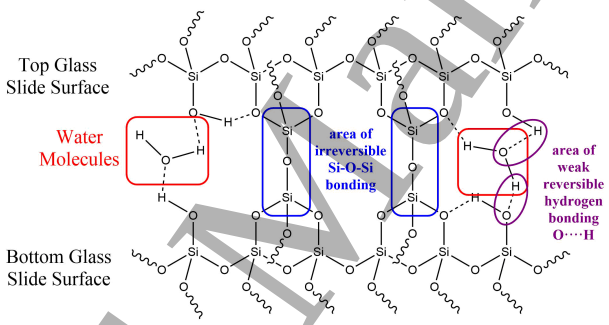

Figure 1: Representation of the irreversible bond between the two glass surfaces formed after annealing. In the middle it can be seen how the Si-O-Si bonds form, while on either side they do not form due to too-great a distance between the surface hydroxyl groups, leaving the weaker hydrogen bonds as the sole force holding the substrates together.

3 Methodology

Bonding was carried out in an ISO class 3 clean room in order to reduce the chance of physical particle contamination. All bonds were performed between 'Extra White Soda Lime Glass' slides (product number: S41014A, brand: Thermo Scientific) that were unmodified after being bought (Composition: 72.20% SiO_2, 14.30% Na_2O, 1.20% K_2O, 6.40% CaO, 4.30% MgO, 1.20% Al_2O_3, 0.03% Fe_2O_3 and 0.30% SO_3). Various chemical treatments (as detailed below) were carried out in dedicated, ultra-clean glassware. Bonding involved pressing two overlapped (about 3 cm of overlap) glass slides together by hand.

The cleaning procedures that were used were:

i Ethanol Rub - The surface of the glass was rubbed with MMRC brand wipes (product number MM-C1-2323). The rubbing involved folding the wipes several times,

soaking them in ethanol and applying some moderate pressure using index and middle fingers, and subsequently rubbing them back and forth over the slide for about 30 seconds until the surface became very reflective. This was followed by drying of the surface using a nitrogen gun.

ii Ethanol Rub + NH_4OH - The ethanol rub was performed as previously described, but additionally the sample was given a bath in a solution composed of 5 parts deionised water, one part ammonium hydroxide (NH_4OH) and one part hydrogen peroxide (H_2O_2) for about five minutes. This solution was heated to 75°C. This solution is a common silica cleaning step and was chosen because it is believed to leave a high density of silanol groups.

iii Piranha + NH_4OH - The samples were given a 5 minute bath in 100 ml of piranha solution, which was stationed on top of a 50°C hot plate, and is composed of three parts sulfuric acid and one part hydrogen peroxide. Subsequently, the samples were rinsed in deionised water and given a bath in the same ammonium hydroxide solution detailed above.

iv Piranha + HCl + NH_4OH - The samples were given a 5 minute bath in piranha solution, rinsed with deionised water, then given a 5 minute bath in hydrochloric acid solution, which was made up of 6 parts deionised water, one part hydrochloric acid (HCl) and one part hydrogen peroxide (also heated to 75°C). They were then rinsed again and finally given a bath in the NH_4OH solution described previously.

The final step for all four cleans was the same: the sample was rinsed in deionised water and subsequently dried with a nitrogen gun. Subsequently, the samples were pressed together using index finger and thumb ($\sim 50-100$N Force [15]) in order to form a temporary bond at room temperature. Within 4 hours of cleaning and room temperature bonding, samples were placed in a ceramic oven at room temperature. The oven tempearture was ramped to 400°C at a rate of 3°C/min, held at 400°C for 10 hours and then allowed to cool (uncontrolled) to less than 100°C. To measure the bonded area, a picture was taken of the sample such that the bonded area, which was surround by Newtons rings, could clearly be seen. Image processing, including thresholding in imageJ was used to measure the bonded area. This can be seen in Figure 2.

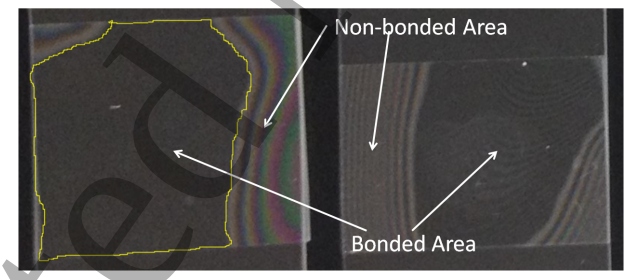

Figure 2: The bonded, outlined in yellow on the left image, can clearly be seen on these two samples. The bonded area is 411mm^2, and 275mm^2 in the left and right images respectively.

In order to test the samples, a compression test was conducted (Figure 3). The tensile testing machine had two compression plates designed to perform compression tests on blocks of material. Two aluminium plates, one which could be screwed to the top compression plate and one with an L-shape which could be rested to the bottom compression plate, were used to apply shear stress to the bonded region. Shear stress is defined as the compressive force applied, divided by the bonded area (Figure 3). The sample was glued to these Aluminium plates using a cyanoacrlyate glue (super glue) and the compression test commenced until the substrates or the bond broke.

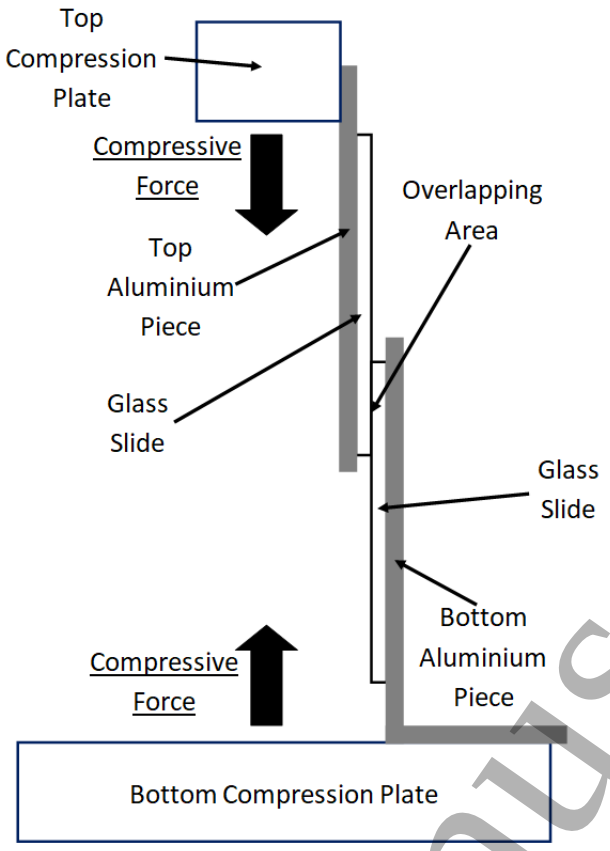

Figure 3: Schematic of testing apparatus showing the compression plates that were used to hold the bonded glass slides. Glass Slide Dimensions: 1 mm ×26 mm ×72 mm. Overlapping area dimensions: ≈ 26 mm ×30 mm.

4 Results

The table below displays all the samples "successfully" tested. A successful test is defined by the bond breaking at the bond interface. Occasionally the glass substrate would yield before the bond. Note that the compressive stress in the unbonded areas is twice that of the bonded area. Figure 4 compares the different cleaning procedures side-by-side according to maximum shear stress.

Cleaning Procedure	Max. Force (N)	Bonded Area (mm^2)	Strain ($\mu\epsilon$)	Max. Shear Stress (MPa)
i	3090	345	9870	8.81
i	1010	129	1890	7.14
i	1270	307	4350	3.90
ii	1350	364	5610	3.45
ii	1860	204	9850	9.10
ii	3970	452	14400	8.77
iii	1800	383	5410	4.71
iii	1050	275	3010	3.79
iii	1360	242	2170	5.45
iv	1100	101	1930	10.9
iv	2080	291	4730	7.16
iv	1620	133	1710	12.2

Table 1: List of all samples successfully tested.

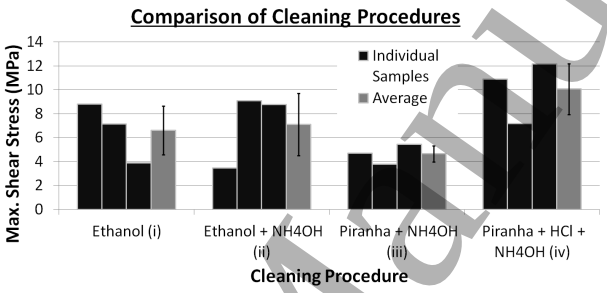

Figure 4: Comparison of bond strengths for all tested cleaning procedures. Error bars represent $+/-1$ standard deviation.

The clear conclusions from Figure 4 are that method iv created the strongest bond. Methods i and ii are of very similar strength, and method iii is the weakest. Hypotheses that can be drawn from our data are 1) the NH_4OH does not significantly improve bonding in our methods, 2) an ethanol rub alone is more effective than a piranha clean alone, and 3) hydrochloric acid in process iv is critical. Therefore, going forward from this project, it would be desirable to try hydrochloric acid and ethanol on their own and/or together.

5 Conclusion

The aim of this project was to find the best cleaning procedure for fusion bonding. This was accomplished by testing 4 different cleaning procedures and mechanically testing the resulting bond strengths. We conclude that the best procedure for fusion bonding is the procedure iv, however, the least hazardous method (procedure i) also performs well.

Interestingly, the mixture of NH_4OH and H_2O_2 is a strong oxidant but exerted no effect on the bond strength. Hence, for the removal of particle contamination ethanol rubbing is perfectly suitable.

At the same time, HCl had a profoundly positive effect on the bond strength when used with Piranha and NH_4OH. These differences could be explained by the etching of Ca^{+2} ions from the glass surface by HCl as reported rather than by cleaning of the glass-glass interface [16] [17]. We believe this Ca-depleted (and consequently SiO_2-enriched)

layer reaches the depth of several nanometers only, but this is enough to introduce more silanol groups and fuse slides better.

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