The Creation of an Anodic Bonding Device Setup and Characterization of the Bond
Interface Through the use of the Plaza Test

A Thesis Presented to the Faculty of California Polytechnic State University, San Luis
Obispo, CA

In Partial Fulfillment of the Requirements for the Degree of Masters of Science in
General Engineering with Emphasis in Materials Engineering

By

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February 21, 2011

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Title: The Creation of an Anodic Bonding Device Setup and Characterization of
the Bond Interface Through the use of the Plaza Test

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Abstract

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Recently there has been an increased focus on the use of microfluidics for the synthesis of different products. One of the products proposed for synthesis is quantum dots. Microfluidics often uses Polydimethylsiloxane for structure in microfluidic chips, but quantum dots use octadecene in several synthesis steps. The purpose of this work was to create a lab setup capable of anodically bonding 4" diameter wafers, and to characterize the bond formed using the Plaza test chip so that microfluidic devices using glass and silicon as substrates could be created.

Two stainless steel electrodes placed on top of a hot plate were attached to a high power voltage supply to perform anodic bonding. A Plaza test mask was created and used to pattern P type silicon wafers. The channels etched were between 300 and 500nm deep and ranged between 1000 μ m and 50 μ m. These wafers were then anodically bonded to Corning 7740 glass wafers. Bonding stopped once the entire surface of the wafer was bonded, determined by visual inspection. All bonds were formed at 400°C and the bond strength and toughness between wafers bonded at 400V and 700V was compared.

A beam model was used to predict the interfacial fracture toughness, and the stress at the bond was calculated with a parallel spring model. By measuring the crack length of the test structures under a light microscope the load conditions of the beam could be found. It was concluded that the electrostatic forces between the wafers give the best indication of what the bond quality will be. This was seen by the large difference in

crack length between samples that were bonded using a thick glass wafer (1 mm) and a thin glass wafer (500 μ m). The observed crack lengths for the thick glass wafers were between 40 and 60 μ m. Thin glass wafers had a crack length between 20 and 40 μ m. The fracture toughness was calculated using the beam model approximation. Fracture toughness of the thin glass wafers was 7MPa m^{1/2}, and of the thick glass wafers was 30 MPa m^{1/2}. The fracture toughness of the thick glass wafers agreed with results found through the use of the double cantilever beam samples in literature. The maximum observed interfacial stress was 70 MPa.

Finally, to measure the change in the size of the sodium depletion zone formed during bonding, samples were placed under a scanning electron microscope (SEM). Depletion zones were found to be between 1.1 and 1.4 μ m for thin glass samples that were bonded at 400 and 700 volts. This difference was not found to have a significant effect on the strength or fracture toughness observed. Thicker glass samples could not have their depletion zone measured due to SEM chuck size.

Keywords: Anodic Bonding, Wafer Bonding, Fracture Toughness, Interfacial Fracture, SEM, Strain Energy Release Rate, Plaza Test, MEMS, Wafer Packaging, Pyrex, Microfluidics, Plaza Test

Acknowledgements

I would like to thank my adviser Dr. Richard Savage for his mentorship and patience while I was testing and writing this document. His perspective always allowed me to walk away with a better understanding of what the goals of a project and my goals as an engineer should be.

I would like to also thank my committee members, Dr. Daniel Walsh and Dr. Kathy Chen, for adding their knowledge to my project and being mentors during my graduate experience.

I would like to thank Dr. Blair London for helping my understanding of fracture mechanics while writing and improving the questions I asked myself to better this project.

To all the graduate students I have worked with, bouncing ideas off of, helping me through the testing and writing process, and making me a better person I would like to give a special thanks; Brian Alvarez, Josh Angell, Patrick Hyland, Adam Olzick, and Mike Marrujo.

Finally I would like to thank my friends and family for telling me to get to work and always being there for me while I went through this wonderful journey at Cal Poly.

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Chapter 1- Introduction

1.1 Quantum Dots

Quantum dots are small semiconducting crystals that absorb and re-emit a photon at a lower energy level, changing their wavelength. The light they emit is affected by the particle size (Figure 1). Quantum dots range from two to ten nanometers in size taking both bulk properties and the properties of individual atoms and molecules, which allows the band gap of the dots to change with particle size. Current applications focus on making light emitting diodes (LEDs) more attractive as a primary lighting sources, causing efficiency increase in photovoltaic cells, and their use in biological imaging.¹

Figure 1: As quantum dots are excited by light with a higher energy wavelength they absorb part of the energy and emit a new wavelength of light based on their size. As the quantum dot grows in size it emits lower energy wavelengths.¹

The wavelength of light emitted depends on the size of the quantum dot. During one common synthesis method for CdSe quantum dots, two flasks of chemicals are mixed at 225°C and then quenched to room temperature after a desired reaction time had been

met.² The quantum dots stop growing as the temperature cools. Temperature uniformity of the flask and the amount of mass being cooled during the reaction prevented the nucleation process from stopping at the same time throughout the flask. The poor temperature uniformity during quenching causes large differences in the size of the quantum dots in the solution. To better control the factors of quantum dot synthesis, such as cooling rate and mixing of synthesis solutions, the use of a microfluidic chip was proposed [Peter Gonsalves, Thesis].

1.2 Microfluidics

Microfluidics is the use and manipulation of small quantities of fluid through a system to achieve a desired effect. It offers the ability to use small sample and reagent quantities with higher efficiency and more control than bulk processes. Because of the amount of reagent being used, microfluidics provides a high amount of control during synthesis processes.³ However, quantum dots synthesized inside of a microfluidic chip could have a more uniform and predictable size if the cooling rate of the chip were controlled, leading to a more uniform emitted wavelength.⁴

Cal Poly microfluidics has focused on Polydimethylsiloxane (PDMS) molds for microfluidic channels because of the ease with which PDMS chips are created, and the cost effectiveness of this method. Quantum dot synthesis uses octadecene (ODE) as an organic solvent during the synthesis. PDMS swells in contact with ODE, and dissolves with extended exposure.⁵ The purpose of this project was to implement anodic bonding as an alternative method of creating microfluidic chips in the Cal Poly lab so that more robust chips could be made from silicon and glass.

1.3 Anodic Bonding

Anodic bonding is a packaging method that bonds materials to silicon at high temperatures (200-500°C) under an applied voltage (300-1000 V).⁶ Metals and glasses form a permanent bond with silicon under these conditions. By attaching a cathode to the glass wafer and an anode to the silicon wafer, covalent bonds are formed (Figure 2).⁷

Figure 2: While the wafers are hot an applied DC voltage across the system creates a depletion zone as sodium ions evacuate. This creates a network of oxygen anions that can diffuse to form covalent bonds between the glass and silicon.

While certain semiconductors, metals, and different types of glasses can be bonded to silicon, this project's scope is to characterize the bond between Corning 7740 (Pyrex) glass and silicon. Bonding bulk glass to silicon is well documented. Most current research into this technology revolves around thin films as an intermediate layer to create an anodic bond at a lower temperature so that more delicate structures may be used or to bond silicon or glass to nitrides or complex material surfaces.^{8,9} A lower temperature processes lowers the residual stress of a system, creating less mechanical interference for the device due to the temperature dependence of the coefficient of thermal expansion (CTE) of the glass.^{10,9}

1.4 Uses of Anodic Bonding

Anodic bonding creates opportunities in the design of micro electrical mechanical systems (MEMS) field by creating hermetic seals without the use of adhesives. In

complex structures like micropumps, alternating Pyrex and silicon wafers are used to create complex structures that can be electrically actuated (Figure 3).¹¹ Intermediate adhesive layers have trouble with generated thermal stresses from differences in CTE, and silicon to silicon wafer bonding techniques require much higher temperature steps (between 800 and 900°C) that create technical limitations in the design of a device such as limiting the types of actuation available. Pyrex's close match of CTE to silicon for most bonding temperatures creates low residual stresses, varying between 100 and -100 ppm over the range of temperatures given. Capacitive sensors can also benefit from anodic bonding.¹² Since capacitive sensors rely on a reference pressure to sense changes in exterior pressure, a hermetic seal about the reference cavity is crucial to accurate readings (Figure 4). The deflection of a membrane changes the distance between two surfaces, changing the capacitance between those surfaces by reducing the distance between them. Anodic bonding was useful in this field originally because it can be used as a batch technique, allowing many devices to be created at once. It is still used as an alternative to direct wafer bonding technologies here, but is not as common. Direct wafer bonding uses higher temperatures and different substrate treatments to bond two wafers together, producing a similar effect.

Figure 3: Alternating wafer stacks during processing allows anodic bonding to be the primary adhesive method between wafers. Here the design uses Pyrex to form a chamber for the fluid flow, and a hermetic cavity for pressure actuation of the membrane.¹¹

Figure 4: A capacitive sensor. External pressure flexing the membrane changes the capacitance of the interior system.¹²

Chapter 2 – Background Information

2.1 Mechanisms of Anodic Bonding

Anodic bonding is a solid state bonding technique often used in MEMS to create a hermetically sealed structure.⁶ The bond formed often benefits any device that might use an airtight seal around a cavity, or a device that requires reactions in extreme conditions like those found during quantum dot synthesis. Usually glass is bonded to silicon or a metal thin film on the silicon's surface.¹³ A DC voltage applied across the wafer stack at high temperatures causes a restructuring of the glass that lets oxygen anions in close contact with the silicon wafer's surface, held by electrostatic forces, bond with the silicon. This bond permanently fuses the glass to the surface of the silicon.¹³

Material choice influences how well the silicon and glass bond to each other. P type silicon is usually used for anodic bonding because the positive dopant increases the electrostatic force during the bonding process, allowing for a stronger bond formed faster than bonds in undoped or N type wafers.¹⁴ This occurs due to local increases in the resistivity of the glass because the negative dopants inside the wafer. Negative ions sitting at the interface slow the migration of sodium in the glass, preventing quick depletion zone formation (Figure 5).

Figure 5: N type silicon slows the migration of sodium in the glass due to local electric affects.

Borosilicate glasses with a coefficient of thermal expansion (CTE) similar to silicon's and a high thermal shock resistance are used (Figure 6). Because Corning 7740's CTE becomes smaller than that of silicon's after 300°C it places the surface of bonded silicon in tension, preventing the buckling of these devices. Glasses are chosen for this quality to reduce residual stress in bonded samples. Residual stress can damage thin devices, causing buckling, or even crack one of the wafers in extreme cases.¹⁵ For a given wafer thickness there is an optimal temperature at which the residual stress is minimized by matching CTE.^{15,14} In addition glasses are chosen for their elemental composition (Table I). Mobile charge carriers in the glass are required for diffusion mechanisms to create sufficient electrostatic force to bring the surfaces into intimate contact. Usually the sodium is the primary mobile charge carrier due to how regularly it appears in glasses, but lithium has been used as an alternative mobile charge carrier to further increase bond quality in some cases.^{16,17} Common glasses, such as soda lime glass, have poor thermal shock resistance and a large CTE, and are not used because of this, but they can still be bonded to silicon using the same mechanism.

Figure 6: Comparison of the coefficient of thermal expansion between Corning 7740, 7070, and 9826. Corning 7740 is the most common glass used in anodic bonding. The difference between CTE is measured in 10^{-6} worth of change in dimension.¹⁸

Table 1: Common glasses and their elemental compositions¹⁹

Glass	Elemental Composition
Corning 7740	80.6 SiO ₂ 12.6B ₂ O ₃ 4.2Na ₂ O 2.2Al ₂ O ₃ 0.1Cl 0.1CaO 0.05MgO 0.04Fe ₂ O ₃
HOYA SD-2	25-70SiO ₂ 20-30Al ₂ O ₃ 10-20ZnO 2-5MgO 1-5Na ₂ O 1-5B ₂ O ₃
Soda-Lime Glass	73 SiO ₂ 14NaO ₂ 9CaO 4MgO 0.15Al ₂ O ₃ 0.1Fe ₂ O ₃ 0.03K ₂ O 0.02TiO ₂

Heating of the glass and silicon allows the electric field to effect the diffusion of sodium ions in the glass. There is little or no creep that occurs during the bonding process because the temperature used during bonding is not close to the glass transition temperature of Corning 7740 (Pyrex) (820°C) and the melting temperature of the silicon (1414°C).¹³ A cathode is attached to the glass while an anode is attached to the silicon to give the silicon a positive charge with respect to the glass. Heat allows the glass to act like an electrolyte during the bonding process.^{7,20} The ionic conductivity of the glass is

high enough at elevated temperatures to allow ion disassociation, causing a migration of positively charged species towards the cathode.^{7,13} Sodium diffuses through the glass' structure towards the cathode. Other positive ion species also participate, such as boron, but their mobility is limited due to their much larger size and arrangement within the glass network.⁷ As ions migrate towards the cathode in the glass, a depletion zone forms at the surface adjacent to the silicon. The depletion zone then restructures itself to a network of oxygen anions to better balance the charge buildup.²¹ Aided by this restructuring, the electrostatic forces of the system cause the two surfaces to contact at a point and form a chemical bond. The bond spreads from this point, producing a bonding front that brings the area surrounding the bond front close enough together to continue the diffusion of oxygen to form new bonds. The surfaces must be clean for this to occur. High roughness or particle contamination prevents the bond front from bringing the surfaces close enough for chemical bonds to form.²²

Monitoring electrical factors shows bond progress. A current vs. time (dI/dt) plot indicates how quickly a depletion zone forms, and indicates the movement of positively charged species away from the interface (Figure 7).²³ Electrically, the depletion zone formation is modeled as a variable capacitor while the glass behaves as a variable resistor (Figure 8).^{24,25} Initially the electrical resistivity of the glass acts as a resistor that decreases in value as a depletion zone forms. The depletion zone eventually acts as a fully charged capacitor because the glass is unable to participate in ionic conductivity in a meaningful manner due to lack of mobile ions in the structure. Initially during the bonding process there is a high flow of current, but as time passes the current decreases

as the capacitor fills. The area under this dI/dt plot indicates how quickly a bond will form and the quality of a bond, most often measured as the percent of area bonded.¹⁰

Figure 7: A dI/dt plot for several factors. The area under the curve indicates how fast a depletion zone forms and indicates the final quality of the bond. This also gives a good indication on the relative effect each factor has on the final product.¹⁰ Changing voltage and temperature have a great effect (a,b). Having a thermally conductive atmosphere containing oxygen also changes the current during bonding (c,d). Increasing the resistance of the glass makes current movement harder as well (e). Chemical factors at the interface did not have a great effect on the current (f)

Figure 8: An electrical model of the wafer stack during the anodic bonding process. Formation of the depletion zone prevents glass from acting as an ionic conductor.²⁶

The voltage applied during bonding, the temperature at which the bonding takes place, the thickness of the glass, the atmospheric conditions, and surface chemistry during the bonding process all have an effect on the final outcome of the procedure (Figure 9).¹⁰ Temperature and voltage are both strong indicators of bond quality. As temperature is raised, it affects the mobility of ions in the glass as diffusion becomes easier throughout the structure. Voltage has a similar effect, greatly increasing the quality of bond per unit during bonding because it is the primary driving force for sodium diffusion. Atmospheric conditions affect the ability of the bond to form as well.

Figure 9: Some of the different factors affecting anodic bonding. Movement up the response scale shows the relative increase in effectiveness from test to test. Downward movement results in decreasing strength. Temperature has the largest effect on the ability to form the bond because it increases the mobility of ions in the glass. The reduction in strength at longer times is associated with errors of the test method.⁸

Atmospheric oxygen aids in the formation of the bond due to an increase in available oxygen for bonding, though the thermal conductivity of the gas also has an effect.

Thickness of the glass reduces the effective voltage at the interface between the glass and silicon, detracting from the strength of the bond by reducing the available electrostatic force at the interface. Silicon surface chemistry also has a large effect on the bond.²⁷

Creating a more hydrophilic surface on both wafers by placing N type silicon and Corning 7740 glass into an ammonium hydroxide solution, bond quality was greatly improved for the same conditions and bond times. By improving the amount of available oxygen and hydrogen at the bond surface, the wafers were able to form higher quality bonds, as measured by a percent of the bonded surface area, when compared to wafers without this surface treatment at the same times. In addition to all these factors changing, the chemical composition of the glass also affects the strength of the bond. Replacing sodium with a more mobile ion, such as lithium in the glass, could increase bond quality and strength.

The network around sodium atoms allows them to participate in the reactions occurring during depletion zone formation.^{10,26} Borosilicate glass networks are composed of silicon atoms connected to boron and aluminum by bridging oxygen atoms. Sometimes these oxygen atoms do not bridge, forming a non-bridging oxygen ion (NBO) in the network (Figure 10). Sodium ions in the solution are bound by $[\text{AlO}_4]^-$ or $[\text{BO}_4]^-$ units in the glass (Figure 11). The size of the structures around the sodium atom causes the activation energy for the movement of sodium ions to be relatively low. The low activation energy leads to sodium's participation in the anodic bonding process. It was found that as

Figure 10: Bridging and non-bridging oxygen in a glass network. The non-bridging oxygens bound sodium ions in the borosilicate glass network.

Figure 11: A borosilicate glass network. The sodium ions are weakly held in the structure, allowing for depletion zone formation. They are generally bound in place by large $[\text{AlO}_4]^-$ or $[\text{BO}_4]^-$ molecules.²⁸

the sodium depletion zone is formed, a large hydrogen drift moved in the same direction as the sodium atoms. A hydrogen depletion zone was found at long bond times (Figure 11). Water molecules that had diffused into the glass through dissolving and leaching effects had disassociated into H^+ and $[\text{OH}]^-$, or $[\text{H}_3\text{O}]^+$ and $[\text{OH}]^-$ increased the sodium atom's mobility by taking its place temporarily.⁶ Hydrogen atoms take the place of sodium atoms as the depletion layer formed resulting in the reactions:

Figure 12: A concentration profile for sodium and hydrogen during the bonding process. Sodium has such high mobility in the glass because hydrogen atoms temporarily take their place during the bonding process, lowering the amount of energy required during the migration.⁶

Hydroxide groups left behind build up and form unstable complex groups that aid in the oxidation reactions to form silicon dioxide bonds at the surface and water.⁶ This is shown in the reactions:

Through these reactions, the two surfaces become covalently bonded (Figure 12). Similar reactions will take place in any anodic bonding process. Both sodium and hydrogen drift play an important part in bond formation between these two surfaces. While other depletion zones form at higher temperatures and voltages, they do not form as readily due to how they are bonded in the structure. In addition the mechanisms of depletion zone

formation, buildup of interfacial oxygen anions, and covalent bond formation are common to all anodic bonding processes.

Figure 13: During the bonding process complex SiO_2 , $[\text{OH}]^-$ structures form to aid in the diffusion of oxygen between the two surfaces. Eventually the $[\text{OH}]^-$ structures reform into H_2O and evaporate away from the bond front.^[26]

Several attempts have been made at improving glasses specifically for the purpose of anodic bonding. One popular area of study is using lithium in aluminosilicate and borosilicate glasses instead to improve the mobility of the diffusing species further. This leads to larger depletion zones at lower temperatures and times. A lithium aluminosilicate- β quartz glass ceramic layer sputtered on a silicon wafer allowed anodic bonding to another silicon wafer at 180°C and 60V in 45 minutes.²⁹ The low temperature and voltage used during this test shows that more delicate devices could benefit from anodic bonding.

2.2 Characterization of the Bond Interface

The quality of an anodic bond can be measured by non-destructive methods relatively easily. Generally ultrasound can be used to determine whether or not areas of a device are fully bonded.³⁰ The ultrasound image shows in higher clarity what areas of the

wafer are bonded. This method is used in industry to examine devices and ensure quality, but it does not tell the mechanical properties of the bond interface. Fracture mechanics and traditional mechanics have both been applied to quantify the mechanical properties of the bond with varying degrees of success.

Strength and toughness are two qualities used to measure other microfabrication wafer bonding techniques.³¹ The purpose of anodic bonding is to fix two surfaces together so it has been graded by these same criteria. Many methods to measure the bond quality have been used. Destructive methods used to measure the bond, such as tensile, shear, and pressure tests often have mechanical problems while measuring the bond. Usually the glass would break when pressure was exerted instead of debonding the interface. In addition residual stresses interfered with accurate measurements of the interfacial strength. Using similar bonding conditions two separate researchers found large differences in their tensile tests. At 900 V and 450°C, bond strengths of 30-40 MPa were found, while testing at 800 V and 500°C, strengths of 10.3-20.7 MPa were found. Samples failed 100-200 μm into the glass from the interface, revealing that the strength found during these tests were a function of the residual stress and strength of the glass.^{23,32}

Fracture mechanics methods of measuring toughness were not more accurate. Chevron-notched (CN) and straight-through-cracked (STC) compact tension tests also found that cracks propagated through the glass wafer. Both of these tests use tension to propagate a crack along the interface. These methods did create reproducible results that were similar in value for similar conditions, but did not measure the toughness of the bond between the two wafers due to crack propagation into the more compliant glass.³³

Nondestructive methods for measuring the toughness of a bond have been more successful in determining properties. One popular test method is to create a double cantilever beam specimen with a spacer of known height inserted between wafers (Figure 14).³¹ While wafer fusion methods often break wafers upon blade insertion, anodically bonded wafers can be fused together with the spacer already present. Because this method does not rely on destructive testing the bond, strength can be more accurately measured without tensile forces causing crack propagation into the glass. The Plaza test is another method that can be used to measure bond mechanics nondestructively.²⁶ The plaza test could tell of the stresses at the interface and the fracture toughness.

Figure 14: A double cantilever beam sample setup. By calculating the surface energy the toughness of the bond can be found through linear elastic fracture mechanics (LEFM).³¹

2.3 The Plaza Test

A nondestructive method was used to measure the strength and toughness of the interface. This method, developed by Plaza et al. can find the strength and the toughness of the bond using a spring model and fracture mechanics model (Figure 15).²⁴ These are

found by inspecting bonded cells of the test. To determine whether or not a cell has been bonded a visual inspection is performed. Cells that were bonded during testing had dark bond areas outlined by the cell's walls (Figure 16).

Figure 15: A device of the Plaza chip. As the width of the cells narrow it becomes harder for the glass and silicon to bond together. The separation between rectangular structures is greater than 500 μm to prevent residual stresses from neighboring structures from interfering with the bonding process.

Figure 16: Bonded and unbonded cells on a Plaza wafer. Above is a cross section of the effect. The bonded cells show thin outlines around the structure. These crack lengths are measured to find the toughness of the bond. Unbonded cells in this picture are colored by diffractive effects.

2.3.1 Bond Strength using the Plaza Test

The strength of the bond can be measured by the elastic restorative force trying to open the cell.²⁶ A bond begins to form when the elastic restorative force of the system and the electrical force of the system are equal to each other:

$$F_{net} = 0 = -F_e + F_k$$

Where F_e is the electrical force attracting the surfaces to each other, and F_k is the elastic restorative force resisting surface contact. If the area remains bonded at room temperature then the strength was assumed to be greater than the elastic restorative force of the material. The electrostatic pressure (P) bringing the two surfaces together is defined by the equation:

$$P = \frac{1}{2} \epsilon_0 \frac{V^2}{h}$$

2

Where ϵ_0 is the permittivity of free space, V is the voltage applied during bonding, and h is the glass thickness. The electrical attractive force (F_e) then is:

$$F_e = PA$$

3

Where A is the area of the bond surface. The elastic restorative force is determined by the geometry of the bonded area and the depth of the channel (Figure 17). The elastic restorative force can be modeled as a spring in series. Both the silicon and glass deflect slightly and try to restore themselves to a neutral position. Narrowing channel width makes bonding more difficult, while increasing depth forces the spring to larger displacements (Figure 18). A bond forms successfully under these conditions when the bond strength is greater than the elastic restorative force.

Figure 17: A cross sectional view of a Plaza test device. As the etch depth, g_0 , increases and the channel narrows the structure becomes harder to bond.

Figure 18: A mechanical model of what occurs during the bonding process. For a bond to form, the electrical force must overcome the elastic restorative force of the material.²⁶

The elastic restorative force tries to pull the bond apart, similar to a spring. This can be modeled as a spring in series. The equivalent stiffness of the system, E_{eq} , is calculated using the equation:

$$E_{eq} = \frac{E_1 E_2}{E_1 + E_2}$$

where E_1 is the Young's modulus of the glass and E_2 is the Young's modulus of the silicon. The force applied by the bond to hold together the parallel surfaces can be calculated using Hooke's Law:

$$F = \frac{-E_{eq}A}{L_0} \Delta L$$

5

Where A is the bond area, L_0 is the thickness of the two wafers minus the etch depth, and ΔL is the full distance from one side of the wafer stack to the other. The spring force of the system can be described by the equation:

$$F_k = k_{eq}g_0 = \left(\frac{E_{eq}A}{L_0}\right)(\Delta L)$$

6

Where g_0 is the etch depth. The stress at the bond interface can be described in the equation:

$$\sigma = \frac{F_k}{l(w - 2a)}$$

7

Where l is the length of the cell (10 mm) w is the width of the smallest bonded cell, and a is the crack length measured at that cell. This equation gives the stress at the bond interface (Figure 19).

Figure 19: The crack length is measured around the bond area at certain widths.

2.3.2 Bond Toughness using the Plaza Test

Linear elastic fracture mechanics can be used to determine the toughness of the bond by finding the strain energy required to bring the surfaces into contact. In this model the energy contained in the bond area prevents strain energy from restoring the two materials to their original position. The bonding of the two surfaces is modeled as a crack closing. Mode I fracture, where the crack opens in the direction of applied force, is assumed to be the primary mechanism acting on the bond (Figure 20). The entire system can be modeled as two beams meeting (Figure 21).

Figure 20: Different modes of fracture. The dominant fracture mode in the case of the plaza sample is mode I where the applied force is normal to the plane of the crack.

Figure 21: The beam model used to find the fracture toughness of the sample.

During bonding the two surfaces coming together and forming covalent bonds acts to close the space between the two surfaces, modeled as a crack in this case. The bond begins in the center of the two surfaces and spreads until the strain energy release rate reaches a minimum value. The energy release rate, G , can be defined as:

$$G = \frac{dW}{dA}$$

8

Where W is the change in potential energy of the crack. G describes the energy dissipated during fracture per unit of new surface area. Each cell bonds with a crack length at $G_{\min}$, the stored strain energy at which the increasing surface area and the strain energy being applied by the structure's wall balance each other. This change in potential energy can be broken down to the equation:

$$W_p = U - W_f$$

9

Where U is the strain potential energy, and W_f is the work done by an external force. Since the system does not have any external forces acting on it W_f is assumed to be zero. Modeling the system as a single beam deflecting allows for an easier calculation of the potential strain energy (Figure 22). The deflection at a distance from the wall is known to

be the channel depth. From this the load profile of the beam can be calculated. Once the loading profile is known the strain energy of the beam (U) can be found with the equation:

$$U = \int \frac{M^2}{2EI} dx$$

10

Where M is the moment acting on the end of the beam and EI is the flexural rigidity of the beam. The moment for each load is calculated separately for one end of the beam and this moment is summed. The strain energy stored in the beam at different crack lengths is calculated to find the strain energy release rate. Beam equations used can be found in Appendix A.

Figure 22: The assumed method of loading for the beam system. This will give an approximation of the strain energy of the beam

To calculate the stress intensity factor, K , which describes the toughness of the bond, the materials are assumed to be linearly elastic, homogeneous, and isotropic at the two interfaces. An Irwin-type relation can be derived between K and $G_{\min}$:

$$G = \frac{|K^2|}{E_L \cosh^2 \pi \varepsilon}$$

11

where ε is the oscillatory index that describes the change in behavior of the crack due to elastic mismatch.³⁴ E_L describes the average modulus and can be found using the equation:

$$\frac{2}{E_L} = \frac{1}{\bar{E}} + \frac{1}{\bar{E}}$$

12

$\bar{E}$ describes the plane strain tensile modulus and is calculated in the equation:

$$\bar{E} = \frac{2\mu}{1 - \nu}$$

13

Where μ is the shear modulus of the materials and ν is Poisson's ratio. The oscillatory index, ε , takes into account different pathological behaviors in linear elasticity solutions for interfacial cracks:

$$= \frac{1}{2\pi} \ln \frac{1 - \beta}{1 + \beta}$$

14

β is the Dundurs elastic mismatch parameter and is defined by:

$$\beta = \frac{1}{2} \frac{(1 - 2\nu_2)/\mu_2 - (1 - 2\nu_1)/\mu_1}{(1 - \nu_2)/\mu_2 + (1 - \nu_1)/\mu_1}$$

15

Where $\mu_{1,2}$ are the shear moduli of each material and $\nu_{1,2}$ are the Poisson's ratios of each material. K , the toughness of the bond, can be solved for using the equation:

$$K = \sqrt{G_{min} E_L \cosh^2 \pi}$$

1616

Chapter 3 – Project Overview

3.1 Long Term Scope

The final goal of this project is to implement a new bonding method for the creation of MEMS devices inside of the Cal Poly cleanroom. Examples of such devices have been given, but the project that required anodic bonding was a microfluidic chip that could produce quantum dots. Currently PDMS is the primary bonding technique of the lab. While anodic bonding will not replace PDMS processes for all microfluidic device creation, certain devices can only be made from glass and silicon because of the service temperatures or chemicals used.

3.2 Previous Work

No previous work on the characterization of anodic bonding has occurred at Cal Poly. At least one author has already tried to characterize anodic bonding through the use of the Plaza test using finite element analysis (FEA).¹⁷ It was revealed that pull in voltage could be calculated for small channel depths using a parallel plate capacitor model, but the model could not accurately predict fracture toughness. Double cantilever beam specimens have been used to predict the fracture toughness of the material. The trend of determining bond quality seems to be nondestructive methods, and the Plaza test is a method that creates great opportunity in quantifying bond strength and toughness. Due to the complex geometry of the crack interface however, accurate measurements of fracture toughness have been difficult to calculate from the Plaza test alone.

3.3 Scope of Current Work

The goal of this project was to produce a device capable of anodic bonding for use in the Cal Poly cleanroom, and add to the overall knowledge and data for the Plaza

test as a method to quantify the mechanical properties of the bond. 4" wafers were allowed to bond over their entire surface for the test. The spring and beam model proposed in the previous section were used to try and find the fracture toughness and strength of the bond.

Chapter 4 – Experimental Procedures

4.1 Anodic Bonding Equipment Setup

To create a device capable of anodic bonding, a heat source and power supply must be used to heat and apply current through a pair of electrodes. Two ½” thick 4.25” wide 302 stainless steel disks were used as electrical contacts. The disk width was chosen for the 4” wafer size the lab used as a standard. The stainless steel disks were surfaced to ensure the lowest possible contact resistance. A hole was drilled and tapped in each for stainless steel screws so that alligator clips could be used to create electrical contacts. The power supply used originally was capable of 300 V and could not produce readable current values during bonding (Less than 0.001 mA). While it was possible to bond at this voltage, bonding occurred much faster at 400+ V. The second power supply, a Hewlett Packard 6515A DC power supply, was capable of generating 1500 V without limiting the current during the bonding process. The highest voltage tested was 900 V at which the gap between electrodes reached its breakdown potential, arcing electricity between the two plates while two 500 µm wafers were between the electrodes. At 800 V there was no breakdown.

The measured interface temperature of this lab setup at maximum temperature was 407°C after 30 minutes of heating by using a surface probe while the hot plate was set to 540°C. All bonding occurred at this temperature to prevent variations in temperature from changing bond strength. Bond temperature should be performed at a minimum of 200°C to aid in the diffusion of charge carriers in the glass and silicon. This occurs at 300°C

Originally aluminum disks were used as electrical contacts. Repeated use at high temperature caused an oxide buildup on the surface of the disks. This increased the contact resistance of the system so that bonding procedures were taking longer amounts of time or bonding did not occur at all. Stainless steel was suggested as a replacement after trying several thin films on the aluminum to prevent further surface degradation.

The anodic bonding device was in ambient atmosphere conditions. It consisted of a pair of stainless steel electrodes, a hotplate, a power supply, a multimeter, and banana clips connecting the system. Stainless steel wires and large copper alligator clips were used to attach to the hot plate because the springs in the alligator clips originally used gave out at the temperatures used.

4.2 Development of the Plaza Test Mask

The plaza test mask was created in AutoCAD (Figure 23). The spacing between each structure on the surface is 500 μm to ensure that the residual stress produced if one structure bonded would not affect adjacent structures.²⁶

Figure 23: The plaza test mask used for the experiments of this thesis. This mask is meant for a 4" wafer. The width of all cells are in microns.

4.3 Plaza Test Wafer Processing

All processing steps were performed in a class 1000 cleanroom. P type wafers 100 mm wide, oriented on the (001) plane were used (Figure 24). P-type wafers significantly decrease the bond time for devices. N type wafers can be used for device creation, but device creation time increases by 10-20 minutes under the same conditions, and the likelihood of forming a bond decreases.

Figure 24: A processing flowchart for sample creation.

4.3.1 Thermal Oxide Growth

Before an oxide was grown, the wafers were dipped in Piranha solution at 70°C for 10 minutes. Piranha is a 9:1 mixture of sulfuric acid to hydrogen peroxide that cleans organics from a surface. After a deionized (DI) water quench and rinse, the wafers were then dipped into a buffered oxide etchant (BOE), removing native oxide. Wafers were then quenched and rinsed again with DI water and nitrogen gun dried.

The wafers were then placed into a quartz boat for oxidation. The boat is loaded so that a dummy wafer protects the device wafers on each exterior to normalize air currents around the device wafers. The furnace is preheated to 900°C before the wafers are placed inside. While the furnace is heating, the DI water is raised to a boil so that the rate of oxide growth can be increased with water vapor. Ultra high purity nitrogen gas is flowed through the chamber while the wafers are present to prevent oxidation at lower than the desired temperature. The furnace is opened and the quartz boat is slid into the furnace tube slowly to prevent warping. After capping the furnace the furnace is heated to the final temperature of 1110°C. The Deal-Grove model was used to find the time after which the oxide thickness would be 5000 Å:

$$t = \frac{X_o^2}{B} + \frac{X_o}{B/A}$$

17

Where X_o is the oxide thickness, and B and A are constants related to the environment during oxidation. The amount of time predicted to grow a 500 nm oxide for the furnace used was 90 minutes. The nitrogen flow is turned off and a flow of O₂ gas through H₂O at 100°C is turned on. This creates a wet oxide which will grow faster than an oxide that was grown with just O₂ gas. After oxide growth the furnace is left to cool with a nitrogen gas flow to prevent oxide from growing at a lower temperature than desired. Once the furnace has cooled the wafers are removed.

Once the wafers were removed the oxide thickness was measured using a Filmetrics reflectometer. After the light source was allowed to heat for 30 minutes the system was calibrated by taking a measurement from bare silicon. The system was then checked against a calibration sample for accuracy. The error of the reading on the

calibration sample was less than 1% each time. The wafers with a new SiO₂ coat were then each measured in several spots around the wafer to check for uniformity of the device.

4.3.2 Spin Coating

After oxide growth the wafers are given a 20 second BOE dip to prepare the surface for spin coating. Positive resist was removed from the storage refrigerator and set out several hours for defrost. Bringing the resist up to room temperature before use ensures that the properties of the resist during coating are as rated. Before being placed into the spin coater, a dehydration bake occurred at 150°C for 60 seconds to remove any surface moisture. Wafers were then allowed to cool. Afterwards the wafer was placed in the spin coater and held on the chuck by vacuum. The surface of the wafer was then treated with a primer to ensure that the surface of the wafer is hydrophobic for the resist. MCC Primer 80/20 was used to change the wafer's SiO₂ surface from hydrophobic to hydrophilic. Approximately 3 mL was syringed onto each wafer before the spin coater started the initial steps of its program. On the third step the machine was stopped and opened so 4 mL of Shipley S1813 photoresist could be added. The spin coater was then allowed to complete its program. After removing the wafer from the machine a soft bake was performed to evaporate some of the solvents in the photoresist to give the photoresist structure for alignment and exposure. This occurred at 90°C for 60 seconds.

4.3.3 Patterning Photoresist

The mercury vapor arc lamp was allowed to heat before samples were placed inside so that the proper amount of energy would be applied during exposure steps. The mask created for this project, a Plaza test mask, was loaded between two glass slides.

Wafers were placed inside of the aligner. The recommended dose for Shipley S1813 is 150 mJ/cm^2 . This dose was applied by the aligner to pattern the photoresist. The aligner uses light integrals to apply dose.

After exposing the photoresist soluble parts of the image are developed away. Microposit MF CD-26 developer was used to develop the wafer. The wafer is placed into the developer for 4 minutes and agitated. Once the wafer was developed it was rinsed with water and nitrogen gun dried. After cleaning each wafer was inspected under a microscope to ensure that the image was transferred properly. This was done to ensure that the photomask was placed in properly, and the pattern had been sufficiently developed. Once the image was inspected the photoresist was hard baked at 150°C for 60 seconds to remove the remaining solvent, giving the photoresist more structure.

4.3.4 Etching Processes

Once the photoresist was hard baked, the pattern was etched into the oxide. Wafers were dipped in BOE for approximately 1 minute for every $1000 \text{ \AA}$ of oxide, with a 10% over etch included in final time. Since device wafers had an oxide layer of $5000 \text{ \AA}$, they were placed in BOE for 5 minutes and 30 seconds. The device wafers were then quenched, and then rinsed with DI water followed by a nitrogen gun dry.

Etching the mask into the oxide allowed the photoresist to be stripped. The photoresist was stripped by using Microposit Remover 1165. The stripper was heated to 60°C , and the device wafers placed in the solution for 5 minutes. The wafers were then quenched and rinsed in DI water before being nitrogen gun dried.

The device wafers, now only comprised of a patterned oxide and bare silicon, were then etched with tetramethylammonium hydroxide (TMAH). Because the etch

depth was so shallow, attempts to characterize the etch rate were unsuccessful. Wafers were etched by trial and error since desired etch depth, 300 to 600 nm, was relatively small when compared to the etch rate, approximately 28 $\mu\text{m}/\text{hour}$ or 77 $\text{\AA}/\text{second}$. Dilution of the TMAH was not an acceptable solution as this increases the etch rate. These desired depths were found experimentally. At 200 nm, all test spaces had bonded; while at 700 nm very few test spaces bonded. TMAH at 25% by weight was used because the device's etch depth was more uniform across the wafer in wet etching than wafers etched using RIE. TMAH was heated to 70°C using a hot plate. After that a resistive heating element was turned on to continue heating the TMAH to 85°C. A stir bar was used to create a uniform temperature throughout the etchant. Once the etchant reached temperature device wafers were etched in groups for 10 to 15 seconds at a time to etch to the correct depth. Temperature was monitored to ensure it did not fall below 80°C during the etching process. Between each etch the wafer was rinsed, dried, and then the etch depth measured by profilometer. The oxide was remeasured in the area around this device to ensure accurate measurements. This cycle was repeated until the average depth of one test cell was between the target depths. Once the wafers were etched, the remaining oxide was removed by using BOE for 5 minutes and 30 seconds to make sure all oxide was removed.

4.4 Profilometer Measurements

The uniformity of the wet etch was poor, so the depths of each cell was measured to more accurately find bond strength and strain energy release rate. To do this, a profilometer was used. The cells of each device were scanned to find the etch depth of a cell. These etch depths would indicate how difficult it would be to bond the cells.

4.5 Anodic Bonding

To anodically bond the plaza test wafer to a glass wafer the anodic bonding lab setup was used. Corning 7740 glass was bonded to silicon. The glass wafers used were either 500 μm or 1mm in thickness. The silicon wafer was placed on the cathode. The glass wafer was placed on top and aligned while the hot plate was cool. The anode was then placed on top of the wafer stack. Before a charge was applied the hot plate was allowed to heat to the maximum temperature to measure bonding time of a hot device. The device reached a peak temperature after 30 minutes. Once the device was at temperature the power supply was turned on. The device was then allowed to sit from 30 minutes to 3 hours depending on glass thickness and applied voltage.

4.6 Crack Length Measurements

The crack length across the middle of each rectangle in the plaza test wafer was recorded. Using an optical microscope at 200X to 500X the crack length was measured. The crack length was averaged for each cell by taking a measurement from each sidewall from the center of the device (Figure 25). Not all devices on a wafer completed a bond. If a portion of the relevant bond area was not bonded due to particulates or other contaminants it was discounted (Figure 26)

Figure 25: A picture of one of the Plaza test cells under a light microscope. The crack length was measured from both walls and averaged for all reported values.

Figure 26: The crack through, and unbonded area around these test cells would prevent it from being counted.

4.7 SEM Work

Samples were then scribed and broken into samples small enough to be placed in the scanning electron microscope (SEM). This was done to take images of the depletion zone formed during the anodic bonding process. While looking at the samples the depletion zone was photographed and measured to compare at different bond times and

glass thicknesses (Figure 27). Due to the size of the chuck only samples that were bonded to the 500 μm thick glass could be photographed.

Figure 27: A SEM image of the depletion zone. This is a cross section of the sample. The black line between the silicon and the glass is where covalent bonding between the two surfaces takes place. The sodium depletion zone is marked by the change in intensity of white between the first micron, and the following thickness of glass. Inside of the depletion zone oxygen anions restructured themselves to better balance the charge of the system.

Chapter 5 – Results and Analysis

5.1 Creation of an Anodic Bonding Lab Setup

The primary goal of this thesis was to implement a device that could anodically bond silicon to glass in the Cal Poly microfabrication lab, and characterize it. This would allow new devices to be fabricated in the lab, and replace adhesives and PDMS for some processes.

Currently a 1.5 kV power supply is with the system. The maximum voltage allowed running on this system is 800 volts. Breakdown occurred above this voltage range due to the overhang of the top electrode. Making the top electrode smaller than the diameter of the wafer being bonded would prevent breakdown of the gap. This would allow higher voltages to be run for the system during the bonding process with a higher degree of safety.

Bonding has only occurred at the maximum temperature of the hot plate, 407°C. This has allowed for faster bond times, but increases the residual stresses at the bond interface due to the CTE's dependence on temperature. While current projects using the lab setup usually create robust devices, other projects could benefit from the use of lower temperatures, or specific calculations to determine what bonding temperature would be best to minimize residual stresses. One important idea to keep in mind while picking new temperatures for bonding is that the CTE of silicon and Pyrex glass are similar until approximately 320°C. At 400°C there is a difference of 100 ppm between the thermal expansion of the materials (Figure 6).

Several electrode types were tried during the creation of the lab setup. Originally two aluminum blocks were used as electrodes. These worked well initially, but eventually

the finished surfaces of the electrodes began to suffer from oxide buildup. Eventually even at high voltages the system was unable to bond wafers together. The mechanisms for the production of alumina as a protective coating for alloying are well understood. One method of alumina production occurs through a cation diffusion mechanism, and though the presence of oxygen anions.³⁵ Due to the high voltages and temperatures that occur during the anodic bonding process, the rate at which alumina grows due to the cation diffusion method could have increased to a point where it inhibited the aluminum's ability to create a smooth, conductive surface contact with the glass. The aluminum was resurfaced several times while looking for a solution. Eventually the aluminum electrodes were replaced by 302 stainless steel disks.

While the stainless steel disks have not grown nonconductive at service temperature, the disks appear to have problems with diffusion of ions in the glass. The electrode in contact with glass has formed spots during the bonding process. These spots are mirrored on the glass. The spots increase in area coverage of the wafer at longer times. This seems to occur because sodium ions and other positive ions in the glass or near the surface migrate to the surface between the negatively charged steel electrode and the glass wafer. Points of surface contact form diffusion channels of positive ion species, creating Kirkendall porosity over the surface of the glass wafer. These spots were very prevalent in the thick glass samples due to the long bond time. This should be kept in mind for complex devices that may need a clean glass surface to operate. Bonding at lower temperatures or shorter times would slow the formation of these diffusion channels.

5.2 Device Creation Times

Initially the anodic bonding system was unable to reliably bond samples together. This occurred due to problems discussed in section 4.1 from the aluminum electrodes. Currently a complete bond forms between two 500 μ m thick wafers in under an hour, while 1mm thick glass wafers take approximately 2 hours to create (Figure 28). During device creation the wafers were allowed to bond over the complete surface before being removed from the anodic bonding device. The large variation in device creation times between thick and thin glass is because the resistance of the glass in the electric system has been doubled. This produces smaller attractive forces at the interface, and results in slower depletion zone formation.

Figure 28: Bond times at varying voltages. Bonds formed much faster with thin glass wafers.

5.3 Bond Strength

Measurements of bond strength during the test calculated the highest stress observed in each cell. Narrower bond areas are harder to bond, and have much more area

missing at the same crack length of other cells (Figure 26). The maximum stress calculated at the bond interface was 70 MPa. The average stress of all bonds was 35 MPa.

Figure 29: The stress at the interface between the two materials. The only force acting to bring the two surfaces apart is the elastic restorative force.

In thick glass wafer samples, the bond was not less strong necessarily, but the electrostatic forces attracting the glass and the silicon together never overcame the elastic restorative force required to bond smaller cells together. This occurred because of the increase in resistance associated with doubling the thickness of the glass wafer. The change in electrostatic attractive force can be approximated by equation 2. Because the surfaces of smaller cells could not become close enough to allow oxygen anions and hydroxide species to bridge the gap and covalently bond to the opposite surface, the bond could not be formed. Bond strength is not a critical factor in determining whether two surfaces will stay in contact or come together, but the amount of time the two surfaces are

in contact with each other to allow for covalent bonds to form, and if the fracture toughness is high enough to hold the cell.

Instead of bond strength measurements, the model could find the pull in voltage required for a two surfaces to contact. This has been done before for small etch depths, on the order of 200 nm, and small depletion zones, but a model that could predict the pull down voltage at various etch depths and depletion zone values is required for when bonds will form had not been made.¹⁷ To define this model, the effect of the depletion zone on the attractive capacitive force would have to be better understood, as well as what causes bond formation after two surfaces contact. It is unknown what caused the contact and bond formation in the one cell that bonded the 100 μm wide channel. If the etch depth of the channel was nonuniform, this could cause contact at one point, which could form a bond over the remaining surface. Crack lengths along this cell were similar in value to the cells around it.

The bonded channels for both of the thin glasses were similar even though one was bonded at a much higher voltage due to the time required to bond a full 4" diameter wafer. Because these wafers are so large compared to many of the samples found in literature, it takes a long time to form a bond over the entire surface of the wafer. During the amount of time required to bond a wafer with this surface area at these temperatures the depletion zone reaches its maximum thickness. The depletion zones of the low voltage and high voltage thin glass samples were photographed using a scanning electron microscope (SEM) (Figure 25, 26). There was not a large difference between the two depletion zones despite the difference in voltage between the two. B. Schmidt et.al. found that the depletion zone did not grow significantly after 80 minutes at temperatures

between 210 and 280°C. At 400°C the depletion zone may hit its maximum size at shorter times than this. The small differences in depletion zone had no proven effect on the strength of the bond.

Figure 30: A SEM of the depletion zone in the low voltage (400 V) bond sample. Here multiple lines can be seen between the bulk glass and silicon. It is unclear whether or not these are additional depletion zones that formed or shadows due to surface contamination. This is an exact perpendicular views.

Figure 31: A SEM of the depletion zone in the high voltage (700 V) sample. The higher voltage caused a small increase in depletion zone thickness, even at a shorter bond time. This is an exact perpendicular views.

The primary problem with this measurement of bond strength is that it is highly dependent on the ability of the electrostatic force to overcome other factors affecting the bond. These include residual stress forcing open a bond, unclean surfaces, and low electrostatic attractive forces for any number of reasons. For any device that can overcome the electrostatic issues, the bond strength can be calculated. While the difference in strength between low and high voltage samples cannot be calculated for this system, there is a significant increase in the number of successfully bonded nodes at smaller channel widths on the high voltage thin glass wafer. This proves that increased attractive force is the primary factor in determining the formation of a bond in a cell. By making a contact over a larger area and holding these surfaces in contact, the electrical forces allow diffusion processes to begin to contribute to the adhesion between surfaces. The best method for predicting contact for a gap is given by the electrostatic attractive force of the whole wafer. The bond strength of the anodically bonded surface should be close to or higher than the flexural strength of bulk pyrex (69 MPa). Due to the small size of the new bond zone formed there exist few flaws at the bond interface, causing the SiO_2 bonds formed to be much stronger than the bulk glass due to a lack of flaws in its volume.

5.4 Bond Toughness

The bond toughness model agreed with values reported by double cantilever beam specimens in the literature for the thick glass samples (Figure 32, 33).¹⁷ The values for the thick glass samples are significantly higher because of the effect that the increased thickness of the glass has on the second moment of inertia, I , and the channel width, but also the maximum diffusion zone size was probably present in these samples due to their

long bond time. Since the crack length of these samples are greater than the crack length in the thin glass samples, and the etch depth is smaller the toughness should be lower, but the increased thickness of the glass in the sample changed the moment of inertia of the beam. The change in crack length between the thin and thick glass indicates that the toughness of a bond is a function of factors that affect the electrostatic force in addition to the crack length and etch depth. If the thin samples were allowed to reach a fully matured depletion zone size then the fracture toughness values may be correct as well.

Figure 32: Due to geometric factors the fracture toughness values for the thin wafers were calculated to be very low compared to the toughness values calculated by the DCB specimens.¹⁷ This is either because of a shortened bond time or because of the geometry used to find the strain energy release rate.

Figure 33: Thick glass samples reported a fracture toughness that was similar to values found using DCB specimens in literature.¹⁷ Reported values for fracture toughness from outside literature lie between 25 and 30.

Because of the way the normal opening force is applied to the crack in the Plaza test, and since the distances measured are much smaller than the crack lengths measured in the double cantilever beam tests, the exact measurement of the crack has a large role to play. If the bonding was allowed to continue then after a maximized depletion zone had formed the surfaces would be able to have the chance they need to form a full bond across the area. The spring force applied in the model assumes that force is applied equally across the entire surface of the bond area, but as the bond approaches the edge of the structure the resistance to the surfaces coming into contact increases greatly. This would mean that at short bond times the whole surface would not receive the chance to come into contact long enough to resist the restorative force towards the edges of the bond. On the other hand the fact that the bond toughness is similar to values calculated for the DCB samples the thick glass wafer samples may only be a coincidence. Using the geometry of the channel, ignoring non mode I fracture sources and other approximations used in the calculations of the beam model may not allow for accurate measurements to

be produced at all values. Correct values for fracture toughness would be seen for thin glass samples if the average crack length were 3 μm shorter in length. All measurements taken from the wafer can be found in appendix B.

Ideally the model would be a double cantilever beam model that took into account that the ends of the beam were not free, and then the surface energy could be calculated. The factors used to calculate the toughness should be the depth of the etched channel and the crack length of the sample, and the toughness of a bond might vary with bonding variables as higher electrostatic attractive forces would allow the cell to overcome the local geometry preventing bonding.

Chapter 6 – Conclusions and Recommendations

Anodic bonding was successfully implemented at Cal Poly, and device creation was studied. The anodic bonding system completes 4” devices in less than an hour. Visual inspection is the only way of knowing if an entire surface has been bonded. Allowing the bond to mature for longer times at higher voltages and temperatures will increase the full area bonding of the wafer.

The calculations for stresses at the interface of the bond were straightforward. The primary predictor in whether or not a bond will form, the electrostatic forces, are more important than stress at the interface. A predictive model as to whether or not a bond will form under an applied electric field that takes into account the diffusion mechanisms in formation of the depletion zone and the formation of the bonds at the interface in addition to other attractive electrostatic forces is required to determine whether or not a bond will form at any given time.

It is currently unknown whether or not the beam model presented can accurately predict the fracture toughness of a bond. Because the model relied on the shape of the structure the values for toughness varied greatly from device to device, and between wafers. Ideally the fracture toughness should be calculated only through the use of the crack length and etch depth of the channel. The fracture toughness would vary with bond parameters, as the electrostatic force at the interface would determine how much area of a structure the bond would cover. Further testing of samples made at long bond times could accurately predict the mechanics of the bonded interface. To determine if the model could accurately predict the fracture toughness of a sample crack length measurements would

have to be made at increasing bond times to see if maximum fracture toughness could be reached after long bond times.

The thickness of the glass affects the maximum strength of the bond by inhibiting depletion zone formation due to a higher sample resistance. The maximum strength of the bond will be greater than the bending strength of Pyrex (69 MPa) glass due to the few flaws in the bond interface. There may be no good way to test the actual strength of the interface because the bond will have fewer flaws than the glass it is made from.

The fracture toughness of the samples was correct at longer bond times. Thick glass samples, which take long times to bond fully, displayed the correct fracture toughness values (Average $30 \text{ Pa m}^{1/2}$). This was believed to be because of a fully matured depletion zone. The $500\mu\text{m}$ thick glass samples had fracture toughness values between 5 and $30 \text{ Pa m}^{1/2}$. If these were placed on the hotplate again at similar voltages, the fracture toughness of the samples may mature to correct values. It is unknown if the thickness of the glass affects the fracture toughness.

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Appendix A – Beam Equations³⁶

$$R = V \dots\dots\dots = P$$

$$M_{\max} \text{ (between loads)} \dots\dots\dots = Pa$$

$$M_x \text{ (when } x < a) \dots\dots\dots = Px$$

$$\Delta_{\max} \text{ (at center)} \dots\dots\dots = \frac{Pa}{24EI} (3\ell^2 - 4a^2)$$

$$\Delta_x \text{ (when } x < a) \dots\dots\dots = \frac{Px}{6EI} (3\ell a - 3a^2 - x^2)$$

$$\Delta_x \text{ (when } x > a \text{ and } < (\ell - a)) \dots\dots = \frac{Pa}{6EI} (3\ell x - 3x^2 - a^2)$$

$$R = V \dots\dots\dots = \frac{P}{2}$$

$$M_{\max} \text{ (at point of load)} \dots\dots\dots = \frac{P\ell}{4}$$

$$M_x \left(\text{when } x < \frac{\ell}{2} \right) \dots\dots\dots = \frac{Px}{2}$$

$$\Delta_{\max} \text{ (at point of load)} \dots\dots\dots = \frac{P\ell^3}{48EI}$$

$$\Delta_x \left(\text{when } x < \frac{\ell}{2} \right) \dots\dots\dots = \frac{Px}{48EI} (3\ell^2 - 4x^2)$$

Appendix B – Wafer Measurements

Cell Number	Least Wide Cell bond (μm)	Crack Length (μm)	Depth of Cell (nm)
Wafer 1: 400 V, 500 μm			33.3
1	200	29	467
2	200	34	476
3	250	35	493
4	150	37.3	498
5	250	26.4	490
6	200	34.2	492
7	150	36.5	506
9	200	35	508
10	250	37.3	496
11	250	38.1	495
13	200	31.1	507
14	200	32.6	506
15	200	36.5	506
16	150	33.4	504
17	150	37.3	509
19	200	35.7	508
20	200	31	502
21	150	31.8	507
22	150	31.1	505
23	150	31.8	507
24	250	27.2	504
25	200	30.3	507
Wafer 2: 700 V, 500 μm			
2	200	38	514
3	150	36.5	508
4	150	39.6	405
7	150	35.7	517
8	150	24.9	520
9	150	34.2	515
11	150	28.7	502
12	150	31.8	511
14	100	34.2	505
15	150	28	510
17	150	32	498
19	150	22.5	503
20	150	31.8	508
21	150	30.3	509
22	150	31.8	503

	24	150	24.1	514
	25	150	27.2	491
Wafer 3: 700 V, 1mm				
	1	500	58.2	290
	2	500	63	297
	3	500	59.8	294
	4	500	59.7	295
	5	500	58.2	291
	6	500	64.5	301
	7	500	73.9	301
	8	500	72.3	302
	9	500	69.2	303
	10	500	55	298
	11	500	58.2	309
	12	500	69.2	302
	13	500	72.3	300
	14	500	62.9	303
	15	500	59.7	294
	16	500	56.6	301
	17	500	56.7	298
	18	500	67.6	297
	19	500	59.8	298
	20	500	62.4	293
	21	500	59.7	302
	22	500	64.5	293
	23	500	64.5	299
	24	500	72.4	292
	25	500	59.7	280
Wafer 4: 400 V, 1mm				
	1	650	62.3	292
	2	500	59.8	318
	3	650	66	316
	4	500	55	314
	5	650	67.6	326
	6	500	58.3	321
	7	500	66	318
	8	650	59.7	318
	9	500	66	318
	10	500	58.1	301
	11	650	70.8	306
	12	650	66	319
	13	250	45.6	321
	14	500	52	317

15	650	61.4	307
17	500	66	312
18	250	45.6	315
19	500	42.4	313
20	750	70.7	313
21	500	62.9	309
22	650	62.9	309