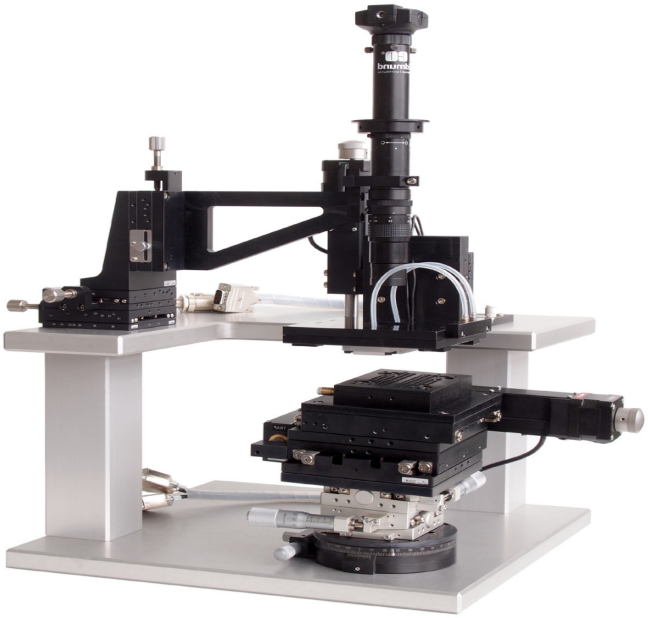
Modification of Microcontact Printing Process for Adhesive and Conductive Ink Printing

A Major Qualifying Project Report
submitted to the Faculty of
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science



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(The Interstate University of Applied Sciences of Technology Buchs)
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Abstract

This project applied the mechanical and chemical characteristics of Microcontact printing to adapt the current printing process at NTB to pattern adhesive and conductive epoxies on non-standard substrates. The process development focused on implementing new methods and process parameters to produce a thin and uniform layer of epoxy. To ensure a reproducible and optimal printing process, a series of printing trials were conducted and the final printed adhesives were characterized.

Executive Summary

The concept of microcontact printing (µCP) is a method of transferring an “ink pattern” on an elastomeric stamp with relief features onto a substrate (Ruiz and Chen, 2007). This method was introduced by the Whitesides group in 1993 and used to pattern gold. As technology developed, microcontact printing has been widely used to transfer multiple “inks” such as water, salt, organic solvents, metals, polymers, DNA, proteins and cells. This process can provide a simple and low-cost surface patterning methodology with high versatility and sub-micrometer accuracy (Perl et al, 2009 and Xia et al, 1998).

Interstate University of Applied Sciences of Technology Buchs (NTB) partnered with the Major Qualifying Project (MQP) group from Worcester Polytechnic Institute (WPI) to develop and optimize the process parameters needed to modify the microcontact printing process for the use of adhesive and conductive inks on both glass and PMMA substrates. The project was focused on an adhesive epoxy (EPO-TEK 302-3M) and a conductive epoxy (EPO-TEK H20E-PFC) as “inks” to be printed on glass and PMMA substrates. In order to accomplish this goal, the following objectives were identified:

Objective 1	• Conduct fabrication of stamps with predefined geometries and functionalization of substrate surfaces using established processes
Objective 2	• Develop methods to create an ink pad for coating the stamp with adhesive and conductive ink
Objective 3	• Design new fixtures for the microcontact tool to ensure reproducibility
Objective 4	• Perform a series of stamping trials to determine an optimal and reproducible process
Objective 5	• Characterize printed structures of adhesives
Objective 6	• Record reproducible procedures for a variety of substrate and ink combinations

Process Development

The following table provides an overview of the steps taken during process development.

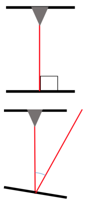
Each step includes the methods used and the end results.

Process Development	Method	Results	
Stamp Fabrication	A pre-made master was used to fabricate PDMS stamps through a standard process	Lateral Dimensions: Minimum Percent Error: 0.20% Maximum Percent Error: 2.51%	
Functionalization	A barrel asher was used to perform an oxygen plasma treatment	The PDMS stamp should be functionalized every 80 minutes	PMMA and glass do not require functionalization
Spin Coating - EPO-TEK 302-3M	A series of trials were performed to determine the relationship among rotation time, speed, and resulting surface area. The thickness of ink pad was measured and analyzed.	As rotation time or speed increases, the resulting surface area increases The thickness of the ink pad has a linear relationship with respect to time	Ink Pad Thickness: 8.8µm - 11.8µm Coefficient of Variation: 0.18% - 0.42% Maximum Wait Time: 15 minutes
Doctor Blading - EPO-TEK H20E-PFC	Two designs were trialed. The final design increased reproducibility by incorporating a built-in blade and sliding stage	Ink Pad Thickness: 2.695µm - 3.395µm Micrometer Screw Value: 18µm	
LabVIEW Trials	Used NTB's stamping tool and LabVIEW program to determine a force and approach distance for the glass plate, PMMA, glass substrate, and silicon wafer	Inking Approach Distance: PMMA/Glass Plate: 23mm Glass/Silicon Wafer: 24.55mm Inking Process: PMMA - Force: 0.85N; Time: 20s Silicon Wafer - Force: 0.4N; Time: 20s Print Approach Distance: PMMA: 23 mm	Printing of EPO-TEK 302-3M: Glass Substrate: Force 1: 0.2N; Time 1: 20s Force 2: 0.1N; Time 2: 20s PMMA Substrate: Force 1: 0.2N; Time 1: 20s Force 2: 0.1N; Time 2: 20s Printing of EPO-TEK H20E-PFC: Glass Substrate: Force 1: 0.65N; Time 1: 20s Force 2: 0.45N; Time 2: 20s PMMA Substrate:

		Glass Substrate: 24.55 mm	Force 1: 0.85N; Time 1: 20s Force 2: 0.65N; Time 2: 20s
Final Prints	Lateral dimensions of the final prints were measured with an optical microscope and compared to the master & stamps	Some measurements were in tolerance and comparable to the master Ones not in tolerance were due to the full pattern not printing on the substrate	
Shear Tests	The shear tester uses a piezo sensor to measure a change in voltage, which can then be converted into a measurement of applied force	Calculated Shear Strength: Conductive Epoxy: Average: 572.703 g Std. Dev: 142.561 g	Calculated Shear Strength: Adhesive Epoxy: Average: 417.816 g Std. Dev: 490.736 g
Resistivity Tests	Conducted through the use of a voltage generator and a multi-meter. An electric current was sent through two opposing corners of the frame, providing the resistivity of the stamp frames	Measured Surface Resistance: Average: 16.7 MΩ Std. Dev: 25.1 MΩ	Calculated Resistivity: Average: 3284.16 Ω-cm Std. Dev: 3182.38 Ω-cm

Future Recommendations

Recommendation	Description
Microscope Slide and Stamp Adhesion	The microscope slide and stamp can be glued together to prevent the stamp from falling off of the slide during inking and printing. Gluing can also aid in preventing any residual contaminants from being trapped.
Master Reproducibility	When changing masters, PDMS can become trapped around the master. There is a high possibility of damaging the mold when the master is changed. An alternative mold tool can help to avoid damage.
Consistency in the Inking Process	Since the thicknesses of the substrates and silicon wafer aren’t equal, multiple approach distances have to be used. This means that after inking, the approach distance must be altered. As a result, the rate of production is lowered. This can be resolved by maintaining consistent thicknesses of substrates and wafer.

Hardware Additions to the NTB Printing Tool	To better control the angle between the stamp and substrate surface, three lasers can be attached to the stamp holder and a mirror can be attached to the substrate platform. When they are parallel, the lasers reflect back to their points of origin. When they are not aligned, the lasers reflect back at an angle.	

Acknowledgments

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1.0 Introduction

The concept of microcontact printing (μCP) was introduced by the Whitesides group in 1993, as a method of transferring an "ink pattern" on an elastomeric stamp with relief features onto a substrate (Ruiz and Chen, 2007). This method was originally used to pattern gold. As technology developed, microcontact printing has been widely used to transfer multiple "inks" such as water, salt, organic solvents, metals, polymers, DNA, proteins and cells. This process can provide a simple and low-cost surface patterning methodology with high versatility and sub-micrometer accuracy (Perl et al, 2009).

Our team partnered with the Interstate University of Applied Sciences of Technology Buchs (NTB) to investigate extended applications of microcontact printing by optimizing NTB's microcontact printing process to print small frames of adhesives for optical component mounting. NTB has a particular interest in using the adhesives in fiber optics and extending optical pathways. Optimization methods are needed for the current printing process to avoid glue entering the optical path while maintaining the adhesive and conductive qualities of the epoxies. In addition, NTB is seeking to move towards further miniaturization of applying conductive and adhesive epoxies. Possible applications include flip chip packaging in memory devices, smart-cards and medical devices for mounting electrical components with conductive epoxy, and semiconductor, optical and medical use for mounting optical components with adhesive inks (Epoxy Technology, 2015).

The goal of this Major Qualifying Project (MQP) was to develop and optimize the process parameters needed to adapt the microcontact printing process to the use of adhesive and conductive inks on both glass and PMMA substrates. Glass is a standard substrate used in optical components. PMMA is a plastic substrate to prepare for further research in the field of microcontact printing. In order to accomplish this goal, the team has identified the following objectives:

1. Fabricate stamps with predefined geometries and functionalize substrate surfaces using established processes
2. Develop methods to create an ink pad for coating the stamp with adhesive and conductive ink
3. Design new fixtures for the microcontact tool to ensure reproducibility
4. Perform a series of stamping trials to determine an optimal and reproducible process
5. Characterize printed structures of adhesives
6. Record reproducible procedures for a variety of substrate and ink combinations

2.0 Background

2.1 Microcontact Printing

Microfabrication has become increasingly common in modern technology as a means of producing microelectronics and optoelectronics. Soft lithography is a class of printing which utilizes patterned elastomers to transfer inked patterns to a wider range of substrates at a much lower cost. Microcontact printing (µCP) is a method of soft lithography that is capable of printing patterns with dimensions at a submicron level and commonly used to form patterned self-assembling monolayers (SAMs) on substrates (Xia et. al, 1998).

2.2 Optical Adhesive

Optical adhesives are widely used in military, commercial, and aerospace applications due to their ability to bond or cement optical components together (Edmund Optics Inc., 2016 and Summers Optical, 2016). Additional advantages of using adhesives rather than other means of attaching optical components, include their flexibility in design and low cost. Previous work with optical components were bonded with purified, filtered Canada balsam due to its transparency and high optical quality. Lenses glued with Canada balsam were also known as cemented lenses. However, Canada balsam was phased out during World War II, when polyester, epoxy and urethane based single and two components adhesives were introduced for bonding optical components (Summers, 2015).

2.3 Epoxy Resin

Epoxy resin is used as the ink for the procedures developed in this report. Epoxy resin is a class of prepolymers and polymers that contain epoxide groups. Epoxy resins can both cross-link within themselves or with other co-reactants. The reactants are widely used in industries because of their excellent mechanical properties, chemical resistance, anti-corrosive properties and thermal stability (Kishi et al, 2016 and Morsch et al, 2015). Epoxies must be mixed in a small container because if surface area to volume ratio is too large then one cannot accurately assess whether the two components obtained homogeneity (Summers, 2015). Two methods to create a thin film with epoxy resin as an ink pad include, spin coating and the use of a doctor blade. The project focused on an adhesive epoxy (EPO-TEK 302-3M) and a conductive epoxy (EPO-TEK H20E-PFC).

2.3.1 Adhesive Epoxy

The adhesive epoxy is EPO-TEK 302-3M, which is a low viscosity, two component adhesive epoxy that is clear in color. The physical, optical, and electrical properties are shown in Appendix A. The low viscosity of this adhesive is desirable for optical, medical, fiber optic, and semiconductor applications. For these applications, this low viscosity adhesive epoxy was chosen for its high shear strength as opposed to the higher viscosity conductive epoxy. Pot time is defined as the amount of time needed for the initial mixed viscosity to double, or to quadruple for lower viscosity products (<1000 cPs) (Epoxy Technology, 2016). Pot time for EPO-TEK 302-3M is 1 hour (Epoxy Technology, 2015).

2.3.2 Conductive Epoxy

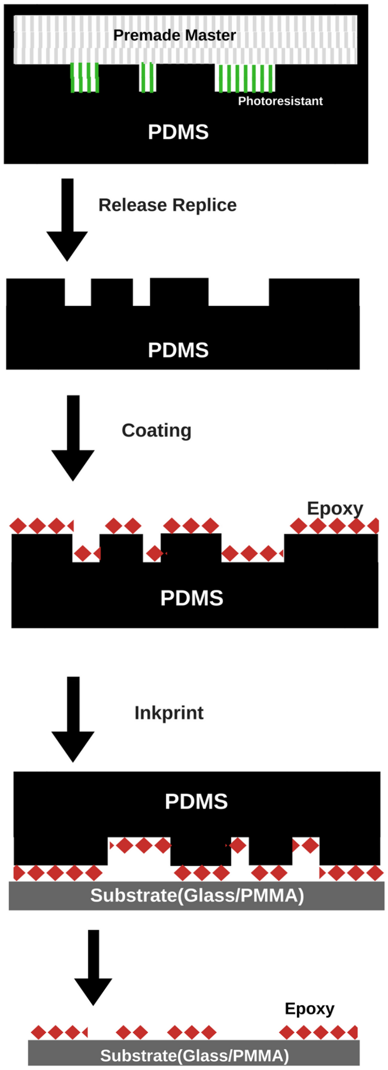
The conductive silver epoxy is EPO-TEK H20E-PFC, which is a high viscosity, two components, semiconductor grade epoxy. The physical, thermal and electrical properties are shown Appendix A. Possible applications for printed conductive adhesives include electrical components used for printed electronics and one way sensors. For these applications, this conductive epoxy was chosen for its high conductivity. The pot time for EPO-TEK H20E-PFC is three days.

3.0 Process Development

The goal of the procedures in the process development section is to determine the effectiveness of the microcontact printing process of adhesive and conductive epoxies. In order to accomplish this goal, the team completed the following objectives:

1. Fabricate stamps with predefined geometries and functionalize substrate surfaces using established processes
2. Develop methods to create an ink pad for coating the stamp with adhesive and conductive ink
3. Design new fixtures for the microcontact tool to ensure reproducibility
4. Perform a series of stamping trials to determine an optimal and reproducible process
5. Characterize printed structures of adhesives
6. Record reproducible procedures for a variety of substrate and ink combinations

The overview of the microcontact printing process is shown in Figure 3-1. The printing process begins with a pre-fabricated master with laminated photoresist patterns provided by NTB. This master is used to replicate the pattern onto a PDMS stamp. Once the PDMS stamp is fabricated, the stamp is pressed into an epoxy ink pad. The inked stamp is then pressed onto the desired substrate. The ink is then ready for bonding and characterization through optical, mechanical, and electrical testing.



Name	Material	Color
Stamps	PDMS	⬛
Premade master Part1	Monocrystalline silicon/Floatglass	⬜
Premade master Part2	Photoresist	🟩
Ink	Epoxy	🟥
Substrate	Glass/PMMA	▨

Figure 3-1 Processes of Fabrication and Printing

The iterative process used to develop the final microcontact printing process from Figure 3-1 is shown in the flowchart in Figure 3-2.

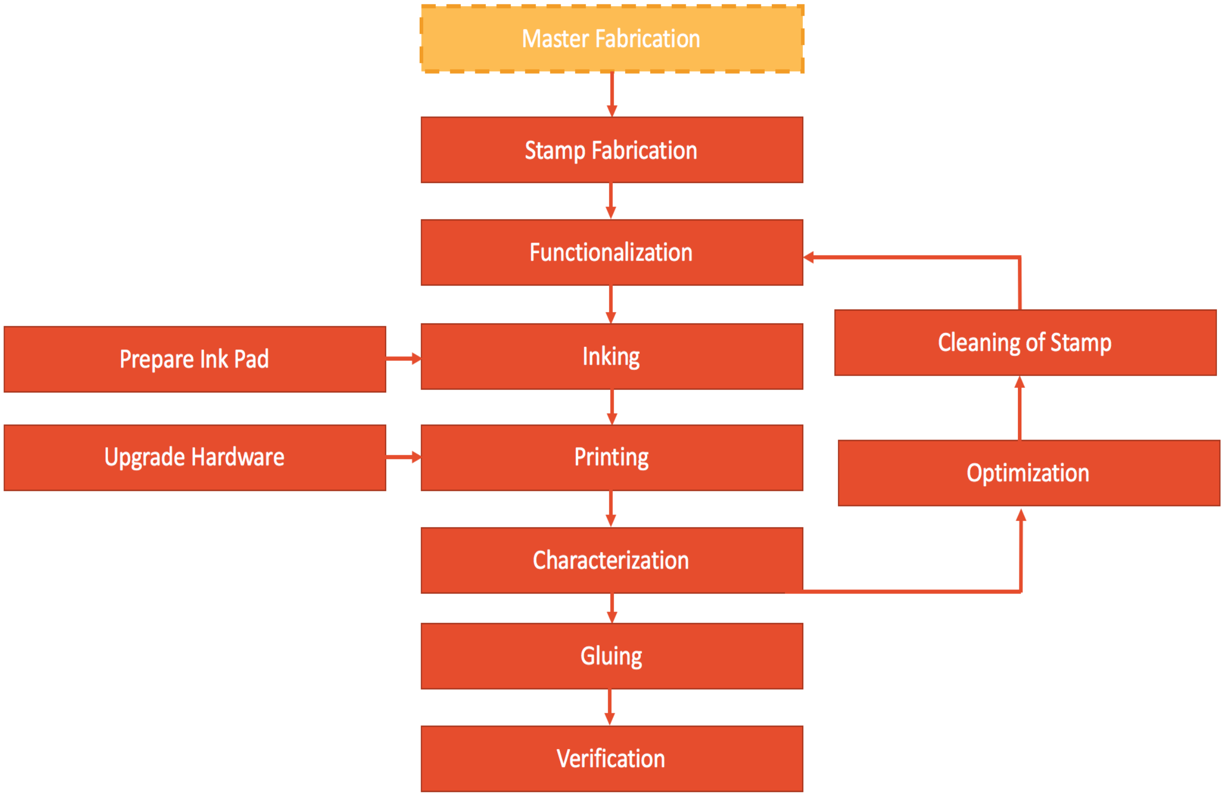


Figure 3-2: Flowchart of Process Development

The pre-made master used to fabricate a PDMS stamp, as shown in Figure 3-3, is created following the negative method of master fabrication. In this method, the photoresist layer is on the surface of silicon glass. A mask with a certain pattern is then placed over the photoresist. The mask is then removed and the desired master is formed.

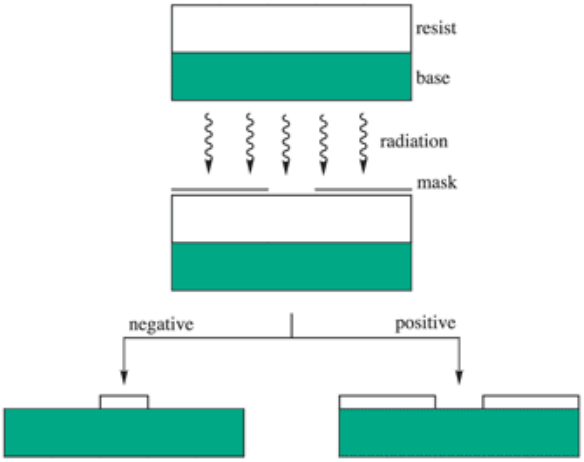


Figure 3-3: Premade Master Process (Sigma-Aldrich, 2016)

After a pattern is replicated, an ink pad is developed to provide a thin layer of ink to coat the PDMS stamp. Surface functionalization of PDMS and PMMA substrates is performed to increase surface adhesion before printing the coated stamp. The contact angle of the surface is measured to determine the duration of surface activation. After functionalization, the microcontact tool is used to print the replicated pattern onto glass and PMMA substrates. The current LabVIEW parameters were modified to bring the stamp in contact during inking and printing. A series of printing trials are needed to ensure a reproducible process. Optimization takes places when necessary throughout the trials and characterization procedures. A small glass die is glued on the final print before hardening the adhesive. The overall thickness of the final print is measured to ensure a uniform and thin layer is produced. Lastly, mechanical and electrical tests are performed to evaluate the characteristics of the adhesive.

Combinations of two different substrates and two types of inks were developed in this study resulting in four different stamping combinations. The substrates included glass and PMMA. The two inks were EPO-TEK H20E-PFC developed for applications that require a conductive adhesive, and EPO-TEK 302-3M developed for applications that require adhesion without electrical conductivity. Figure 3-4 outlines the different inks and substrates used. Multiple stamps can be fabricated from one master, and multiple prints can be printed from one stamp.

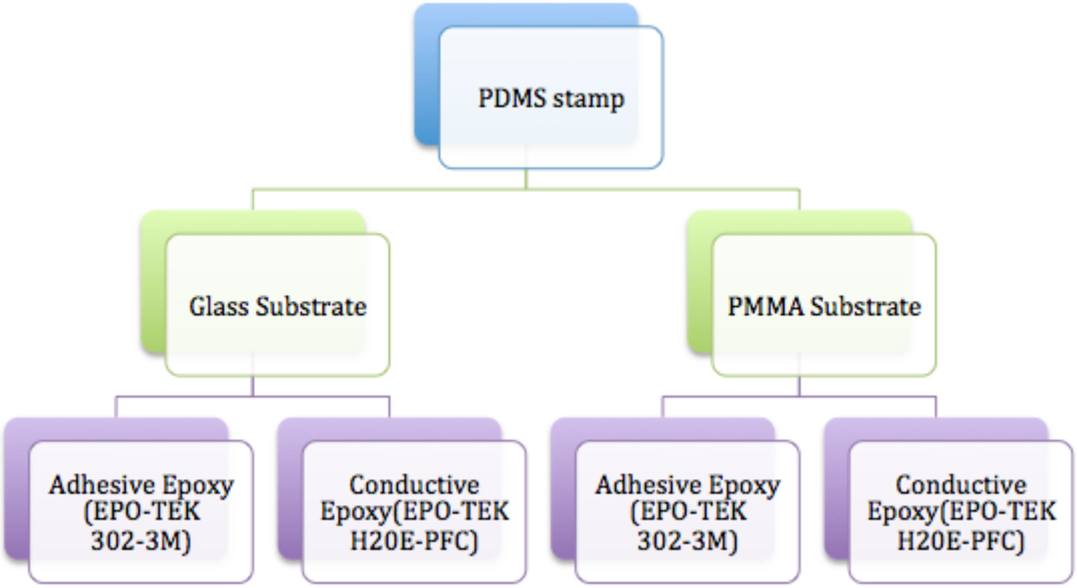
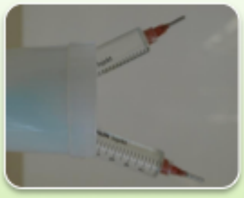


Figure 3-4: Substrate & Ink Combinations

3.1 Stamp Fabrication

The standard procedure for microcontact printing is to create a master template through photolithography, as shown in Appendix B. That master template is then used to produce PDMS stamps, which serve as inverted copies of the master. This is accomplished through a standard stamp fabrication process, as shown in Table 3-1. The PDMS requires precise measurement and mixing during the stamp fabrication process. An aluminum mold tool holds the master during the PDMS stamp fabrication process. The mold tool is cleaned in order to remove impurities and dirt that can contaminate the surface. A silanization procedure is used to cover the surface of the master with two drops of trichlorosilane 97% molecules and form bonds to ensure proper PDMS stamp pattern replication and to prevent sticking. The stamp is molded by forming a layer of PDMS over the master and allowing it to harden into a flexible solid state. After peeling the stamp away from the master, the stamp is ready for use. Multiple stamps can be fabricated from one master. Cooling the master to room temperature during the curing process is important to ensure the proper hardening of the stamp. Stamp fabrication trials were conducted until the lateral dimensions of the stamp pattern were comparable with a tolerance of +/- 0.001 mm (1 µm), to those of the master.

Table 3-1: Stamp Fabrication Procedure

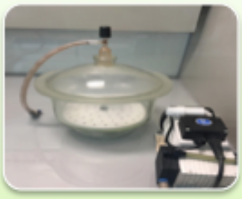


1. Prepare PDMS

- Mix PDMS (Sylgard 184) with a 10:1 (resin:hardener) in the speedmixer for 30 s at 1000 rpm and 120 s at 2000 rpm
- Fill syringes with 3-4ml of PDMS with black tip
- Store syringes in the freezer overnight

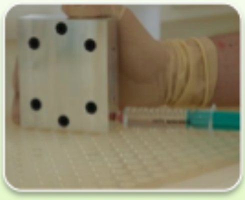
2. Mold Tool Treatment

- Clean the aluminum housing of the master with first Acetone and then Isopropanol to remove dirt on the surface



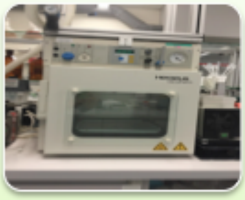
3. Silanization of the Mold-Tool

- Place the mold tool in a desiccator for 30 min at 0.2 bar with two drops of (Tridecafluoro-1,1,2,2-tetrahydroctyl)trichlorosilane 97%



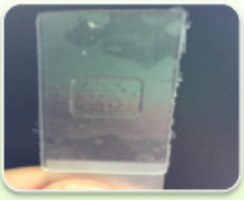
4. Molding Process

- Close the mold-tool, and gently tighten the screws
- Mount the red tip on the syringe (filled with PDMS) and push excessive air out of the syringe.
- Insert the syringe into the mold tool and slowly inject PDMS until full.



5. Curing Process

- Leave the syringe in the tool during polymerization
- Place the master with the attached syringe in the oven for 12 h @ 60°C



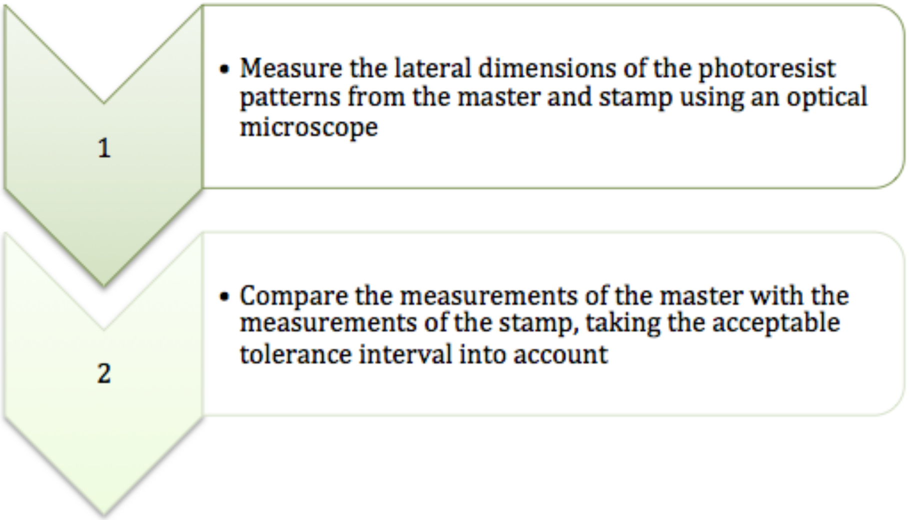
6. Mold Removal

- Remove the mold and let cool to room temperature
- Once cooled, remove the stamp from the mold-tool
- Place the stamp onto a microscope slide and store in a dry, clean place
- Fabricate stamps until the lateral dimensions of the pattern are comparable to the master

3.1.1 Optical Inspection: Lateral Dimensions of the Pattern

The lateral dimensions of the stamp must be equivalent to the corresponding dimensions of the master, with a tolerance interval of +/- 0.001 mm (1 micron). If the dimensions are not within this tolerance interval, the process for the fabrication of the stamp is considered to be not reproducible. The PDMS stamp inspection procedure is as follows in Table 3-2:

Table 3-2: Optical Microscope Procedure



1

- **Measure the lateral dimensions of the photoresist patterns from the master and stamp using an optical microscope**

2

- **Compare the measurements of the master with the measurements of the stamp, taking the acceptable tolerance interval into account**

3.1.2 Optical Testing Results

A master with a pattern optimized for shear testing was selected to fabricate three PDMS stamps. The lateral dimensions of the fabricated stamps matched the lateral dimensions of the master used, as shown in Figure 3-5. In Table 3-3, the lateral dimension percent error is shown. The equation used in determining these values is shown below, where L_s and L_m represent the lateral dimensions of the stamp and master, respectively.

$$\%error = \frac{Ls - Lm}{Lm} * 100\%$$

In this testing procedure, three dimensions were measured. These points were labeled as a, x and y, as seen in Figure 3-6. Stamp 3 had the lowest percent error of 0.67% for a, 0.91% for x, and 0.20% for y, followed by Stamp 2, and Stamp 1. The % maximum error required to maintain a 0.001 mm (1 micron) tolerance of the master are 0.67%, 0.23%, 0.20% for width a, x, and y respectively. Numbers are highlighted in red if they did not meet this requirement. Stamps 3 and 2 were shown to be reproducible with width a and y since they were in the tolerance defined. None of the stamps were in the tolerance value for width x.

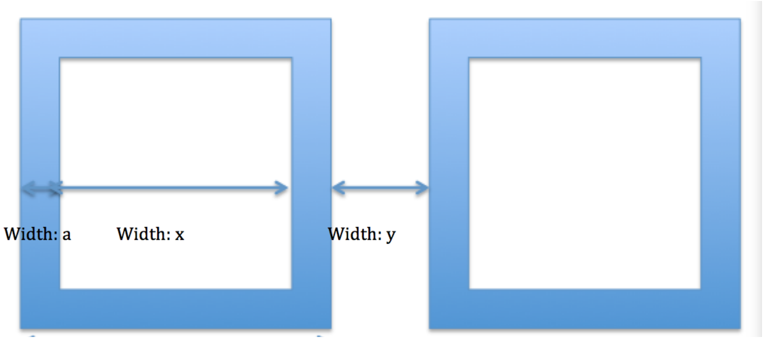
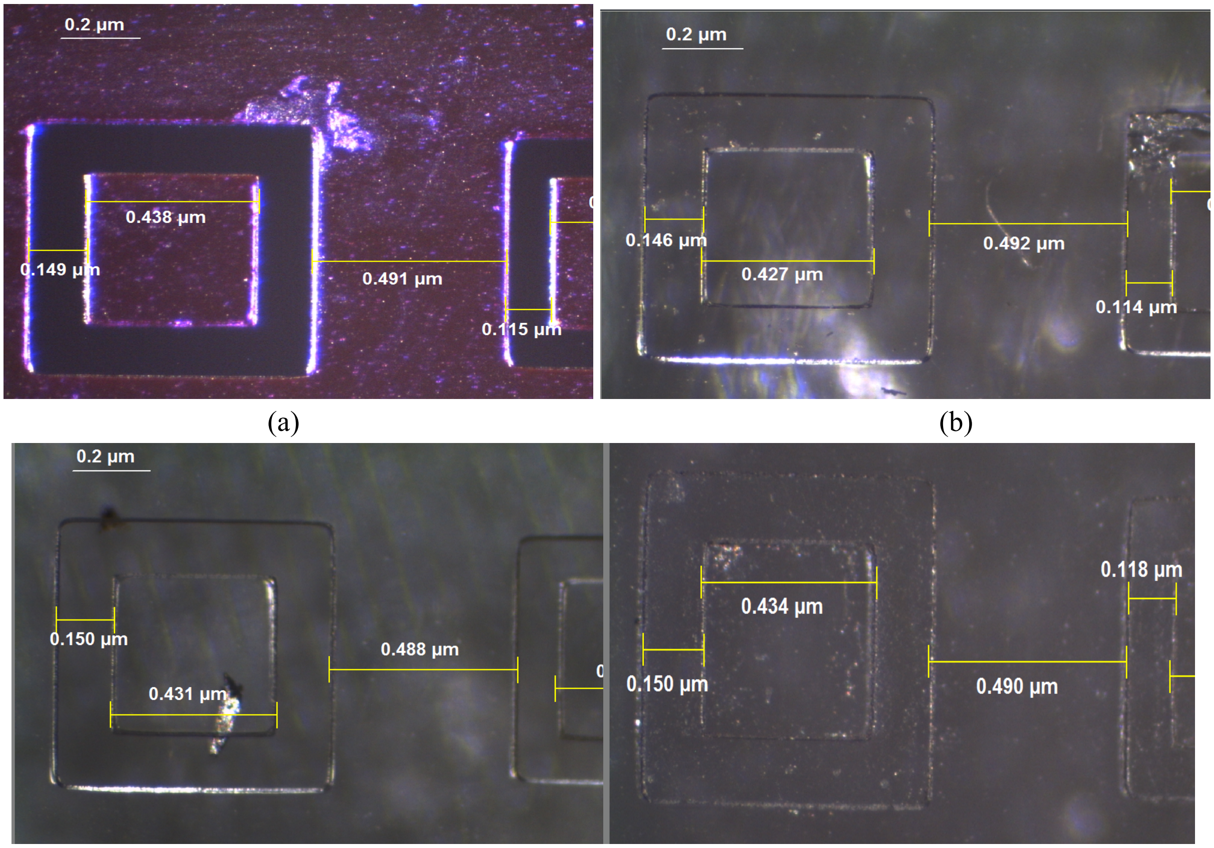


Figure 3-5: Demonstration Lateral Dimensions Measured



(a) (b)

(c) (d)

Figure 3-6: Lateral Dimensions (a) Master 1 (b) PDMS stamp 1 after fabrication (c) PDMS stamp 2 after fabrication (d) PDMS stamp 3 after fabrication

Table 3-3: % Error Between Lateral Dimension Measurements

	a (mm)	% error of a	x (mm)	% error of x	y (mm)	% error of y
Master (a)	0.149	N/A	0.438	N/A	0.491	N/A
Stamp 1 (b)	0.146	2.01%	0.427	2.51%	0.492	0.20%
Stamp 2 (c)	0.150	0.67%	0.431	1.60%	0.488	0.61%
Stamp 3 (d)	0.150	0.67%	0.434	0.91%	0.490	0.20%

3.2 Surface Preparation

The surfaces of the substrates must be cleaned to remove contaminants, and functionalized to increase the ink's surface adhesion by creating a hydrophilic layer on the surface of the substrate. The final printed epoxy cannot be used as an optical component if it cannot adhere to the surface or if any contamination to the surface exist. A hydrophobic surface repels water and will not allow the ink to stick. The purpose of having a hydrophilic surface is to increase surface adhesion for the applied adhesive. The adhesive will not bond to the stamp if the surface is hydrophobic.

3.2.1 Surface Wettability

A surface's hydrophobic or hydrophilic nature is based on the wettability of the surface as determined by the contact angle. Contact angle is defined as the angle between the liquid-vapor (water) interface and the solid, as shown in Figure 3-7.

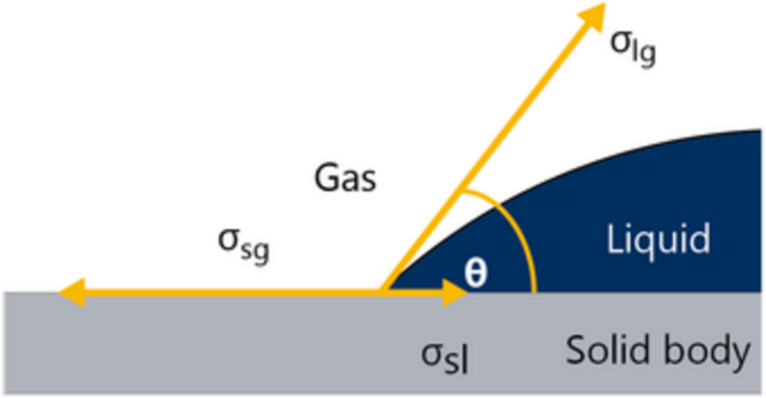


Figure 3-7: Contact Angle (Kruss, 2016)

According to Young's equation, the contact angle, θ, can be expressed as

$$\sigma_s = \sigma_{sl} + \sigma_l * \cos(\theta)$$

Where σ_s is the surface free energy of the solid, σ_{sl} is the interfacial tension between water and solid and σ_l is the surface tension of the liquid.

If the contact angle is close to 0°, the water is almost completely spread even on the surface, which indicates high wettability. This phenomenon is known as superhydrophilic. A hydrophilic solid has a contact angle of less than 90°. The surface with the contact angle of $90° \leq \theta \leq 150°$ is called a hydrophobic surface. If the contact angle is greater than 150°, the water only rests on the surface without spreading. This condition is known as a superhydrophobic surface. Different situations of wetting are demonstrated in Figure 3-8.

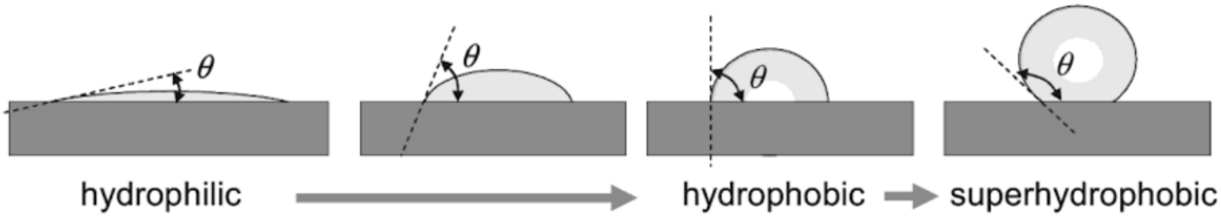


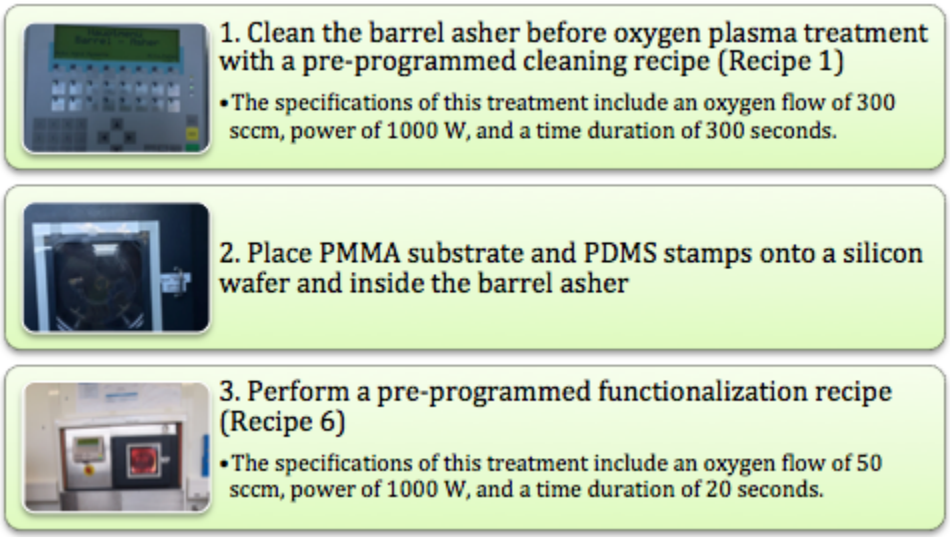
Figure 3-8: Different Levels of Wettability of Surface (Forch, 2009)

Oxygen plasma is one of the most common ways to treat substrate surfaces. First, oxygen plasma removes the organic contaminants by reacting with oxygen radicals. Then, energetic oxygen ions promote surface oxidation by reacting with OH groups (Harrick Plasma, 2016). However, the activation of the surface via oxygen plasma is not permanent, and the maintenance of hydrophilicity is varied from case to case. In order to optimize the timing of functionalization procedures, a series of contact angle measurements were performed where the contact angle of the PMMA substrates and PDMS stamps was measured over a series of varying time intervals.

3.2.2 Functionalization of Surfaces

The surfaces of the PDMS stamps that contact the adhesive inks are hydrophobic, whereas the surfaces of PMMA substrates are hydrophilic. Both of surfaces used an oxygen plasma treatment to activate the surface and increase the wettability properties. The functionalization process is performed through the use of a barrel asher, which can be seen in Appendix O. The steps used for surface functionalization are shown below in Table 3-4. When this procedure is performed, a contact angle of less than 5° is targeted.

Table 3-4: Functionalization Procedure



1. Clean the barrel asher before oxygen plasma treatment with a pre-programmed cleaning recipe (Recipe 1)

- The specifications of this treatment include an oxygen flow of 300 sccm, power of 1000 W, and a time duration of 300 seconds.

2. Place PMMA substrate and PDMS stamps onto a silicon wafer and inside the barrel asher

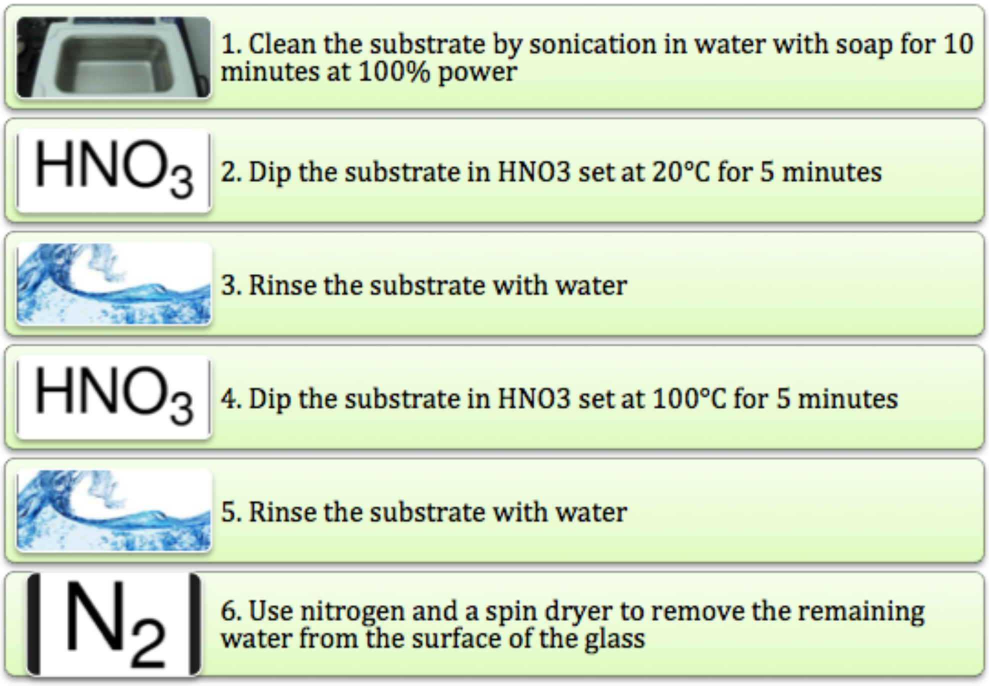
3. Perform a pre-programmed functionalization recipe (Recipe 6)

- The specifications of this treatment include an oxygen flow of 50 sccm, power of 1000 W, and a time duration of 20 seconds.

3.2.3 Glass Cleaning

Correct substrate preparation is essential in the successful bonding of optical components. Optical components cannot be bonded unless excess dirt and residue are removed (Summers, 2015). The glass substrates do not require functionalization due to their hydrophilicity. Only the glass substrate required cleaning before any treatments. The PMMA substrate was functionalized with oxygen plasma and does require cleaning since oxygen plasma removes any impurities. The steps used to clean the glass surface are outlined below in Table 3-5 (Maechler, 2016).

Table 3-5: Glass Cleaning Procedure



1. Clean the substrate by sonication in water with soap for 10 minutes at 100% power
2. Dip the substrate in HNO_3 set at 20°C for 5 minutes
3. Rinse the substrate with water
4. Dip the substrate in HNO_3 set at 100°C for 5 minutes
5. Rinse the substrate with water
6. Use nitrogen and a spin dryer to remove the remaining water from the surface of the glass

3.2.4 Contact Angle Measurement for Hydrophilicity Procedure

Since oxygen plasma produces a temporary surface activation, the surface only remains hydrophilic when the contact angle is less than 90°. A KRÜSS EASYDROP DSA20E, as shown in Figure 3-9, was utilized to measure the contact angle of the substrate and stamp surfaces through the use of water droplets. The following procedure shown in Table 3-6 was used to measure contact angles and to optimize the PMMA, glass, and PDMS surface treatments:

Table 3-6: Contact Angle Measurement Procedure

1. Measure the contact angles of the substrates (PMMA and glass) and PDMS stamps before functionalization and cleaning
2. Functionalize the PDMS stamps and the PMMA substrates
3. Clean the glass substrates as outlined in Section 3.2.3 and measure the contact angle
4. Wait for 15 minutes, 20 minutes, 35 minutes, 45 minutes, 60 minutes after functionalization for PMMA. Measure the contact angle after each time interval
5. Wait for 15 minutes, 30 minutes, 45 minutes, 60 minutes, 90 minutes, and 120 minutes after functionalization for PDMS. Measure the contact angle after each time interval
6. For each substrate or stamp, measure several arbitrary points until three values are within a tolerance interval of +/- 8º

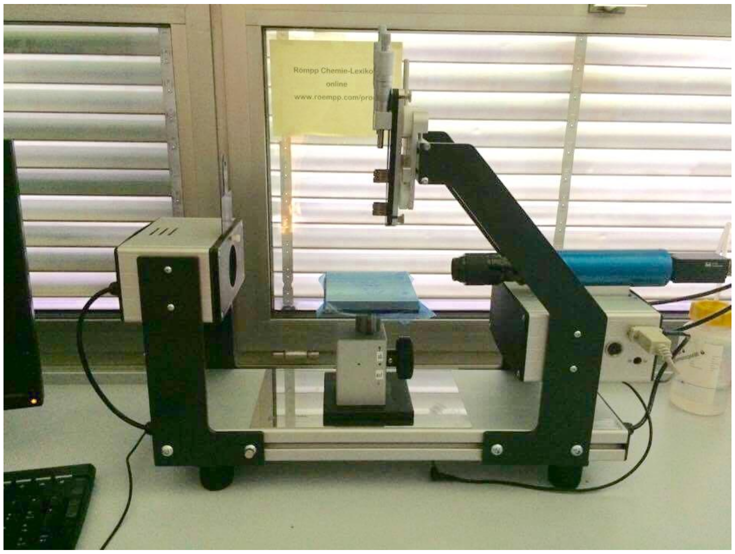


Figure 3-9: Kruss Easydrop DSA20E

3.2.6 Contact Angle Measurement Results

Measurement data from the contact angle trials of the PMMA substrates and PDMS stamps are shown in Appendix D and Appendix E, respectively. The average values of three contact angle with tolerance of 8 degrees are graphed, as shown in Figure 3-10. The first measurement taken 15 minutes post-functionalization revealed that the contact angle of PMMA decreased by 30 degrees. Before functionalization, the contact angle of PMMA was 71.9º, indicating a hydrophilic surface. After functionalization, the contact angle was measured at 40º. However, the contact angles experienced a rapid increase within one hour of functionalization. Figures 3-11 (b) and (c) show that there is a 30º difference in the measured contact angles between the time interval of 15 min and 45 min. After one hour, the contact angle is equal to that of the PMMA before functionalization. Since PMMA always has a hydrophilic surface, it does not require functionalization.

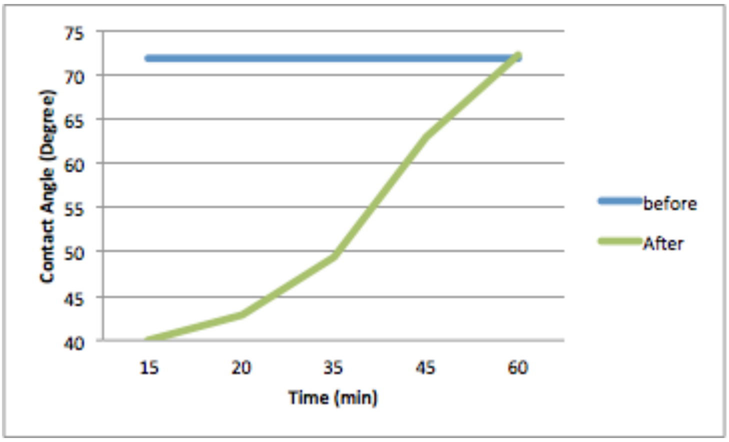
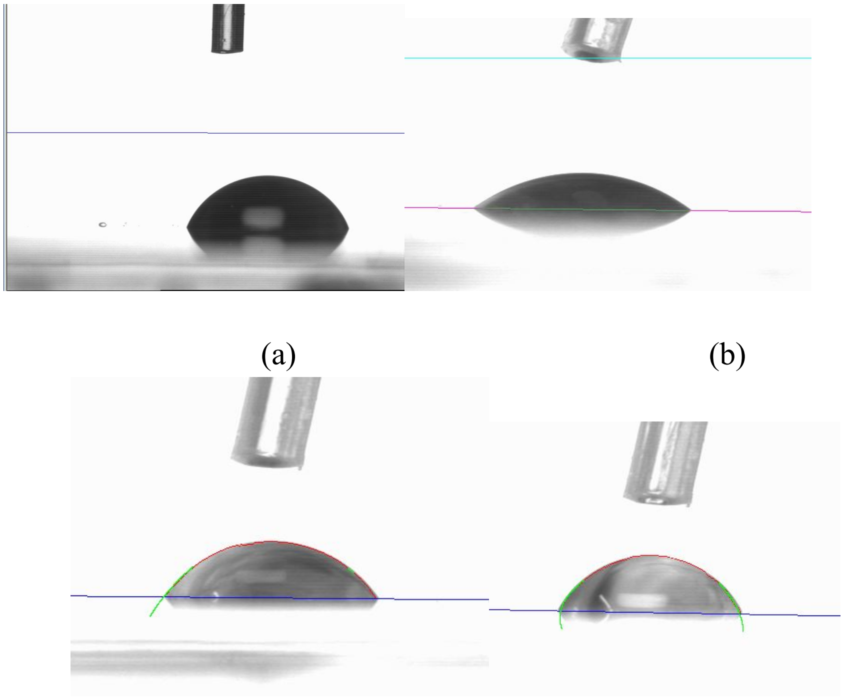


Figure 3-10: PMMA Contact Angle



(a) (b)

(c) (d)

Figure 3-11: (a) PMMA before functionalization (b) PMMA post functionalization 15 min (c) PMMA post functionalization 45 min (d) PMMA post functionalization 60 min

Before functionalization, the PDMS had a hydrophobic surface with a 112 º contact angle. The PDMS stamp was functionalized to change the surface from hydrophobic to hydrophilic. The average values of three contact angles with a tolerance of 8 degrees were plotted over time, shown in Figure 3-12. The contact angle of the PDMS stamp measured at 39.5º 15 minutes after functionalization. However, the contact angle experienced a rapid increase within two hours after the functionalization procedure was performed. Images demonstrating the measured contact angles before and after functionalization are shown in Figure 3-13.

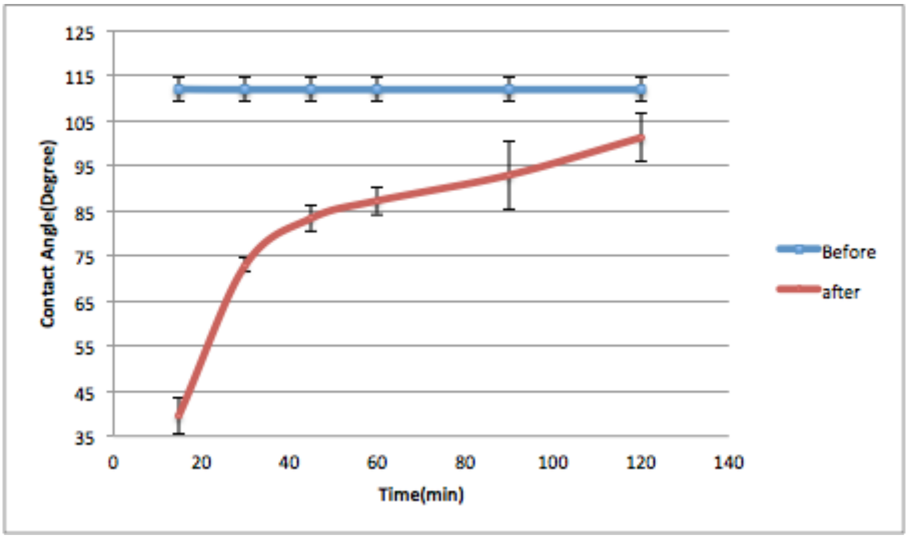


Figure 3-12: PDMS Contact Angle

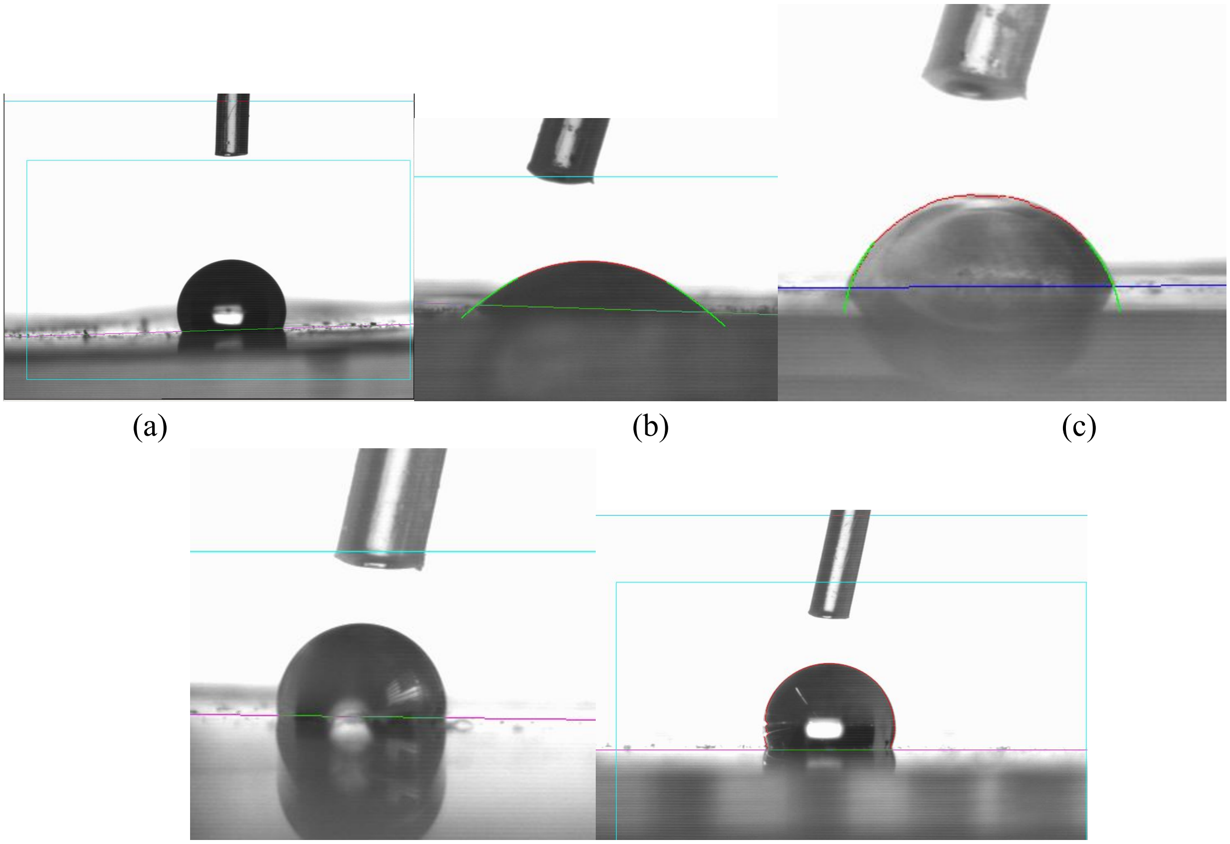
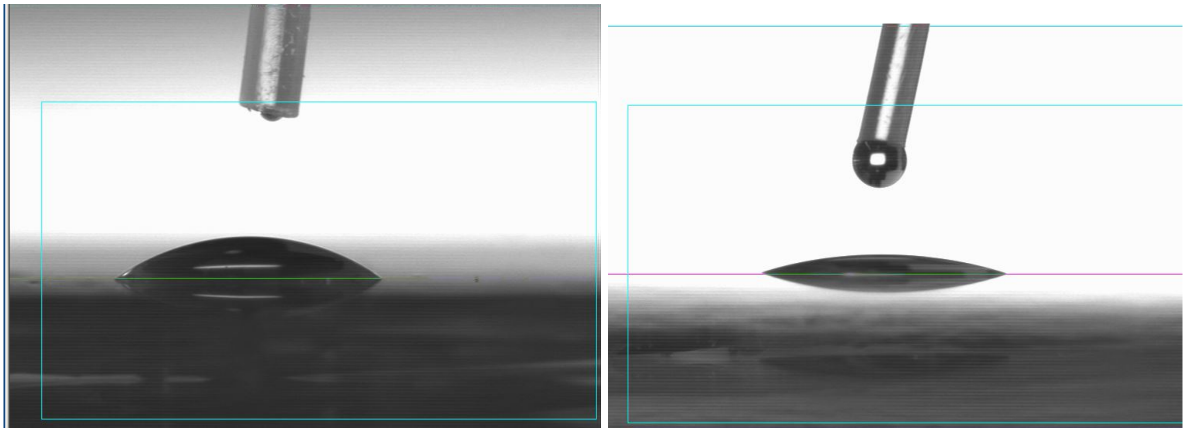


Figure 3-13: (a) PDMS before functionalization (b) PDMS post functionalization 15 min (c) PDMS post functionalization 30 min (d) PDMS post functionalization 90 min (e) PDMS post functionalization 120 min

The contact angle was measured for the glass substrate using two different cleaning procedures shown is Figure 3-14. The first procedure utilized acetone and isopropanol (Procedure A), and the second procedure was the standard process provided by NTB, as shown in Section 3.2.3 (Procedure B). The measured contact angle data for the glass substrates is shown in Appendix F. The glass substrate that was cleaned with acetone and isopropanol had a contact angle of 41.2 º, which was 22 º larger than the contact angle of 19.2 º of the glass cleaned with the standard process. Therefore, all the glass substrates must be cleaned with the standard process. Images demonstrating the measured contact angles are shown in Figure 3-14, where Procedures A and B are shown respectively.



(a) (b)

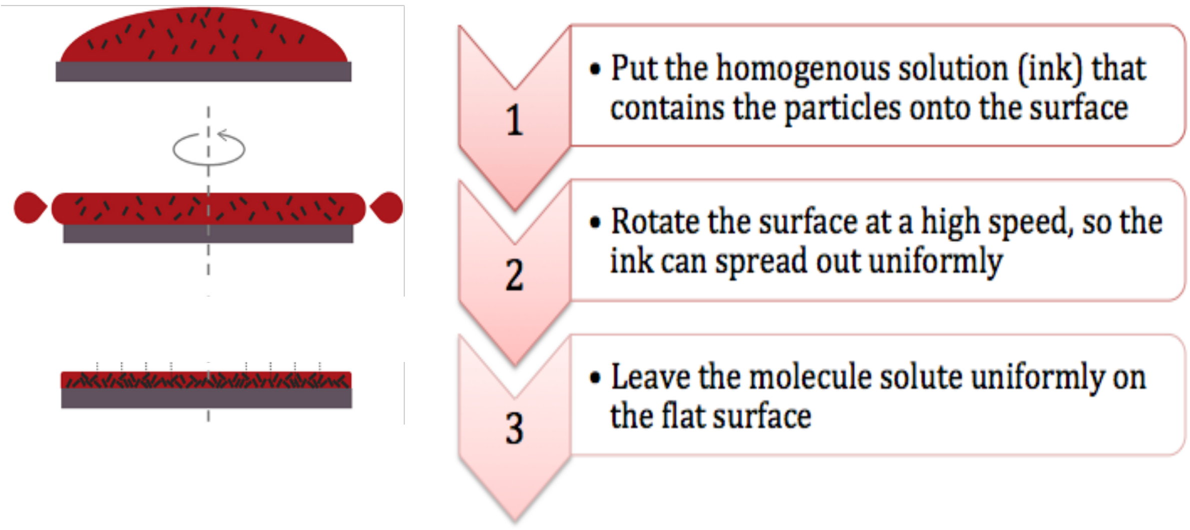
Figure 3-14: (a) Glass cleaned by hand (b) Glass by the standard clean room process

3.3 Ink Pad Development

There is no ink pad needed for NTB's current printing process for small molecules. An ink pad is necessary for epoxies since they cannot be applied to the stamp uniformly with the current process using a syringe. The purpose of the ink pad is to provide a thin uniform region of adhesive or conductive ink that can be collected by the stamp during the inking process. Different methods of ink pad creation are required depending on the viscosity of the ink. The spin coating process creates thin layers of liquid materials with low viscosities. This procedure was well suited for the generation of an adhesive ink pad on a silicon wafer. The process of doctor blading can also be used to create a thin uniform layer of ink for liquids with higher viscosities. This procedure is well suited for the high viscosity conductive ink on a glass wafer. Once the ink pad is generated, the stamp can be coated with the either the adhesive or conductive ink for use in the later steps of the stamping process.

3.3.1 Spin Coating Background

Spin coating is one of most common techniques to deposit a thin, solid polymeric film onto the flat surface of substrates (Ossila, 2016 and Uddin et al, 2004). Spin coating has been widely used in industry because this process quickly and easily makes uniform micrometer films. Generally, there are three steps involved in this technique, as shown in Figure 3-15.



1 • Put the homogenous solution (ink) that contains the particles onto the surface

2 • Rotate the surface at a high speed, so the ink can spread out uniformly

3 • Leave the molecule solute uniformly on the flat surface

(a) (b)

Figure 3-15: (a)Spin coating graph of a Solid Polymeric Film (Ossia, 2016) (b) Corresponding steps

The thickness of the film “d” can be calculated from the empirical relationship

$$d = k\omega^{\alpha}$$

Where k and α are the constants related to the properties of solute, solvent and the surface, while ω is the angular velocity of the surface (Krebs, 2009). The fast spin speed and high airflow can result in uniform solvent particles on the surface in both macroscopic and nano-length scales. However, there are disadvantages in this technique. First, there is a relatively low throughput compared with other techniques, since each substrate is handled individually (Ossila, 2016). Second, it is difficult to spin coat a uniform film on a large wafer. Third, the ink waste ratio is high, with only about 10% of ink retained during the second step of the process, while the remaining ink is propelled from the surface. A desirable layer for adhesive epoxy is uniform with a thickness of less than 10 micrometers.

3.3.2 Spin Coating Procedure of Adhesive Epoxy

The spin coater machine, as shown in Appendix O, is used to create a thin layer of adhesive epoxy.

A clean surface before spin coating is a key step to make a uniform ink layer. Steps for cleaning is shown in Table 3-7:

Table 3-7: Cleaning Procedure for Spin Coating

	1. Place the silicon wafer into a glass container that is filled with acetone
	2. Place the glass container into a sonicator and run it for ten minutes
	3. Remove the silicon wafer from the container and clean with isopropanol
N_2	4. Dry the silicon wafer with nitrogen
	5. Place the silicon wafer onto a hot plate at 100 °C for three minutes

The total ink, V_{total}, desired is dependent on the surface area of the spin coated surface and the target thickness of the final ink pad. The relationship is represented in the equation below, where A and r are the surface area and radius of the silicon wafer, respectively, while d is the expected thickness of the ink pad.

$$V(ink) = V(total) * \eta$$

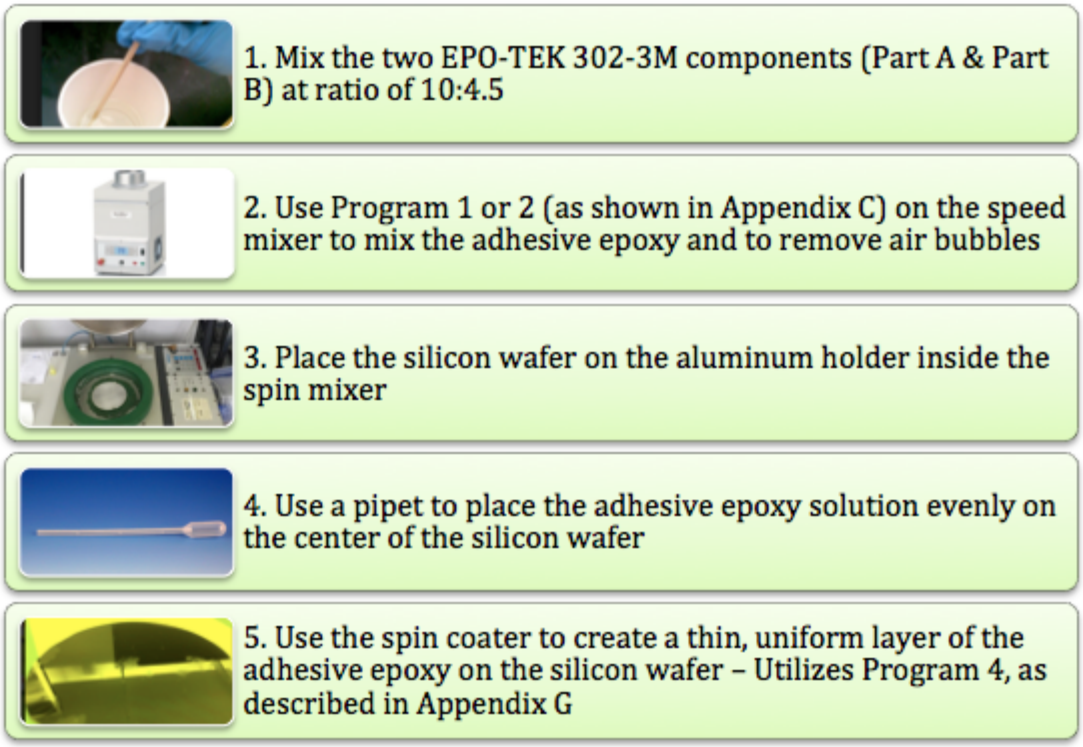
$$V(total) = V(ink)/\eta$$

$$V(total) = A * d/\eta$$

$$V(total) = \pi r^2 * d/\eta$$

The method of spin coating has an efficiency (η) of around 10%. The efficiency was calculated by using the radius of the silicon wafer, r = 10 cm, and the measured thickness of the spin coated ink, d = 10 µm. The desired amount of ink used in the experiment is around $3.14 * 10^{-5}$ m^3. The spin coating procedure is as follows shown in Table 3-8:

Table 3-8: Spin Coating Procedure for Adhesive Epoxy



1. Mix the two EPO-TEK 302-3M components (Part A & Part B) at ratio of 10:4.5

2. Use Program 1 or 2 (as shown in Appendix C) on the speed mixer to mix the adhesive epoxy and to remove air bubbles

3. Place the silicon wafer on the aluminum holder inside the spin mixer

4. Use a pipet to place the adhesive epoxy solution evenly on the center of the silicon wafer

5. Use the spin coater to create a thin, uniform layer of the adhesive epoxy on the silicon wafer – Utilizes Program 4, as described in Appendix G

There were four parts of the spin coating procedure. The first part was to explore the effect of the air bubbles produced in the process. To do this, Program 1 with vacuum and 2 without vacuum (shown in Appendix C) of the speed mixer were used to mix the two components of adhesive epoxy.

The second part was to explore the effect that waiting time had on forming a thin layer. To achieve this goal, the silicon glass was spin coated after 0.5 min, 5 min, 10 min and 25 min of mixing.

The third part was to find the relationship between spin coating time and surface area, and spin coating speed and surface area. Multiple self-defined programs with different rotation time and speed were used.

The fourth part was to determine the thickness of the layer by using Program 4 defined by NTB. Three wafers were spin coated after 5 min, 10 min and 15 min of mixing; this process was repeated for three times. A prism coupler, as shown in Figure 3-16, was used in the clean room to measure the thickness of the ink pad.

Figure 3-16: Prism Coupler (Filmetrics, 2016)

The silicon wafer was divided into eight portions, as shown in Figure 3-17, including 4 inner areas (1-4) and 4 outer areas (5-8). During the measurements, one point from each area was measured.

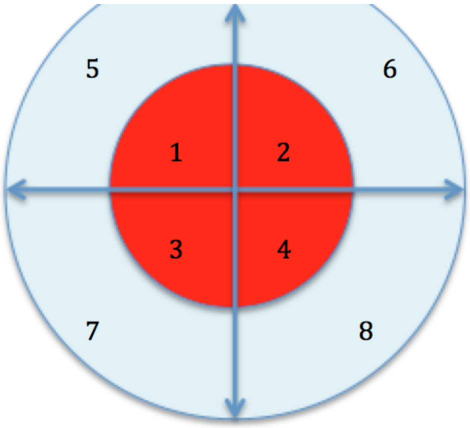


Figure 3-17: Division of Wafer

3.3.3 Spin Coating Results: Part 1

Figure 3-18 illustrates program 1 with vacuum (a) and program 2 without vacuum (b). The results showed that using program 1 successfully reduced the air bubbles inside of the adhesive epoxy, and formed a relatively more uniform ink pad compared the ink pad with program 2.

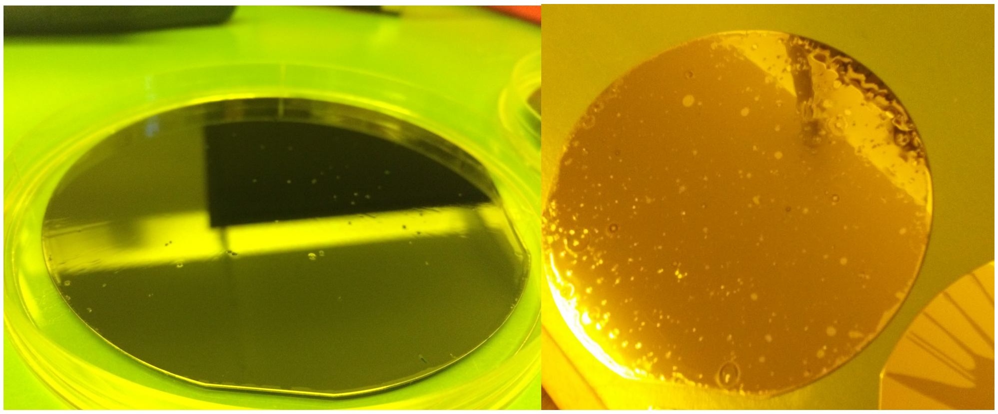
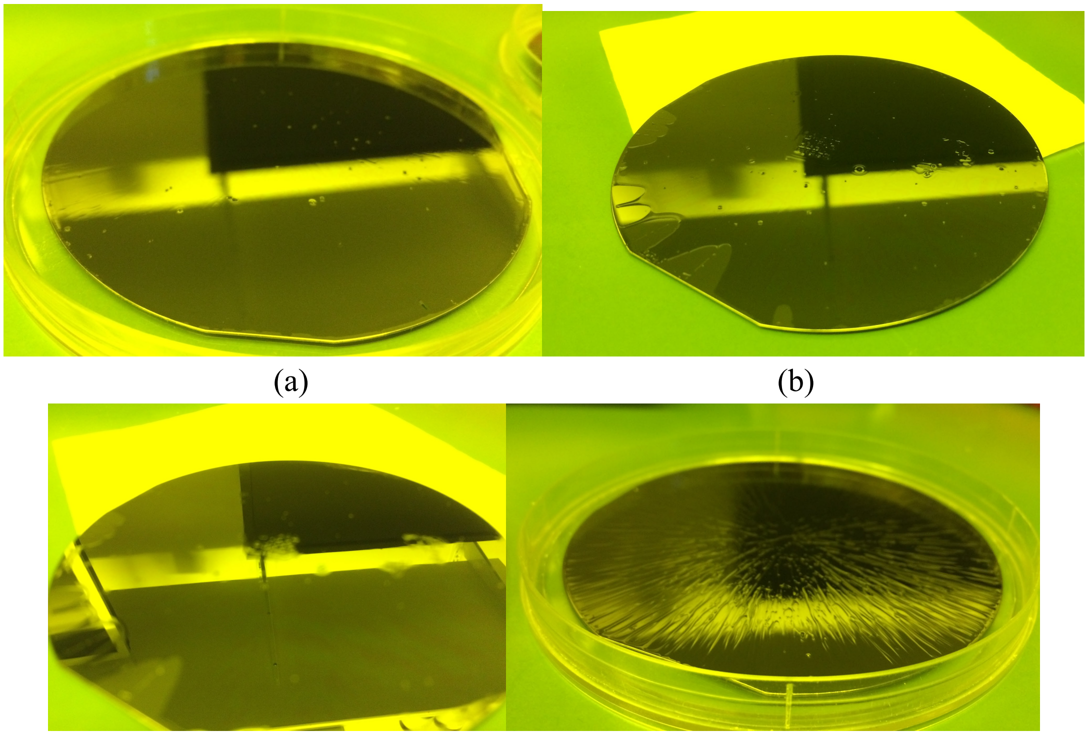

(a) (b)

Figure 3-18 (a) Program 1 with Vacuum (b) Program 2 without Vacuum

3.3.4 Spin Coating Results: Part 2

The effect of wait time between mixing and spin coating was studied, since Part A and Part B of the adhesive would polymerize after mixing. These trials demonstrated the effects of polymerization on the formation of a thin ink layer, as well as when the tipping point occurred and the ink pad fabrication process was no longer effective. The silicon glass wafer was spin coated after wait times of 5 minutes, 10 minutes, 15 minutes, and 20 minutes after Part A and Part B was mixed. The spin mixing process was completed with Program 1, and the spin coating process is completed using Program 4. The results of the delay time trials show that spin coating forms a uniform layer by using the adhesive epoxy within 15 minutes of the time of mixing. However, the surface roughness increased after 20 min of mixing, as shown in Figure 3-19. Therefore, the time between mixing and spin coating should be limited to 15 minutes.



(a) (b)

(c) (d)

Figure 3-19: Spin coating with a delay time of (a) 5 minutes after mixing (b) 10 minutes after mixing (c) 15 minutes after mixing (d) 20 minutes after mixing

3.3.5 Spin Coating Results: Part 3

According to the equation $V(total) = \pi r^2 * d/\eta$, the amount of epoxy required is $3.14 * 10^{-5}$ m^3. However, more adhesive epoxy was need to cover the surface of the silicon wafer. Trials were conducted using varying ink volumes set at 1 mL, 2 mL, 3 mL, and 4 mL of adhesive epoxy. The results show that 3 mL of epoxy proved to give optimal results, as this volume covered the total surface of the silicon wafer without wasting too much epoxy. 1 mL of epoxy was placed on the surface for self-defined studies, and 3 mL of epoxy was placed on the surface for the final ink pads created using Program 4.

Self-defined programs were also used to explore the relationship between the rotation speed, elapsed time, and the final ink pad surface area. 1 mL of adhesive epoxy was placed on the wafer in each self-defined program. In the first trial using self-defined programs 1 to 3, rotation speed was the independent variable and acceleration was the constant variable. The relationship between time and spread area was explored by changing the spinning time, shown in Table 3-9. As a result of these programs, the ink pattern stays in the center without spreading. In this case, the centripetal force was not sufficient enough to overcome the shear force due to high viscosity of the epoxy ink.

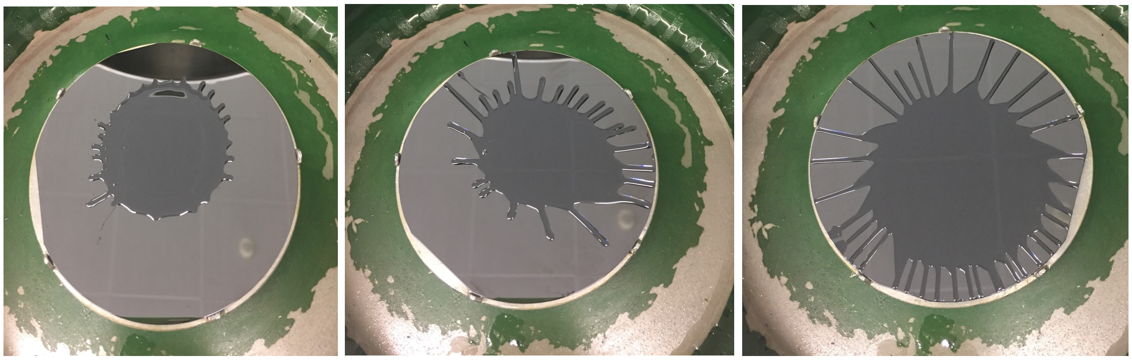
Table 3-9: Low Acceleration with Varying Time Durations

Program	Step #	RPM(*10)	Acceleration	Time (s)
Self-Def 1	1	10	1	20
Self-Def 2	1	10	1	40
Self-Def 3	1	10	1	60

The second trial, used a higher constant speed, 1000 RPM, and kept time as the independent variable, as shown in Table 3-10. Even though Self-Def 4 can spread out the ink in the middle, the rapid stop of the rotation broke the silicon wafer. The second step of Self-Defined Program 4 included a step to reduce the rotational speed to slow down the wafer and avoid damage. Self-Defined Programs 5 to 7 with a constant rotation speed and different rotation time. The results illustrated that as time increased, the spread out area increased as shown in Figure 3-20.

Table 3-10: High Acceleration with Varying Time Durations

Program #	Step #	RPM(*10)	Acceleration	Time (s)
Self-Def 4	1	100	8	2
Self-Def 5	1	100	8	2
	2	50	1	10
Self-Def 6	1	100	8	8
	2	50	1	10
Self-Def 7	1	100	8	16
	2	50	1	10



(a) (b) (c)

Figure 3-20: (a) Self- Def 5 (b) Self- Def 6 (c) Self- Def 7

The third trial, used speed as the independent variable, and the time as a constant variable, as shown in Table 3-11. Similarly, Self-Defined Programs 8 and 9 were performed. By comparing the results of Self-Defined Programs 7 to 9, if time is a constant, as rotation speed increases, the ink pad surface area increases.

Table 3-11: Varying RPM and Acceleration, Constant Time

Program #	Step #	RPM(*10)	Acceleration	Time (s)
Self-Def 7	1	100	8	16
	2	50	1	10
Self-Def 8	1	70	8	16
	2	50	1	10
Self-Def 9	1	50	8	16
	2	50	1	10

The fourth trial used Program 4, a pre-defined program by NTB, as shown in Table 3-12. By observation of the steps of Program 4, a relatively low speed in the beginning spread the epoxy over the whole surface of the wafer. Then the higher speed can propel the excess ink from the surface to create a thin layer. In the end the slow speed safely stops the rotation. After investigating the relationship between time and speed through various trials, it became apparent that Program 4 provided the best results for a uniform layer, as shown in Figure 3-21.

Table 3-12: NTB Spin Coater Program 4

Program #	Step #	RPM(*10)	Acceleration	Time (s)
4	1	250	8	5
	2	800	6	20
	3	2000	8	90
	4	2000	8	90
	5	100	6	5

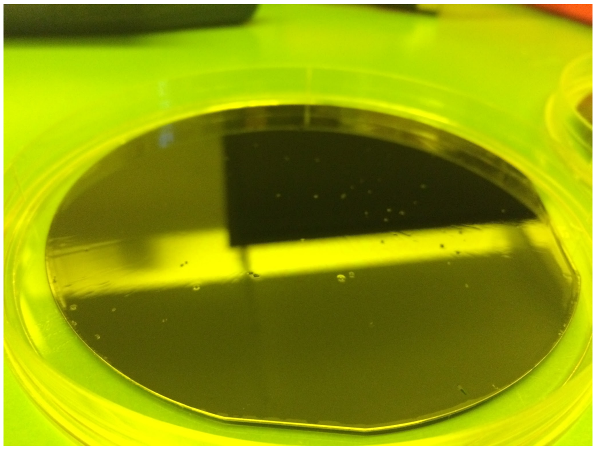
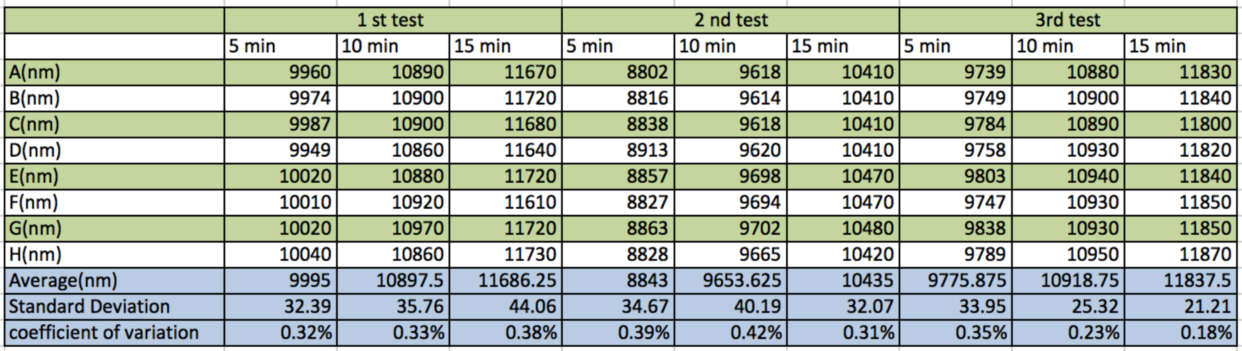


Figure 3-21: Spin Coated Wafer Using Program 4

3.3.6 Spin Coating Results: Part 4

Since program 4 gave the best results for spin coating, the thickness of the ink pad was measured through various trials to determine the repeatability. The comparison of points A through H on an inked wafer are shown in Table 3-13. The first to the third column in each of the tests show the thickness of the ink pad coated of 5, 10 and 15 minutes after part A and part B was mixed. The standard deviation of the thickness is within the range of 21 nm to 44 nm, and the coefficient of variation is between 0.18% and 0.42%, which is less than 1%. Therefore, spin coating formed a uniform ink pad layer. The thickness of inkpad is desirable since it is less than the thickness of photoresist, which is 50 micrometers. Figure 3-22 plotted the thickness of ink pad from 8 different areas in three tests, where the x-axis numbers 1 to 8 corresponding to the points 1 to 8.

Table 3-13: Thickness of Ink Pad - Spin Coated Using Program 4



	1 st test			2 nd test			3rd test		
	5 min	10 min	15 min	5 min	10 min	15 min	5 min	10 min	15 min
A(nm)	9960	10890	11670	8802	9618	10410	9739	10880	11830
B(nm)	9974	10900	11720	8816	9614	10410	9749	10900	11840
C(nm)	9987	10900	11680	8838	9618	10410	9784	10890	11800
D(nm)	9949	10860	11640	8913	9620	10410	9758	10930	11820
E(nm)	10020	10880	11720	8857	9698	10470	9803	10940	11840
F(nm)	10010	10920	11610	8827	9694	10470	9747	10930	11850
G(nm)	10020	10970	11720	8863	9702	10480	9838	10930	11850
H(nm)	10040	10860	11730	8828	9665	10420	9789	10950	11870
Average(nm)	9995	10897.5	11686.25	8843	9653.625	10435	9775.875	10918.75	11837.5
Standard Deviation	32.39	35.76	44.06	34.67	40.19	32.07	33.95	25.32	21.21
coefficient of variation	0.32%	0.33%	0.38%	0.39%	0.42%	0.31%	0.35%	0.23%	0.18%

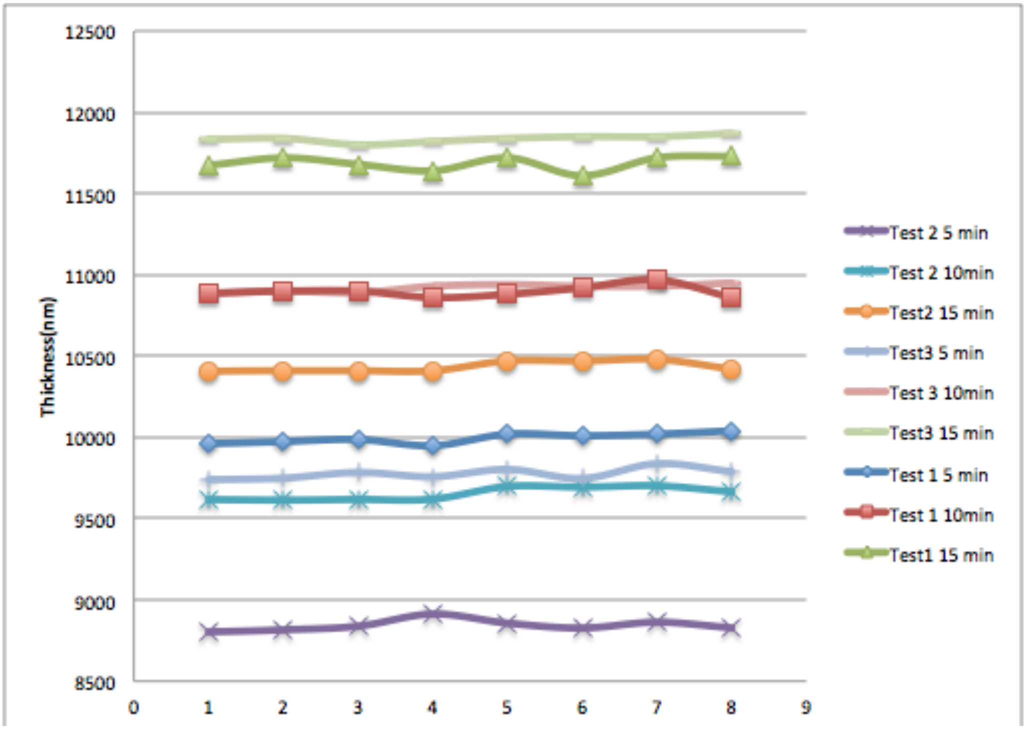


Figure 3-22: Thickness of Ink Pad From 8 Different Areas

Figure 3-23 illustrates the average thickness of the ink pad in each test, with respect to time. The relationship of time and thickness can be expressed as following:

$$y1 = 169.13x + 9168.3$$

$$y2 = 206.16x + 8782.4$$

$$y3 = 159.2x + 8051.9$$

Where y1, y2, and y3 correspond to Test 1, Test 2, and Test 3, respectively, and x (0<x<20) is the time after mixing. Therefore, the thickness of the ink pad is shown to had a linear relationship with respect to time:

$$y = ax + b$$

where a is the coefficient, x is time and b is a constant value

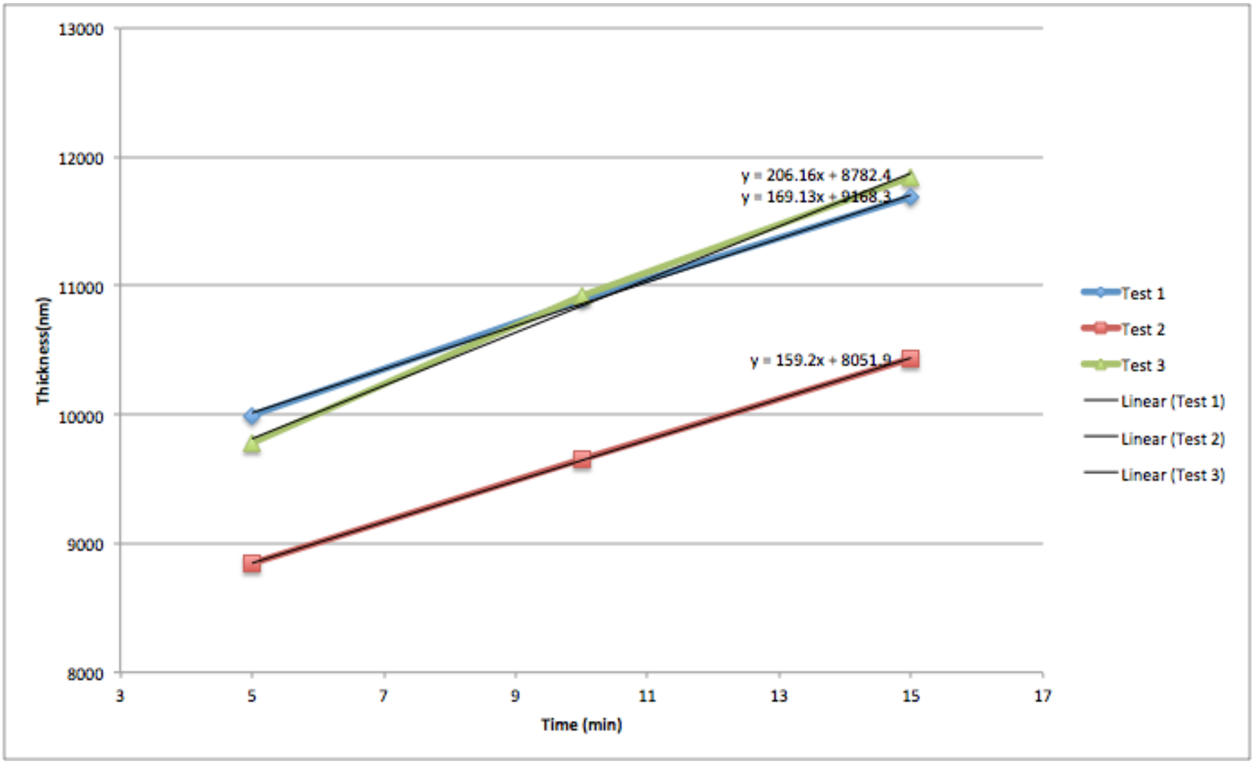
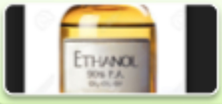
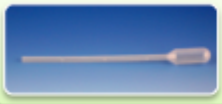


Figure 3-23: Average Thickness of Each Test with Respect to Time

3.3.7 Spin Coating Procedure of Conductive Epoxy

The conductive epoxy was spin coated to see if the same method would give similar results as the adhesive epoxy. The procedure for the speed mixing and spin coating of the conductive epoxy is as follows in Table 3-14:

Table 3-14: Spin Coating Procedure for Conductive Epoxy

	1. Mix parts A and B of the EPO-TEK H20E-PFC epoxy at a 1:1 weight ratio
	2. Dilute the conductive epoxy with 20%wt of ethanol
	3. Use Program 2, as shown in Appendix C, in the speed mixer to mix the two parts of the epoxy
	4. Place the silicon wafer on the aluminum holder inside the spin mixer
	5. Use a pipet to place 1 mL of the EPO-TEK H20E-PFC epoxy solution on the center of silicon wafer
	6. Use the spin coater to create a thin, uniform layer of the EPO-TEK H20E-PFC epoxy on the silicon wafer Program 4

3.3.8 Spin Coating Results of Conductive Epoxy

As a result, the resulting spin coated ink pad is not uniform since the mixed solution is not entirely homogeneous, and the conductive components of the EPO-TEK H20E-PFC epoxy does not dissolve in ethanol. This method will not be used in the final inking and printing procedures since the stamp requires inking on a uniform homogenous layer. A sample result of spin coating the EPO-TEK H20E-PFC epoxy is shown in Figure 3-24.

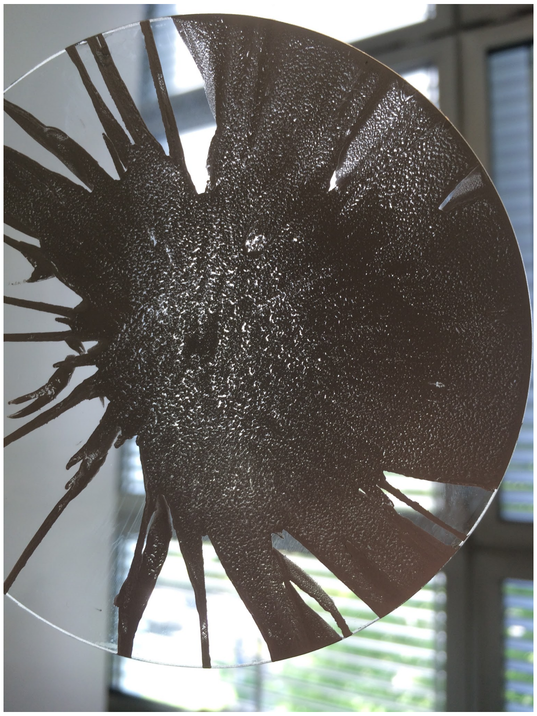


Figure 3-24: Spin Coating Conductive Epoxy

3.3.9 Doctor Blade Background

The second method of creating the EPO-TEK H20E-PFC ink pad uses a doctor blade. Doctor blading, also known as knife coating or blade coating, is a process used in the application of creating thin ink films on the surface of rigid or flexible substrates. Figure 3-25 demonstrates the coating process through the use of a doctor blade. A sharp blade is placed above the surface of a substrate at a fixed distance, g, which is usually 10 µm - 500 µm (Krebs, 2009). The ink is placed above the substrate and in front of the blade. The thickness of the film, d, can be calculated by the equation:

$$d = \frac{1}{2}(g * \frac{c}{\rho})$$

Where ρ is the density of the final film and c is the concentration of solid particles in the ink. The thickness, d, is in the range of twenty to several hundred microns (Berni, 2004). The doctor blade method scrapes off excess ink in the creation of the ink pad and reduce ink waste to less than 5%, which reduces the volume of ink needed for ink pad creation compared with spin coating (Krebs, 2009). However, drawbacks to this technique include the need for multiple trials in order to determine the optimal conditions for coating, specifically the required quantity of ink and the applied force needed.

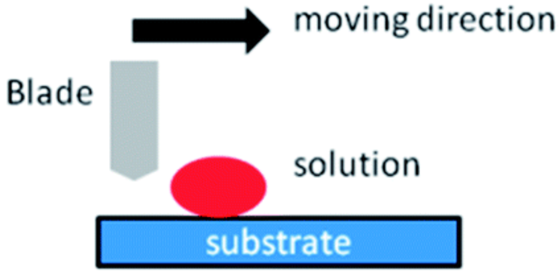


Figure 3-25: Doctor Blade (Burgues-Ceballos, 2014)

3.3.10 Doctor Blade Initial Design

NTB provided two doctor blade constructions. In the initial doctor blade design, Construction 1, micrometer foil was used to maintain a height of 10 µm between the blade edge and the surface of a glass plate, as shown in Figure 3-26. This method removes the excess ink through "wiping" a blade across the surface of a glass wafer by hand. The two ends of the blade are run across the micrometer foil, thereby keeping the blade edge elevated above the plate surface.

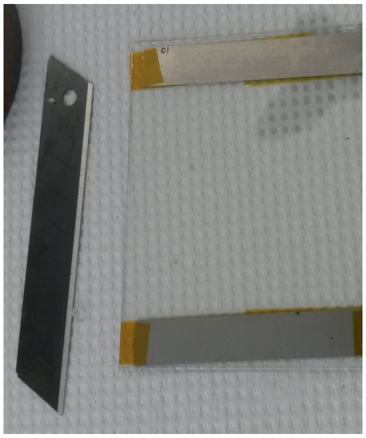
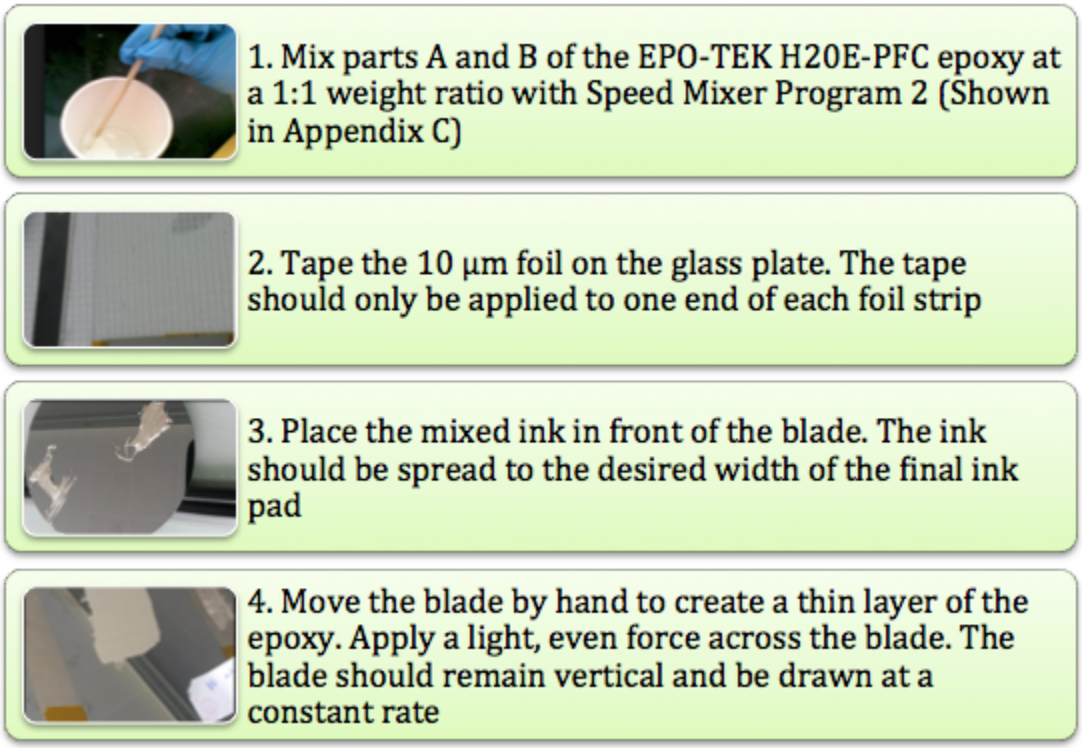


Figure 3-26: Doctor Blade - Construction 1

The procedure for the formation of the ink pad using Construction 1 is as follows in Table 3-15:

Table 3-15: Procedure for Doctor Blade of Construction 1



1. Mix parts A and B of the EPO-TEK H20E-PFC epoxy at a 1:1 weight ratio with Speed Mixer Program 2 (Shown in Appendix C)
2. Tape the 10 μm foil on the glass plate. The tape should only be applied to one end of each foil strip
3. Place the mixed ink in front of the blade. The ink should be spread to the desired width of the final ink pad
4. Move the blade by hand to create a thin layer of the epoxy. Apply a light, even force across the blade. The blade should remain vertical and be drawn at a constant rate

3.3.11 Doctor Blade Final Design

Construction 1 of the doctor blade produced ink pad layers of uniform thickness during initial trials, as shown in Figure 3-27. However, due to the high potential for variability in blade angle, force application, and draw speed, a more controlled system was needed to increase the degree of consistency between trials.

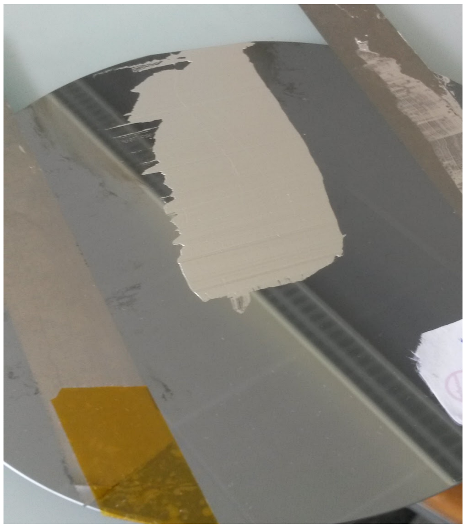


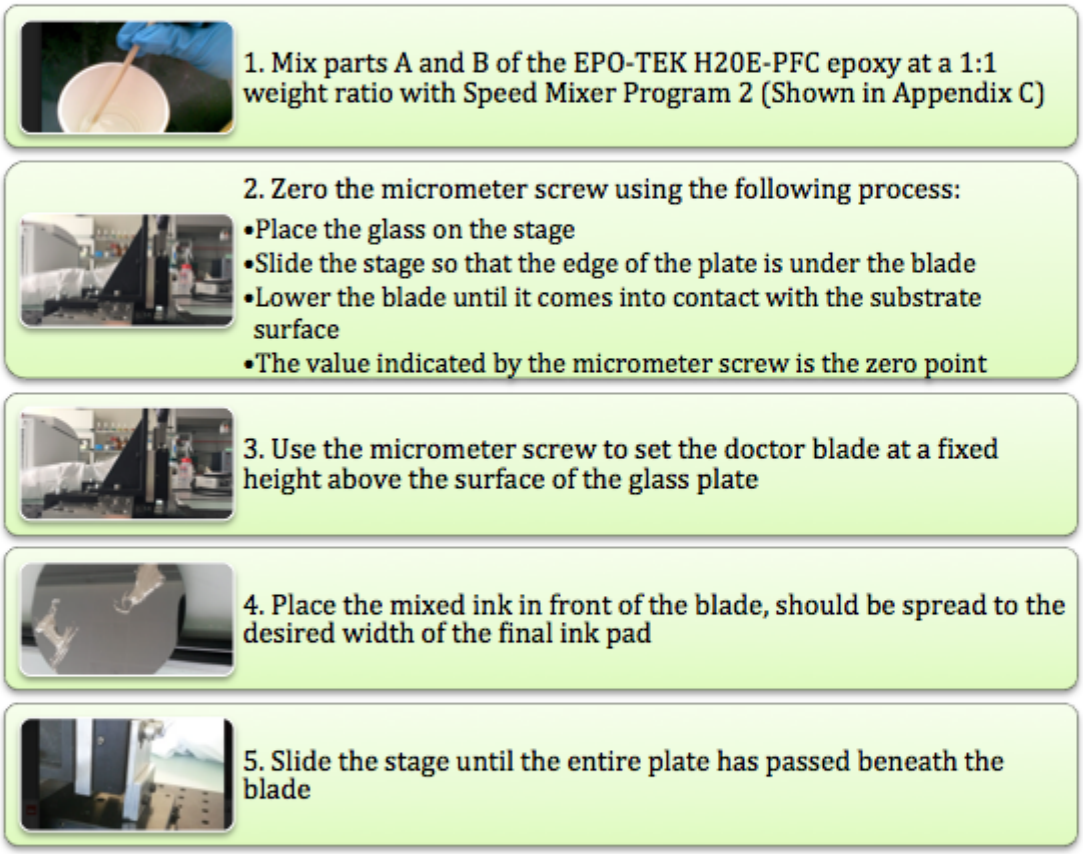
Figure 3-27: Ink Pad Result (Construction 1)

To improve the consistency and repeatability of the doctor blading procedure, a second design, Construction 2, was developed, as shown in Figure 3-28. This design utilizes a micrometer screw to control the height between the blade and the surface of the glass plate. A movable stage was used to move the glass wafer and produce a thin uniform layer of the adhesive. Through these alterations, Construction 2 addressed the high variability in the doctor blading process. The addition of a fixed blade mount provided control for the angle and force applied, and a sliding stage improved control of the draw speed. Construction 2 also utilized a micrometer screw which provided the user with a more flexible control of the height adjustment process.

Figure 3-28: Doctor Blade - Construction 2

The procedure for the formation of the ink pad using Construction 2 is as follows in Table 3-16:

Table 3-16: Doctor Blade Procedure for Construction 2



1. Mix parts A and B of the EPO-TEK H20E-PFC epoxy at a 1:1 weight ratio with Speed Mixer Program 2 (Shown in Appendix C)

2. Zero the micrometer screw using the following process:
   - Place the glass on the stage
   - Slide the stage so that the edge of the plate is under the blade
   - Lower the blade until it comes into contact with the substrate surface
   - The value indicated by the micrometer screw is the zero point

3. Use the micrometer screw to set the doctor blade at a fixed height above the surface of the glass plate

4. Place the mixed ink in front of the blade, should be spread to the desired width of the final ink pad

5. Slide the stage until the entire plate has passed beneath the blade

3.3.11 Doctor Blade: Ink Pad Results

In initial trials, setting the micrometer screw to 20 μm provided an optimal ink pad thickness. A comparison of initial micrometer screw value trials can be seen in Figure 3-29 where (from top to bottom) the micrometer screw is set to 15 μm, 20 μm, and 17 μm. At lower height settings, the applied force of the blade on the ink reaches a tipping point and pulls ink away from the plate surface. At greater height settings, the spacing between the blade edge and the plate surface causes in increase in the ink pad thickness.

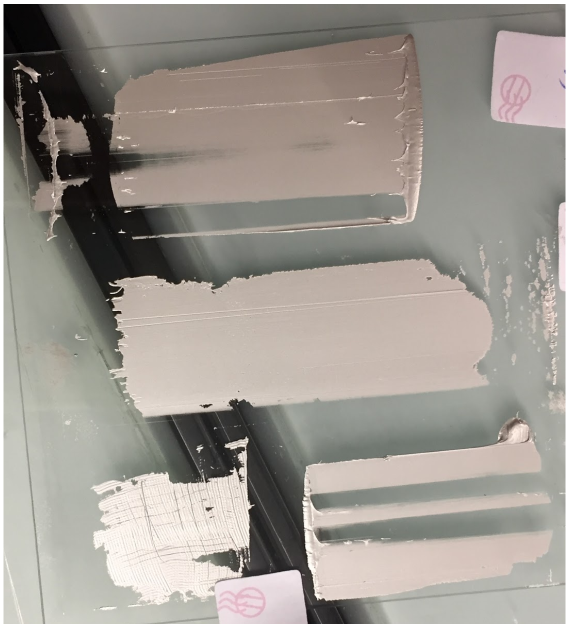


Figure 3-29: Ink Pad Results with Various Micrometer Screw Inputs (Construction 2)

Using white light interferometry, the thickness of various EPO-TEK H20E-PFC conductive epoxy ink pads were measured. The procedure for measuring ink pad thickness is as follows in Table 3-17:

Table 3-17: Ink Pad Measurement Procedure

1. •Prepare an EPO-TEK H20E-PFC conductive epoxy ink pad using a doctor blade (Construction 2) following the procedure outlined in Section 3.3.10
2. •Position the fabricated ink pad under the white light interferometer lens (EPI 10X-N) so that the field of view includes both the ink pad and the plate. The plate will serve as the baseline for the thickness measurement
3. •Prepare for image acquisition with the following settings:
   - •Image Type: Topography
   - Field of View: 768 x 576 data points
   - •Objective: EPI 10X-N
   - Confocal Z Scan: 80.0 µm
4. •Acquire image and open in contour view
5. •Use the three point term setting to set the plate baseline
6. •Open the image in profile view and compare the average baseline height to the average ink pad height to determine the ink pad thickness

As shown in Table 3-18, the resulting thicknesses was not equivalent to the value of the micrometer screw used to create each ink pad. Rather, the ink pad thicknesses were measured to be between 2.695 µm and 3.395 µm. Each ink pad showed a high degree of uniformity under the white light, as shown by the images in Appendix J.

Table 3-18: Doctor Bladed Ink Pad Thickness Results

Ink Pad	Micrometer Screw Value (µm)	White Light Thickness Measurement (µm)
1	15	3.395
2	17	2.695
3	20	2.860

From these results, it was determined that the micrometer screw should be set to 18 μm to form a thin, uniform ink pad using the EPO-TEK H20E-PFC epoxy with doctor blade design Construction 2. This height provides a spacing large enough to effectively remove the excess ink, while maintaining a low enough applied force so that the ink pad remains uniform.

3.4 Time Constraints of Printing

The surfaces of PMMA, PDMS and glass should keep their hydrophilicity during printing to ensure a good print output. Because both PMMA and glass always have hydrophilic surfaces, the time constraint depends on functionalizing PDMS. Thus, PDMS should be re-functionalized within every 80 min according to the results in Section 3.2.

Also, the inking process should be finished within pot time. Therefore, the time starting from adhesive mixing to final inking must be limited to 1 hour. Meanwhile, for conductive epoxy the time between mixing and printing is constrained to 3 days. Lastly, the spin coating process for adhesive epoxy is constrained to 15 min after mixing of Part A and Part B to ensure the surface flatness. The summary of the time constraints is shown in Table 3-19.

Table 3-19: Time Constraints

Names	Time
Stamps	80 min
Pot time of Adhesive Epoxy	60 min
Pot time of Conductive Epoxy	3 days
Time between spin coating and mixing	15 min

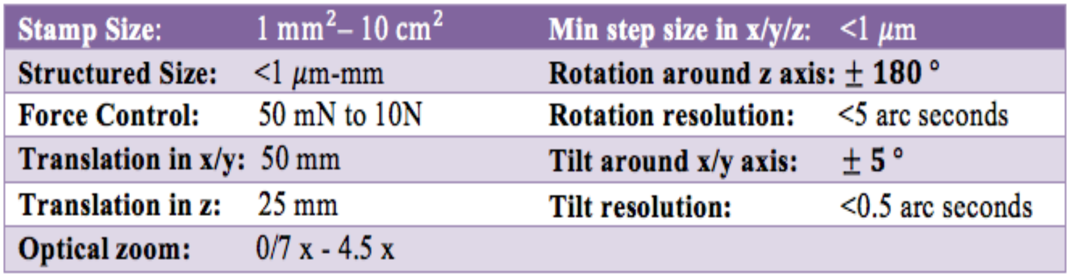
3.5 Series of Stamping Trials for an Optimal and Reproducible Process

The microcontact printing tool is used along with a pre-programmed LabVIEW program to bring the stamp into contact with a substrate. Multiple parameters were tested to provide a broad set of data and determine the best inputs for the program. The data determined whether the process was already reproducible or if it needed continued refinement.

3.5.1 NTB’s Microcontact Printing Tool

The purpose of NTB’s microcontact printing tool is to print a pattern on a substrate through conformal contact. High accuracy, resolution, and low cost are all advantages of this tool. Its motorized translation stages and gyroscope allow for alignment in all degrees of freedom (DOF). The integrated sensors provide precise regulation, and flexibility is provided from the modular design and open source software. The tool specifications can be seen in Table 3-20. During the print process, a polymer stamp is coated with molecular ink through contact with or immersion in an ink pad, and SAMs are stamped with conformal contact with the stamp and substrate. A LabVIEW program was created to control the movement of the tool and for receiving the force-measurement data. Possible applications with this tool include, protein patterns for cell growth experiments, metal layer patterning, and surface functionalization (Maechler, 2016).

Table 3-20: Specifications of NTB's Microcontact Printing Tool (Maechler, 2016)



Stamp Size:	$1\ mm^2 – 10\ cm^2$	**Min step size in x/y/z:**	<1 μm
Structured Size:	<1 μm-mm	**Rotation around z axis:**	± 180 °
Force Control:	50 mN to 10N	**Rotation resolution:**	<5 arc seconds
Translation in x/y:	50 mm	**Tilt around x/y axis:**	± 5 °
Translation in z:	25 mm	**Tilt resolution:**	<0.5 arc seconds
Optical zoom:	0/7 x - 4.5 x		

The microcontact printing tool consists of a holder plate for a glass substrate which is screwed onto the stage shown in Figure 3-30. The holes in the holder plate allow for the use of the vacuum to maintain the position of the substrate on the holder during printing. Holes for pins are also included in the holder plate to help maintain the position of the substrate.

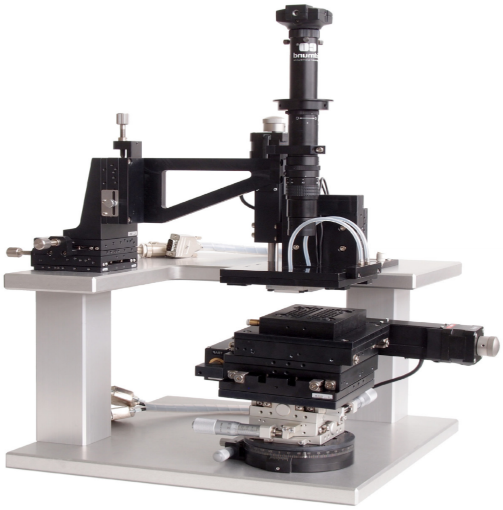


Figure 3-30: NTB's Microcontact Printing Tool (Maechler, 2016)

The current holder for the microcontact printing tool supports a glass substrate with dimensions of 50 mm x 50 mm shown in Figure 3-31.

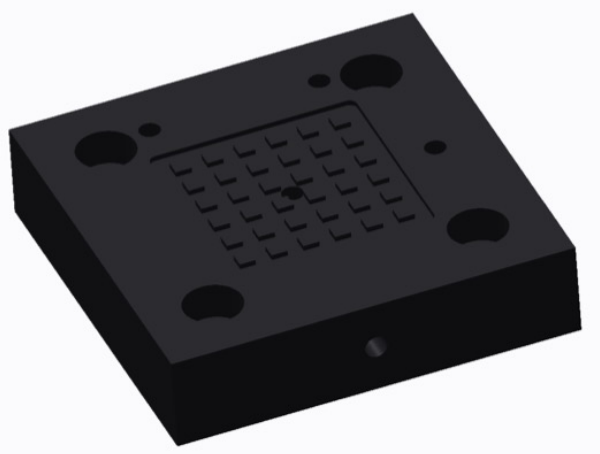


Figure 3-31: CAD Model of Glass Holder

3.5.2 Fixture for NTB Tool

In order to fit the 30 mm x 40 mm PMMA substrate, the holder design was modified through the use of the CAD program Creo. The CAD model created in Creo can be viewed in Figure 3-32. The stage plate on the NTB tool has multiple dimensions of the holes to secure the holder, ranging from 30 mm x 30 mm to 70 mm x 70 mm. The dimensions of the holder screws were modified from 70 mm x 70 mm to 50 mm x 50 mm to reduce material costs. The middle square of the holder was modified to fit the 30 mm x 40 mm plate. The pins were dimensioned to the edge of where the PMMA holder will be placed to help control any movement that may occur during printing. The mount for the vacuum was adjusted so that both the input and output locations remained centered with respect to the changed dimensions. Once manufactured out of metal, the PMMA holder was mounted to the stage on the tool with four screws. The stamping tool was modified in order to support the PMMA substrate and ensure reproducibility.

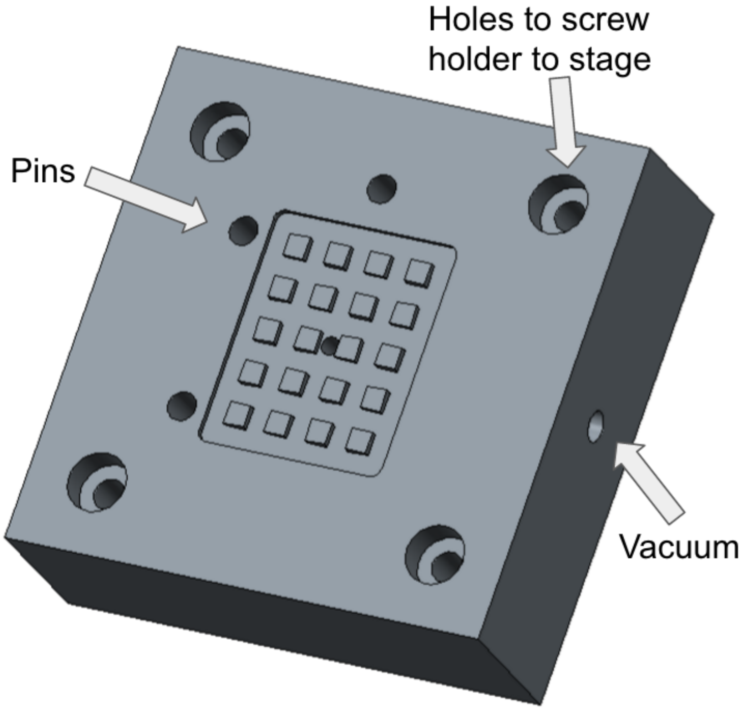


Figure 3-32: CAD Model of the PMMA Holder Fixture

3.5.3 LabVIEW Inputs

A LabVIEW program was pre-made for the NTB tool. The program includes an initial setup to align the stages to the home orientation, enable the camera, and initialize the force sensors. Once the stages are enabled, the program allows the user to begin the stamp alignment. Inputs to the program include an applied force and approach distance for the stamp to come into contact with the substrate or ink pad. The setup and steps of the LabVIEW program are shown in Appendix H. A diagram of the tool setup is shown in Figure 3-33.

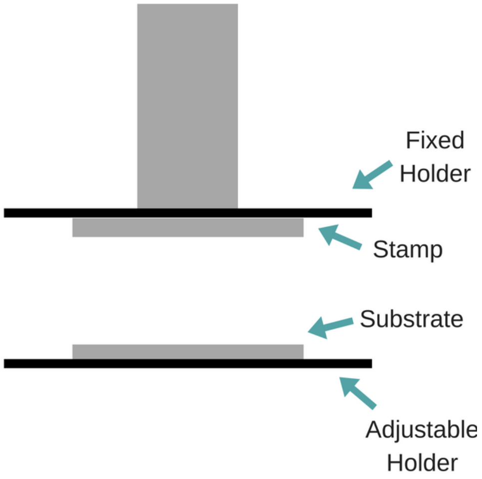


Figure 3-33: NTB Tool Setup

3.5.4 Initial Stamp Cleaning Process

It is necessary to keep the stamp clean and dry every time before inking. The process of cleaning the adhesive and conductive epoxy from the stamp is as follows in Table 3-21:

Table 3-21: Stamp Cleaning Procedure

N_2

Adhesive Epoxy
- 1. Spray ethanol on the stamp
- 2. Use nitrogen gas to dry the stamp

Conductive Epoxy
- 1. Spray ethanol on the stamp
- 2. Clean the stamp with tissue
- 3. Put the stamp into the sonication for one minute
- 4. Dry the stamp with nitrogen gas

3.5.5 Stamping Production

The procedure for the microcontact printing process is as follows in Table 3-22:

Table 3-22: Microcontact Printing Procedure

1	•Initialize stages, camera, and force sensors
2	•Start alignment
3	•Turn the vacuum on and load the stamp and ink pad onto the tool
4	•Input parameters for an approach distance and applied force in the LabVIEW program
5	•Ink the PDMS stamp through a controlled application to the surface of the ink pad
6	•Turn the vacuum off and remove the ink pad
7	•Insert the substrate to which the print will be stamped and turn on the vacuum
8	•Input parameters for an approach distance and applied force in the LabVIEW program
9	•Print with the inked PDMS stamp through a controlled application to the surface of the substrate
10	•Turn the vacuum off and remove both the stamp and the printed substrate
11	•Clean the stamp in between printing procedures

3.5.6 LabVIEW Results

Once the stages, camera, and force sensors were enabled on the LabVIEW program, the alignment and printing procedures were tested through a series of trials. The force and approach distance were used at inputs to ensure a reproducible process. A flashlight was used to ensure the angle of contact between the substrate and stamp was parallel shown in Figure 3-34.

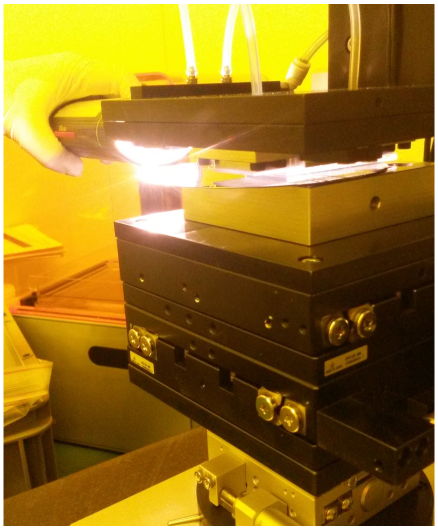


Figure 3-34: Flashlight Alignment Setup

The trials used NTB's stamping tool and LabVIEW program to determine a force and approach distance. Numerous trials were performed to determine a suitable approach distance and applied force. These variables were tested for the contact of inking the stamp to the inkpad, as well as printing the stamp to the substrate (Appendix I). A distance too close to the substrate would result in a collision and a thick non uniform layer created. The same result occurred when the applied force was too large. The ink pads and substrates required different approach distances due to their varying sizes in heights. The final approach distance determined to produce the best results for inking and printing are shown below in Table 3-23.

Table 3-23: Approach Distance for Inking & Printing

	Glass Plate	**Silicon Wafer**
Approach Distance for Inking	23 mm	24.55 mm
	Glass Substrate	**PMMA Substrate**
Approach Distance for Printing	24.55 mm	23 mm

The higher viscosity conductive adhesive required a higher force and longer time to ensure the stamp was fully covered in the ink. Stamps 1.2, 1.3, and 1.4 from Master 1 were used in the trials based on the quality of the stamp. A one-step force and time were used in the inking process to bring the stamp into contact with the ink pad. A two-step force during printing is normally used and gave better results when printing a uniform layer. The first step has a higher force to establish contact, and the second step uses a lower force to bring the epoxy to the surface. The conductive epoxy required a higher force to pick up the ink and print it due to the high viscosity. The parameters tested that resulted in a uniform layer of the final print are shown in Table 3-24.

Table 3-24: LabVIEW Parameters

Conductive Epoxy(EPO-TEK H20E-PFC)					
Inking (glass plate)		**Printing (glass substrate)**			
Force (N)	**Time (s)**	**Force 1 (N)**	**Time 1 (s)**	**Force 2 (N)**	**Time 2 (s)**
0.85	20	0.65	20	0.45	20
Inking (glass plate)		**Printing (PMMA substrate)**			
Force (N)	**Time (s)**	**Force 1 (N)**	**Time 1 (s)**	**Force 2 (N)**	**Time 2 (s)**
0.85	20	0.85	20	0.65	20
Adhesive Epoxy(EPO-TEK 302-3M)					
Inking (silicon wafer)		**Printing (glass substrate)**			
Force (N)	**Time (s)**	**Force 1 (N)**	**Time 1 (s)**	**Force 2 (N)**	**Time 2 (s)**
0.4	20	0.2	20	0.1	20
Inking (silicon wafer)		**Printing (PMMA substrate)**			
Force (N)	**Time (s)**	**Force 1 (N)**	**Time 1 (s)**	**Force 2 (N)**	**Time 2 (s)**
0.4	20	0.2	20	0.1	20

3.6 Final Printed Adhesive

The three stamps from master 1 were used to print the patterns onto both the PMMA and glass substrates. Due to some minor errors with the microcontact printing tool such as mishandling and inaccurate inputs, some prints were not distinguishable and not included in the data. Each stamp had the same lateral dimensions as the master and were comparable to each other. The use of three stamps was to decrease waiting time in between stamp trials. Stamp 1.2 produced seven prints, Stamp 1.3 produced fourteen, and Stamp 1.4 produced three. Each fabricated stamp was used multiple times to produce more sets of data. The key in Figure 3-35 explains the numbering system. Table 3-25 shows the number of final prints for each epoxy.

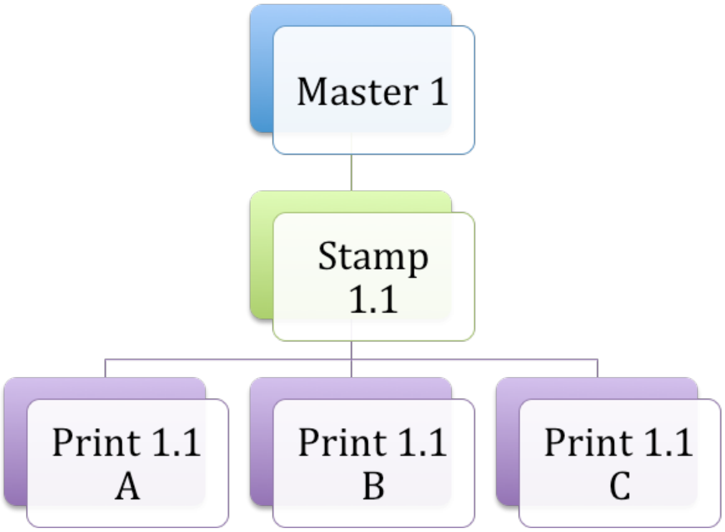


Figure 3-35: Stamp and Print Numbering System

Table 3-25: Final Prints

Conductive Epoxy(EPO-TEK H20E-PFC)		
Substrate:	**Glass Substrate**	**PMMA Substrate**
Stamp 1.2	1.2 C, 1.2 D, 1.2 E, 1.2 F	1.2 A, 1.2 B
Stamp 1.3	1.3 C, 1.3 H, 1.3 I, 1.3 J, 1.3 K	1.3 A, 1.3 B, 1.3 F, 1.3 G
Stamp 1.4	-	1.4 A
Adhesive Epoxy(EPO-TEK 302-3M)		
Substrate:	**Glass Substrate**	**PMMA Substrate**
Stamp 1.2	1.2 G, 1.2 I, 1.2 J, 1.2 L, 1.2 M	1.2 H, 1.2 K
Stamp 1.3	1.3 D, 1.3 E, 1.3 H, 1.3 L, 1.3 M, 1.3 O, 1.3 P, 1.3 Q	1.3 N, 1.3 M
Stamp 1.4	1.4 C, 1.4 D, 1.4 F, 1.4 H,	1.4 E, 1.4 G

3.6.1 Adhesive Curing

The adhesives were hardened for characterization after printing to avoid the pattern from smudging. Adhesives can be cured in a batch oven for both epoxies. Heat cured adhesives can be either one-part or two-part products. The two adhesives in this procedure were EPO-TEK H20E-PFC, and EPO-TEK 302-3M. Curing occurred once the stamp was printed onto the substrate. Both epoxies were cured using an oven, as shown in Appendix O. EPO-TEK 302-3M was capable of a low temperature cure at 23°C in the oven for 23 hours, or a temperature of 65°C for 3 hours, as shown in Appendix A. EPO-TEK H20E-PFC was cured at 120°C in the oven for 15 minutes or 80°C for 3 hours for glass substrate. However, PMMA substrates can only be cured at 85°C for 3 hours in order to prevent disfigurement of the substrate, as shown in Appendix A.

3.6.2 Characterization of Printed Structures

The optical microscope is the tool used to measure the lateral dimensions of the master photoresist pattern, the stamp pattern, and the final print pattern. The white light interferometer is the tool used to measure the thickness of 3-D structures after curing, as shown in Appendix O (Michel, 2001). This tool was used in quantifying the varying characteristics between the trial samples to allow for an objective analysis of the different inking and stamping methods.

After the ink stamp was applied to the surface of the substrate, the produced stampings were characterized in order to provide an objective method of comparison between trials. This objective was accomplished through the measurement of physical features, such as the thickness, conductivity, and shear strength of the finished print.

In characterizing the produced prints, variables available for optimization became apparent. As this occurred, improvements were verified through further cycles of testing.

3.6.3 Optical Testing: Lateral Dimensions of Final Prints

The final prints were viewed under the optical microscope to compare the lateral dimensions to the master and stamp, as well as determine the quality of the epoxy after printing, as shown in Appendix M. Figure 3-36 illustrates the widths that were measured on the prints, and The percent error was also calculated between the final prints and the master. The equation used is shown in below, where Lm and Lp represent the lateral dimensions of the master and final print.

$$\%error = \frac{|Lp - Lm|}{Lm} * 100\%$$

$$\%error\ total = \%error\ a + \%error\ x$$

The data in Table 3-26 includes the measured lateral dimensions of a and x, as well as the calculated percent error of a, x, and total. The maximum percent error allowed to maintain the tolerance of +/- 0.05 mm of the master are 33.56% and 11.42% for a and x respectively. Numbers highlighted in red indicate values that are not within the tolerance.

One reason the prints were not in the tolerance is because the stamp and substrate did not make parallel contact. Since the whole pattern did not fully print on the substrate, the exact square previously measured was not readable shown in Figure 3-37. Some prints were not visible or did print each pattern uniformly during the initial trials and caused difficulty in measuring the same square as the master. A solution to this problem in the future would be to use a master pattern with one square to measure, instead of a master with different sizes.

The lowest percent error for a and x consisting of the adhesive epoxy printed on a PMMA substrate, was 30.87% and 4.79% error respectively. The lowest % error for adhesive epoxy on glass was 10.74% error for a, and 0.91% for x. The conductive epoxy resulted in a lower % error of 2.01% error for a, and 2.74% error for x on PMMA, and 2.01% error for a and 7.76% error on glass.

Print 1.2 B had a slightly higher inking and printing force than Print 1.3 B and resulted in a less uniform print. A higher force used could smudge the pattern and not create a thin uniform layer when inking and printing (Appendix M). Both Print 1.2 J and Print 1.2 L used the same force parameters for inking and printing, but Print 1.2 J did not fully replicate the pattern as well as Print 1.2 L. The two prints were inked from the same spin coated wafer, but a small air bubble may have been the cause for the difference in data. Further development in the printing process is needed since NTB's current process for printing molecules has very good accuracy and reproducibility in producing the same shape of the pattern.

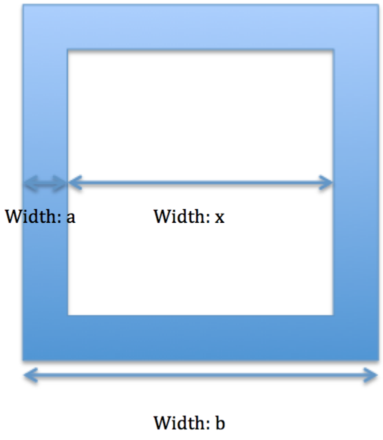


Figure 3-36: Lateral Dimensions Measured

Figure 3-37: Print Pattern on Substrate

Table 3-26: Percent Error Between Lateral Dimension Measurements

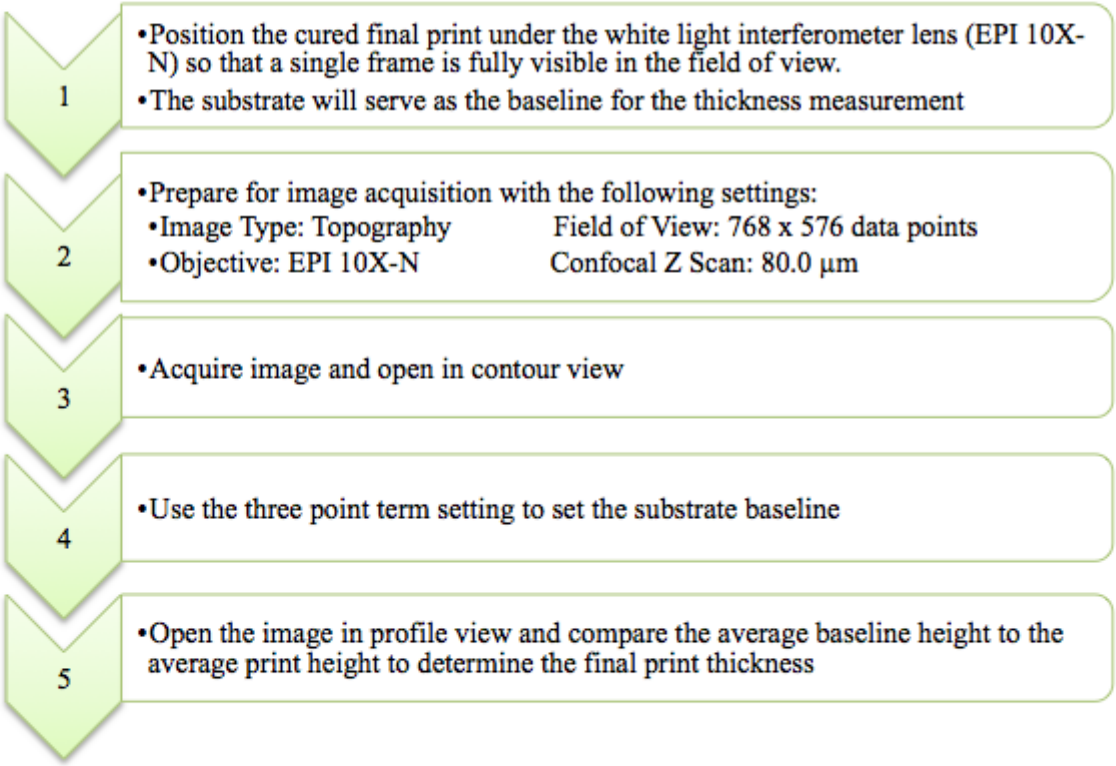
	a (µm)	% error of a	x (µm)	% error x
Master(a)	0.149	N/A	0.438	N/A
Conductive Epoxy (Glass substrate)				
1.2 C	0.106	28.86%	0.476	8.68%
1.2 E	0.117	21.48%	0.518	18.26%
1.2 F	0.131	12.08%	0.513	17.12%
1.2 D	0.135	9.40%	0.500	14.16%
1.3 H	0.146	2.01%	0.560	27.85%
1.3 I	0.166	11.41%	0.543	23.97%
1.2 J	0.161	8.05%	0.472	7.76%
1.3 K	0.128	14.09%	0.509	16.21%

Conductive Epoxy (PMMA substrate)				
1.2 A	0.0967	35.10%	0.4553	3.95%
1.2 B	0.152	2.01%	0.502	14.61%
1.3 F	0.119	20.13%	0.507	15.75%
1.3 G	0.102	31.54%	0.450	2.74%
Adhesive Epoxy (Glass Substrate)				
1.2 L	0.092	38.26%	0.442	0.91%
1.2 J	0.045	69.80%	0.474	8.22%
1.3 N	0.133	10.74%	0.553	26.26%
1.3 O	0.101	32.21%	0.588	34.25%
1.3 P	0.125	16.11%	0.506	15.53%
1.3 Q	0.109	26.85%	0.456	4.11%
1.4 F	0.0967	35.10%	0.506	15.53%
1.4 H	0.112	24.83%	0.514	17.35%
Adhesive Epoxy (PMMA Substrate)				
1.4 E	0.0938	37.05%	0.5342	21.96%
1.2 H	0.0488	67.25%	0.4082	6.80%
1.2 K	0.0811	45.57%	0.4929	12.53%
1.3 M	0.103	30.87%	0.417	4.79%
1.4 G	0.0986	33.83%	0.4704	7.40%

3.6.4 Optical Testing: Thickness of the Printed Structure

After printing on NTB's microcontact printing tool, the thickness of the frames was measured using a white light interferometer, shown in Appendix O, in order to characterize the final prints and further optimize the printing procedure. The procedure for measuring the print thicknesses is as follows in Table 3-27:

Table 3-27: Thickness Measurement Procedure



1
- Position the cured final print under the white light interferometer lens (EPI 10X-N) so that a single frame is fully visible in the field of view.
- The substrate will serve as the baseline for the thickness measurement

2
- Prepare for image acquisition with the following settings:
  - Image Type: Topography
  - Field of View: 768 x 576 data points
  - Objective: EPI 10X-N
  - Confocal Z Scan: 80.0 µm

3
- Acquire image and open in contour view

4
- Use the three point term setting to set the substrate baseline

5
- Open the image in profile view and compare the average baseline height to the average print height to determine the final print thickness

The measured results are shown in Table 3-28. These measurements ranged from 0.118 µm to 4.574 µm for the EPO-TEK H20E-PFC conductive epoxy, and from 2.795 µm to 7.850 µm for the EPO-TEK 302-3M adhesive epoxy. Appendix K and Appendix L show the images for these results. The results of the thickness and LabVIEW inputs were not comparable since the tests used different ink pads. Since the homogeneity did not look as we wanted it to, more development in the coating process is needed to use the prints for production.

Table 3-28: Thickness of the Final Prints

EPO-TEK H20E-PFC (Conductive)		EPO-TEK 302-3M (Adhesive)	
Print Number	Thickness (µm)	Print Number	Thickness (µm)
1.2B	0.784	1.3N	7.850
1.2E	2.896	1.4H	4.536
1.3F	3.502	1.3O	3.355
1.3G	4.574	1.2L	2.795
1.3B	1.756	1.4F	5.371
1.3C	3.373	1.2I	4.101
1.2D	1.074	1.2K	3.153
1.3I	0.657	1.3D	3.271
1.2C	0.118	1.3E	4.033
1.3J	0.945		
1.2F	0.900		
Average:	1.871	Average:	4.274
Std. Dev:	1.465	Std. Dev:	1.559

Shown in Figure 3-38 and Figure 3-39 are the graphical representations of the EPO-TEK H20E-PFC conductive epoxy and the EPO-TEK 302-3M adhesive epoxy print thicknesses, respectively. As shown, the two epoxies have a degree of overlap in measured thickness. However, the EPO-TEK 302-3M adhesive epoxy had an average thickness of 4.274 µm and produced thicker final prints than the EPO-TEK H20E-PFC conductive epoxy, which had an average thickness of 1.871μm. The difference in print thickness was potentially caused by the greater thickness of the spin coated inkpad, as well as the epoxy's comparably lower viscosity. As a result, these two factors allowed the stamp to pick up more ink and to create a thicker print without sacrificing its uniformity. Within the sets of prints for each adhesive, the discrepancy may be a result of the use of different ink pads, or the variation in wait time between the fabrication of the ink pad and the inking process.

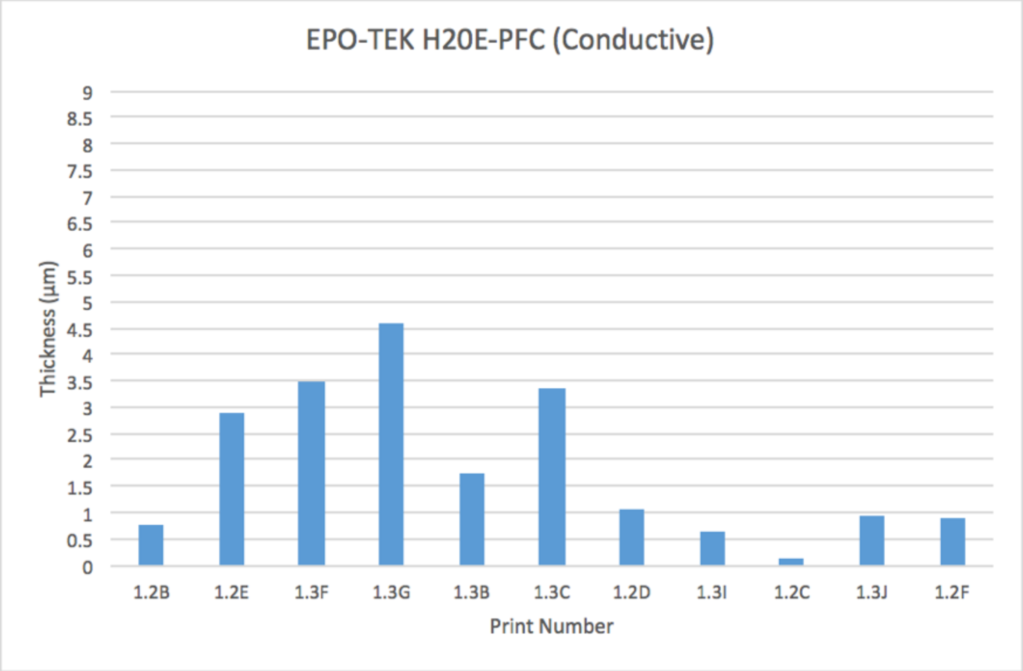


Figure 3-38: Thickness of EPO-TEK H20E-PFC Prints

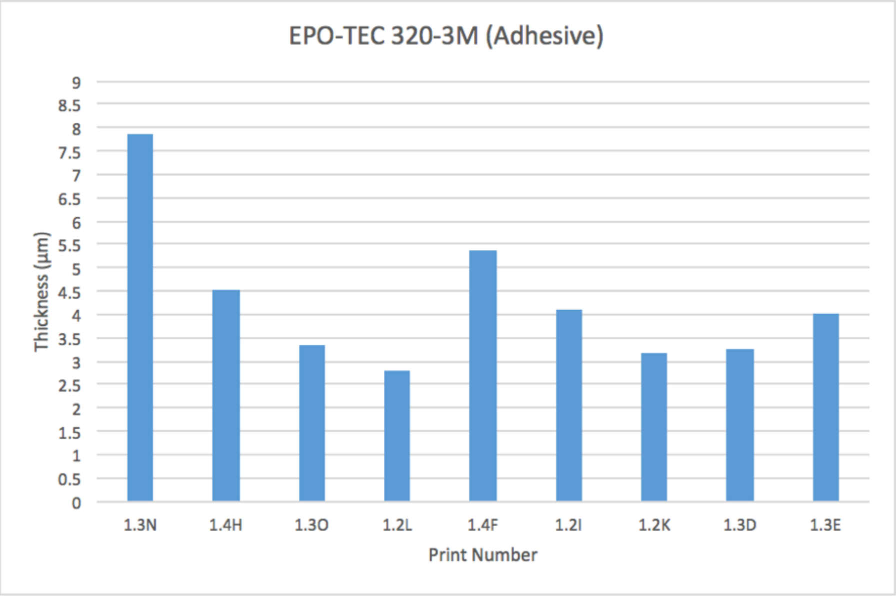


Figure 3-39: Thickness of EPO-TEK 302-3M Prints

3.7 Gluing of the Stamped Product

Once the inking and stamping processes were optimized, a final set of stampings were produced. A series of mechanical tests were conducted to determine the effectiveness of the adhesives. To perform the test, a glass die was first glued to one of the square patterns on the final print, as shown in Figure 3-40. This was accomplished by using tweezers to place a glass die on a single frame of each print. The print was then hardened through the curing processes defined in Section 3.6.1.

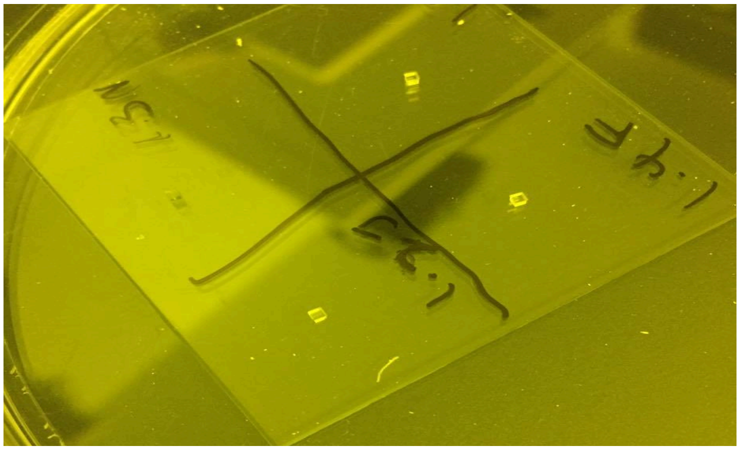


Figure 3-40: Glass Die Glued to Final Print

The glued die allowed for mechanical tests to be performed to determine the shear strength of the final prints. In order for the tests to be optimal, the glass die needed to be precisely placed on its frame. The process of gluing the die was difficult since the squares did not stick until fully cured, and would slide across the substrate during transferring, as shown in Figure 3-41.

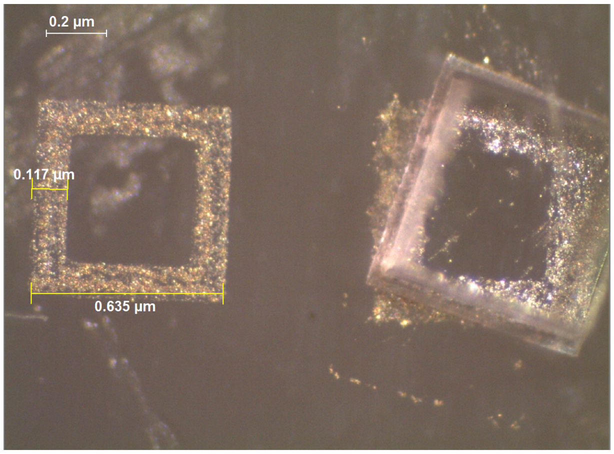


Figure 3-41: Glued Die After Curing

3.7.1 Shear Testing Calibration

Mechanical testing was conducted once a desirable thickness for the printed structure was achieved. Since the thickness of the inkpad was between 8.8 µm and 11.8 µm for spin coating and 2.5 µm and 3.5 µm for doctor blading, the final print thickness should be within the range of its respective ink pad. Samples were put through a shear testing procedure to determine the strength of the hardened epoxy. Before testing, an additional glass substrate was fixed to an individual printed frame and the epoxy was cured. For use on the shear tester, only the glass substrate can be glued and tested due to the smaller geometry of the PMMA substrates. When mounted to the tool, the shear tester isn't able to fully impact the die on the PMMA until interference occurs with another component of the tool.

The shear testing equipment was calibrated using a series of weight measurements. The shear tester uses a piezo sensor to measure a change in voltage, which can then be converted into a measurement of applied force. To determine the conversion rate, a series of weights were strung so that they applied a linear force to the arm which would measure the shear strength of the epoxies, as shown in Figure 3-42.

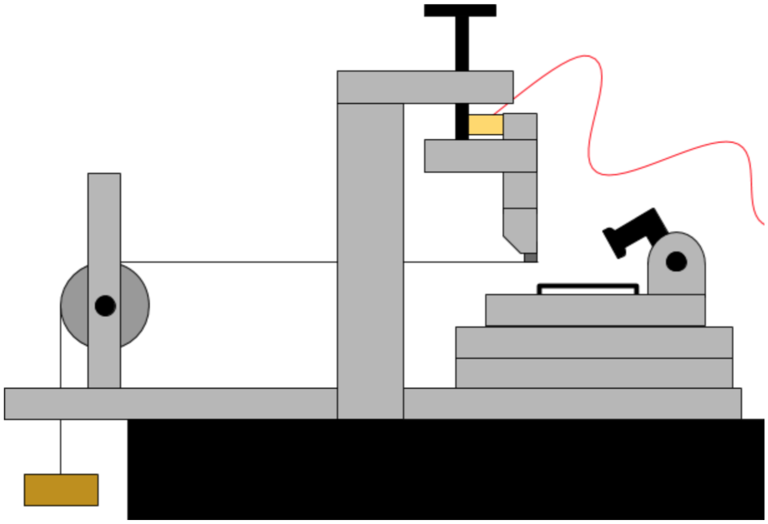


Figure 3-42: Shear Testing Machine

The calibration procedure is as follows in Table 3-29:

Table 3-29: Calibration Procedure

1	•Lower the sensor arm so that the point of the shearing tool is in line with the top of the pulley. Move the stage as needed if interference occurs
2	•Attach a cord (looped on each end) to the point of the shearing tool and lay the other end over the pulley
3	•Ensure that the cord, when under tension, is fully horizontal from the point of the shearing tool to the pulley
4	•Measure the voltage over a series of weight trials. For the team's measurements, six weights were used over three trials for a total of 18 data points
5	•Chart the data points as voltage against force and establish a trend line
6	•Use the trend line to establish an equation that relates voltage to force

The calibration data for each of the testing trials can be seen in Appendix N. For the initial shear test trial, the calibration data provided the below conversion function, where V1 is the measured voltage (in mV) and F1 is the calculated shear force:

$$F1 = -\frac{V1 + 12.982}{0.1776}$$

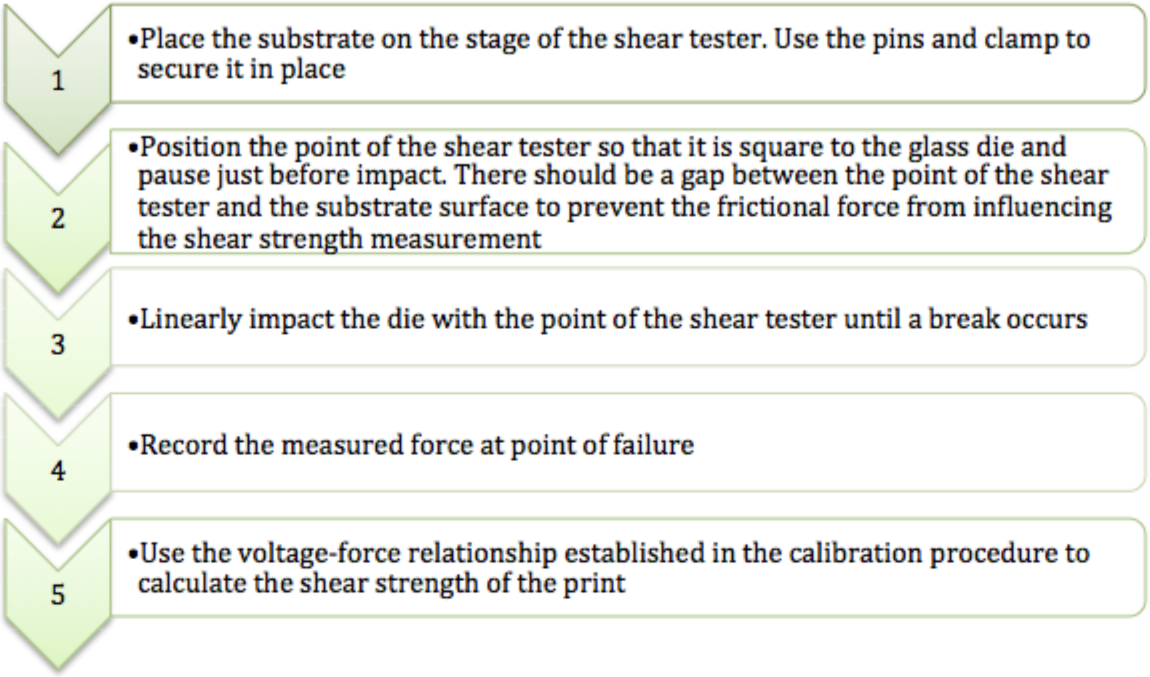
For the second shear test trial, the calibration data provided conversion function below, where V2 is the measured voltage (in mV) and F2 is the calculated shear force:

$$F2 = -\frac{V2 - 58.597}{0.1798}$$

3.7.2 Shear Testing Results

The Procedure for shear testing is shown in Table 3-30. After calibration, the shear test data, as seen in Table 3-31, was collected for a sample of prints for each epoxy on a glass substrate.

Table 3-30: Shear Test Procedure



1 •Place the substrate on the stage of the shear tester. Use the pins and clamp to secure it in place

2 •Position the point of the shear tester so that it is square to the glass die and pause just before impact. There should be a gap between the point of the shear tester and the substrate surface to prevent the frictional force from influencing the shear strength measurement

3 •Linearly impact the die with the point of the shear tester until a break occurs

4 •Record the measured force at point of failure

5 •Use the voltage-force relationship established in the calibration procedure to calculate the shear strength of the print

The initial tests were performed on Prints 1.3D, 1.3E, and 1.4C, and the second shear test trial included the remaining prints. While data was collected for the EPO-TEK H20E-PFC conductive epoxy, the primary focus of this test was placed on the EPO-TEK 302-3M adhesive epoxy for its potential use in future optical applications.

Table 3-31: Shear Test Data of Final Prints Using Both Calibration Functions

EPO-TEK H20E-PFC (Conductive)			EPO-TEK 302-3M (Adhesive)		
Print Number	Measured Voltage (mV)	Calculated Shear Load (g)	Print Number	Measured Voltage (mV)	Calculated Shear Load (g)
1.3I	-62.500	673.509	1.3D	-11.250	-9.752
1.2D	-26.250	471.897	1.3E	6.250	-108.288
			1.4C	-140.625	718.711
			1.3O	17.500	228.571
			1.3N	-198.125	1427.820
			1.2I	-45.000	576.179
			1.4F	17.500	228.571
			1.2J	8.125	280.712
	Average:	572.703		Average:	417.816
	Std. Dev:	142.561		Std. Dev:	490.736

As seen in Table 3-31, the shear test data of the EPO-TEK 302-3M adhesive epoxy has a high standard deviation, as well as negative values. These signs, paired with the variation between the y-intercepts in the functions shown prior in Section 3.7.1, indicate a “drift” in the measurements taken by the oscilloscope in the original calibration. To account for this, all of the data was calculated using only the second calibration function.

Table 3-32: Shear Test Data of Final Prints Using Second Calibration Function

EPO-TEK H20E-PFC (Conductive)			EPO-TEK 302-3M (Adhesive)		
Print Number	Measured Voltage (mV)	Calculated Shear Load (g)	Print Number	Measured Voltage (mV)	Calculated Shear Load (g)
1.3I	-62.500	673.509	1.3D	-11.250	388.471
1.2D	-26.250	471.897	1.3E	6.250	291.141
			1.4C	-140.625	1108.020
			1.3O	17.500	228.571
			1.3N	-198.125	1427.820
			1.2I	-45.000	576.179
			1.4F	17.500	228.571
			1.2J	8.125	280.712
	Average:	572.703		Average:	566.186
	Std. Dev:	142.561		Std. Dev:	455.568

As seen in Table 3-32, the shear test data of the EPO-TEK 302-3M adhesive epoxy has a high standard deviation. This points to either an inconsistency in the gluing process or to an inconsistency in the printing process. The gluing process may affect the shear strength, as the gluing is done by hand and the samples are then moved to a different room for the curing process. During the application process and in transfer, there is a possibility of the dice shifting so that they are no longer in the correct position on the frame. In addition, inconsistencies in the final prints could also cause a high degree of variance in the measured shear strengths. If there is low uniformity in the glued frame, or an irregular thickness compared to other samples, the shear strength could measure higher or lower than in other tests. As seen in the epoxy property tables in Appendix A, the die shear strength value for each epoxy at 23°C are as follows:

EPO-TEK H20E-PFC: ≥ 5 kg / 1,700 psi

EPO-TEK 302-3M: ≥ 10 kg / 3,400 psi

This indicates that the EPO-TEK 302-3M adhesive epoxy should have a higher shear strength than the EPO-TEK H20E-PFC conductive epoxy.

3.7.3 Electrical Testing Procedure

In addition to mechanical and optical evaluation, the EPO-TEK H20E-PFC conductive epoxy required electrical testing for the characterization. This process was conducted through the use of a voltage generator and a multi-meter. By sending an electrical current through two opposing corners of the frame, as seen in Figure 3-43, a parallel circuit was created. In combination with a multi-meter, this provided a resistivity of the stamp frames.

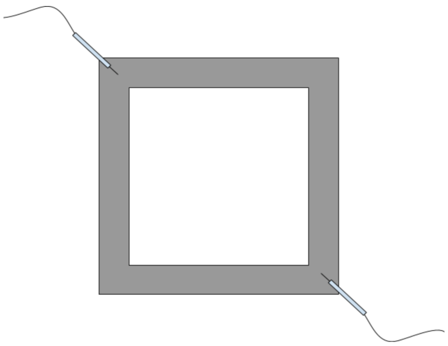
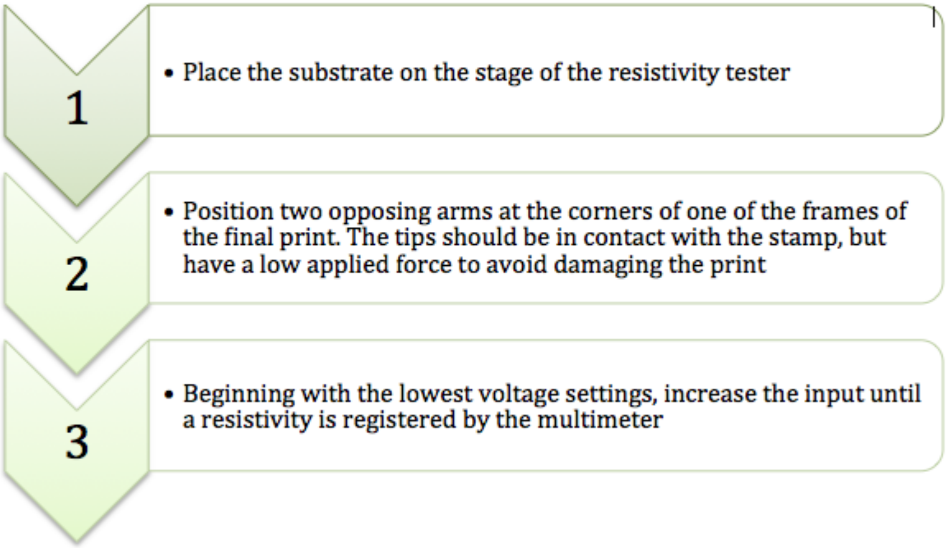


Figure 3-43: Parallel Circuit with Print Frame

The procedure used is as follows, shown in Table 3-33:

Table 3-33: Electrical Testing Procedure



1
- Place the substrate on the stage of the resistivity tester

2
- Position two opposing arms at the corners of one of the frames of the final print. The tips should be in contact with the stamp, but have a low applied force to avoid damaging the print

3
- Beginning with the lowest voltage settings, increase the input until a resistivity is registered by the multimeter

3.7.4 Electrical Testing Results

The electrical test procedure yielded the results as seen in Table 3-34.

Table 3-34: Electrical Test Data for EPO-TEK H20E-PFC

Conductive (EPO-TEK H20E-PFC)	
Print Number	Measured Surface Resistance (MΩ)
1.3C	8.5
1.3F	0.11
1.2A	5.3
1.2D	67.3
1.3G	12.7
1.2B	6.1
Average:	16.7
Std. Dev:	25.1

From the measured surface resistance and the measured thickness of the stamps, as shown in Section 3.6.4, the resistivity of the sample frames could be calculated. The following equation demonstrates the relationship between these measurements and the calculated resistivity:

$$\rho = Rs * d$$

where ρ is the calculated resistivity, R_s is the measured surface resistance and d is the print thickness

Table 3-35: Electrical Test Data for EPO-TEK H20E-PFC

Conductive (EPO-TEK H20E-PFC)		
Print Number	Print Thickness (cm)	Calculated Resistivity (Ω-cm)
1.3C	0.0003373	2867.05
1.3F	0.0003502	38.52
1.2A	N/A	N/A
1.2D	0.0001074	7228.02
1.3G	0.0004574	5808.98
1.2B	0.0000784	478.24
Average:	0.0002661	3284.16
Std. Dev:	0.0001652	3182.38

The resulting calculated resistivities can be seen in Table 3-35. According to the EPO-TEK H20E-PFC conductive epoxy data sheet, as seen in Appendix A, the specified resistivity at 23°C is as follows:

Volume Resistivity: ≤ 0.0004 Ω-cm

When compared to the calculated values, it can be seen that the conductivity of the EPO-TEK H20E-PFC conductive epoxy is much lower after printing than would be expected. This may be a result of the low thickness of the prints, as well as possible interruptions in the continuity of each print. Both of these factors could be solved in future printing trials and optimization.

4.0 Reproducible Procedures for a Variety of Substrate and Ink Combinations

This objective was accomplished through a formal record of the procedures to deliver a stamped product which met the benchmark mechanical, optical, and electrical criteria. By following a thorough optimization and verification process, as stated in the prior methodology, written procedure was developed for each of the substrate and ink combinations tested.

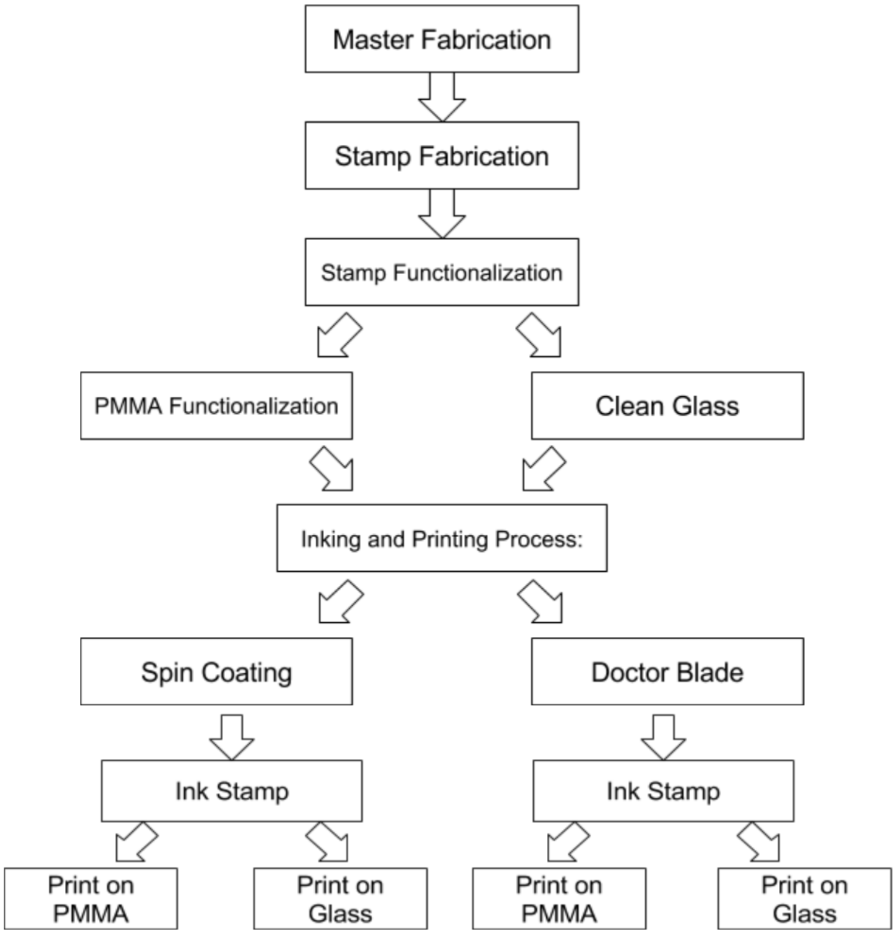


Figure 4-1: Flowchart of Deliverable

4.1 Procedure Combinations

Procedures for the following combinations are outlined below:

1. Non-conductive epoxy on PMMA substrate
2. Conductive epoxy on PMMA substrate
3. Non-conductive epoxy on glass substrate
4. Conductive epoxy on glass substrate

4.2 Initial Procedure Steps

In each procedure provided, master preparation, stamp fabrication, and stamp functionalization will occur. These steps are as follows in Table 4-1:

Table 4-1: Initial Procedure Steps

1. Master Fabrication	A pre-fabricated master is given and used to fabricate the stamp
2. Stamp Fabrication	Prepare PDMS ● Mix PDMS (Sylgard 184) with a 10:1 (resin: hardener) in the speed mixer for 30 s at 1000 rpm and 120 s at 2000 rpm ● Fill syringes with 3-4 ml of PDMS with the black tip ● Store syringes in the freezer overnight
	Mold-Tool Treatment ● Clean the aluminum housing of the master first with acetone and then isopropanol to remove dirt on the surface
	Silanization of the Mold-Tool ● Place the mold tool in a desiccator for 30 min at 0.2 bar with two drops of (Tridecafluoro-1,1,2,2-tetrahydroctyl) tricholorosilane 97%
	Molding Process ● Close the mold-tool, and gently tighten the screws ● Mount the red tip on the syringe (filled with PDMS) and push excessive air out of the syringe ● Insert the syringe into the mold-tool and slowly inject PDMS until full
	Curing Process ● Leave the syringe in the tool during polymerization ● Place the master with the attached syringe in the oven for 12 h @ 60 C

	Mold Removal ● Remove the mold and let cool to room temperature ● Once cooled. remove the stamp from the mold-tool ● Place the stamp onto a microscope slide and store in a dry, clean place ● Fabricate stamps until the lateral dimensions of the pattern are comparable to the master
3. Stamp Functionalization	Oxygen Plasma Treatment in Barrel Asher ● Perform Recipe 1: Cleaning ○ The specifications of this treatment include an oxygen flow of 300 sccm, power of 1000 W, and a time duration of 300 seconds. ● Perform Recipe 6: Surface Activation ○ The specifications of this treatment include an oxygen flow of 50 sccm, power of 1000 W, and a time duration of 20 seconds.

4.3 Procedure One: PMMA and EPO-TEK 302-3M

Table 4-2: Procedure One

Time Constraints	Stamp: ● Use the stamp for printing within 80 min of functionalization Epoxy: ● Spin coat the epoxy within 15 min of mixing ● Print with the epoxy within 60 min of mixing
Surface Preparation	Silicon Wafer Cleaning: ● Place silicon wafer into glass container filled with acetone ● Place glass container into a sonicator and wait for 10 min ● Remove silicon wafer from the container and clean with isopropanol ● Dry the silicon wafer with nitrogen ● Place silicon wafer onto hot plate at 100 °C for 3 min
Ink Pad Creation	Steps to Create Ink Pad: ● Speed Mixer: Program 1 ● Spin Coat Settings: Program 4
Stamp Inking	LabVIEW Settings: ● Distance: 24.55mm ● Force: 0.4 N, Time: 20 s
Stamp Printing	LabVIEW Settings: ● Distance: 23mm ● Step1: Force: 0.2 N, Time: 20 s ● Step2: Force: 0.1 N, Time: 20 s
Stamp Cleaning	Steps to Clean Stamp: ● Spray ethanol on the stamp ● Use nitrogen gas to dry the stamp
Adhesive Curing	Two Options for Curing: Room Temperature ● Time: overnight Oven: ● Temperature: 65°C ● Time: 3 hours

4.4 Procedure Two: PMMA and EPO-TEK H20E-PFC

Table 4-3: Procedure Two

Time Constraints	Stamp: ● Print with the stamp within 80 min of Functionalization Epoxy: ● Print with the epoxy within 3 days of mixing
Surface Preparation	Glass Plate Cleaning: ● Clean glass surface with acetone and isopropanol
Prepare Ink Pad	Speed Mixer: ● Program 2 Doctor Blade Settings: ● Set micrometer screw to 18 m ● Apply 2 - 2.5 mL of EPO-TEK H20E-PFC to substrate surface at the width of the desired ink pad
Ink Stamp	LabVIEW Settings: ● Distance: 23 mm ● Force: 0.85 N, Time: 20 s
Print with Stamp	LabVIEW Settings: ● Distance: 23mm ● Step 1: Force: 0.85 N, Time: 20 s ● Step 2: Force: 0.65 N, Time: 20 s
Clean Stamp	Steps to Clean Stamp ● Spray ethanol on the stamp ● Clean the stamp with tissue ● Put the stamp into the sonication for one minute ● Dry the stamp with nitrogen gas
Adhesive Curing	Oven: ● Temperature: 80°C ● Time: 3 hours

4.5 Procedure Three: Glass and EPO-TEK 302-3M

Table 4-4: Procedure Three

Time Constraints	Stamp: - Print with the stamp within 80 min of functionalization Epoxy: - Spin coat with the epoxy within 15 min of mixing - Print with the epoxy within 60 min of mixing
Surface Preparation	Glass Substrate Cleaning: - Clean the substrate by sonication in water with soap for 10 minutes at 100% power - Dip the substrate in HNO3 at 20°C for 5 minutes - Rinse the substrate with water - Dip the substrate in HNO3 at 100°C for 5 minutes - Rinse the substrate with water - Use nitrogen and spin dryer to remove water from the surface - Put glass substrate into the container Silicon Wafer Cleaning: - Place silicon wafer into glass container filled with acetone - Place glass container into a sonicator and wait for 10 min - Remove silicon wafer from the container and clean with isopropanol - Dry the silicon wafer with nitrogen - Place silicon wafer onto hot plate at 100 °C for 3 min
Prepare Ink Pad	Speed Mixer: - Program 1 Spin Coat Settings: - Program 4
Ink Stamp	LabVIEW Settings: - Force: 0.4 N, Time: 20 s, - Distance for silicon wafer: 23 mm
Print with Stamp	LabVIEW Settings: - Distance: 24.55mm - Step 1: Force: 0.2 N, Time: 20 s - Step 2: Force: 0.1 N, Time: 20 s
Clean Stamp	Steps to Clean Stamp - Spray ethanol on the stamp - Use nitrogen gas to dry the stamp
Adhesive Curing	Room Temperature - Time: Overnight *or* Oven: - Temperature: 65°C - Time: 3 hours

4.6 Procedure Four: Glass and EPO-TEK H20E-PFC

Table 4-5: Procedure Four

Time Constraints	Stamp: ● Print with stamp within 80 min of functionalization Epoxy: ● Print with epoxy within 3 days of mixing
Surface Preparation	Glass Substrate Cleaning: ● Clean the substrate by sonication in water with soap for 10 minutes at 100% power ● Dip the substrate in HNO3 at 20°C for 5 minutes ● Rinse the substrate with water ● Dip the substrate in HNO3 at 100°C for 5 minutes ● Rinse the substrate with water ● Use nitrogen and spin dryer to remove water from the surface ● Put glass substrate into the container Glass Plate Cleaning: ● Clean glass surface with acetone and isopropanol
Prepare Ink Pad	Speed Mixer: ● Program 2 Doctor Blade Settings: ● Set micrometer screw to 18 m ● Apply 2 - 2.5 mL of EPO-TEK H20E-PFC to substrate surface at the width of the desired ink pad
Ink Stamp	LabVIEW Settings: ● Distance: 23 mm ● Force: 0.85 N, Time: 20s
Print with Stamp	LabVIEW Settings: ● Distance: 24.55mm ● Step 1: Force: 0.65 N, Time: 20 s ● Step 2: Force: 0.45 N, Time: 20 s
Clean Stamp	Steps to Clean Stamp ● Spray ethanol on the stamp ● Clean the stamp with tissue ● Put the stamp into the sonication for one minute ● Dry the stamp with nitrogen gas
Adhesive Curing	Oven: ● Temperature: 120°C ● Time: 15 minutes *or* ● Temperature: 80°C ● Time: 3 hours

5.0 Future Recommendations

Due to the limited time constraint of this project, the microcontact printing process of adhesives could not be fully refined. As such, the team has created a set of recommendations for future improvements. Some of these refinements are specific to the different steps of the process, and primarily include more trials and research. Other refinements include alterations or additions to some of the tools that were used during the process.

5.1 Variable Isolation

Multiple variables needed to be controlled in the process, and made it difficult to produce a repeatable process. As a result, the final thickness measurements of the adhesive were not comparable to the other parameters used in the process. One variable should be isolated at a time to aid in optimization and provide better results.

5.2 Microscope Slide and Stamp Adhesion

The microscope slide and stamp can be glued together to avoid the PDMS stamp from falling off of the microscope slide during printing and inking. The occurrence of this situation was rare but can help reduce any additional error during the process. In addition to this complication, gluing of the slide and the stamp can also aid in preventing any residual ethanol, ink, or air from being trapped between the slide and the stamp.

5.3 Master Reproducibility

An alternative mold tool can help to avoid damaging the master during substitution. When changing masters, PDMS can become trapped around the master, making it difficult to remove the master without damage. There is a high possibility of damaging the mold each time the master is removed. In addition, the mold tools are only useful when one master is being used and does not need to be changed.

5.4 Consistency in the Inking Process

Since the thicknesses of the PMMA substrate, glass substrate, and silicon wafer are not equal, multiple approach distances have to be used during the inking and printing processes. This requires the approach distance to be altered each time after inking. As a result, the rate of production is lowered. This problem can be avoided by maintaining a consistent thickness between each of the substrates used in the inking and printing processes.

5.5 Hardware Additions to the NTB Printing Tool

In order to better control the angle of applied force between the stamp and the surface of the substrate, three lasers can be attached to the stamp holder and a mirror can be attached to the substrate platform. When the stamp and substrate are parallel, the lasers will reflect back to their respective points of origin. When they are not aligned, the lasers will reflect back at an angle. This can be seen in Figure 5-1.

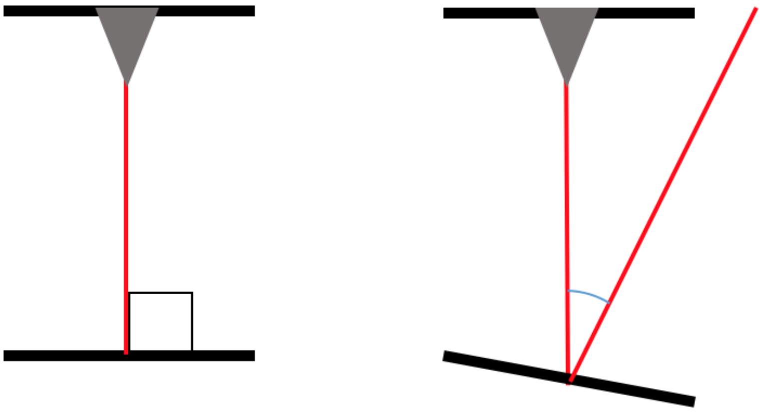
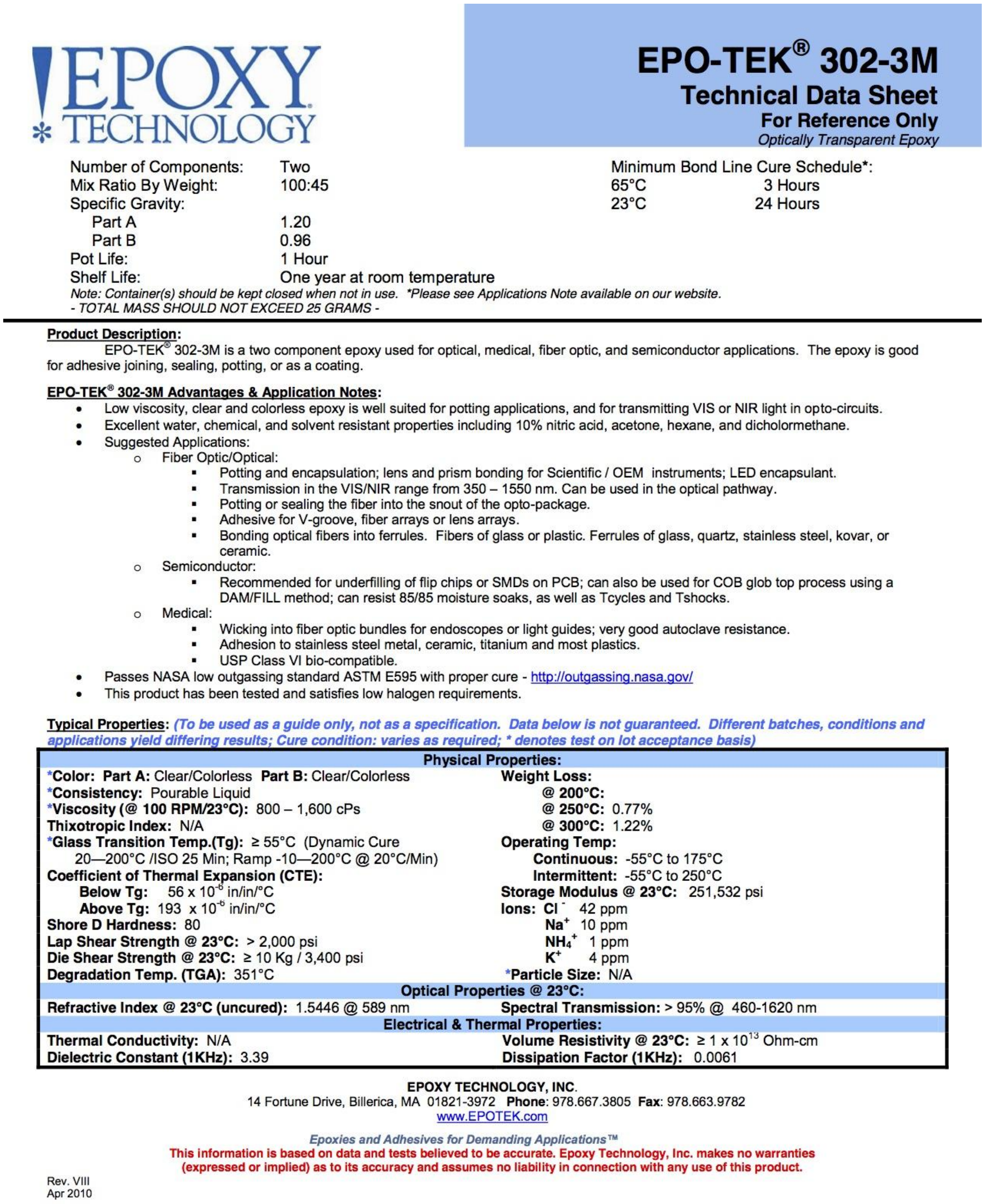


Figure 5-1: Laser Alignment System

6.0 Appendices

Appendix A: EPO-TEK Epoxy Data Sheets

EPO-TEK 302-3M



EPOXY TECHNOLOGY

EPO-TEK® 302-3M
Technical Data Sheet
For Reference Only
Optically Transparent Epoxy

Number of Components: Two
Mix Ratio By Weight: 100:45
Specific Gravity:
  Part A 1.20
  Part B 0.96
Pot Life: 1 Hour
Shelf Life: One year at room temperature

Minimum Bond Line Cure Schedule*:

65°C	3 Hours
23°C	24 Hours

*Note: Container(s) should be kept closed when not in use. *Please see Applications Note available on our website.*
- TOTAL MASS SHOULD NOT EXCEED 25 GRAMS -

Product Description:
EPO-TEK® 302-3M is a two component epoxy used for optical, medical, fiber optic, and semiconductor applications. The epoxy is good for adhesive joining, sealing, potting, or as a coating.

EPO-TEK® 302-3M Advantages & Application Notes:

- Low viscosity, clear and colorless epoxy is well suited for potting applications, and for transmitting VIS or NIR light in opto-circuits.
- Excellent water, chemical, and solvent resistant properties including 10% nitric acid, acetone, hexane, and dicholormethane.
- Suggested Applications:
  - Fiber Optic/Optical:
    - Potting and encapsulation; lens and prism bonding for Scientific / OEM instruments; LED encapsulant.
    - Transmission in the VIS/NIR range from 350 – 1550 nm. Can be used in the optical pathway.
    - Potting or sealing the fiber into the snout of the opto-package.
    - Adhesive for V-groove, fiber arrays or lens arrays.
    - Bonding optical fibers into ferrules. Fibers of glass or plastic. Ferrules of glass, quartz, stainless steel, kovar, or ceramic.
  - Semiconductor:
    - Recommended for underfilling of flip chips or SMDs on PCB; can also be used for COB glob top process using a DAM/FILL method; can resist 85/85 moisture soaks, as well as Tcycles and Tshocks.
  - Medical:
    - Wicking into fiber optic bundles for endoscopes or light guides; very good autoclave resistance.
    - Adhesion to stainless steel metal, ceramic, titanium and most plastics.
    - USP Class VI bio-compatible.
- Passes NASA low outgassing standard ASTM E595 with proper cure - http://outgassing.nasa.gov/
- This product has been tested and satisfies low halogen requirements.

Typical Properties: ***(To be used as a guide only, not as a specification. Data below is not guaranteed. Different batches, conditions and applications yield differing results; Cure condition: varies as required; * denotes test on lot acceptance basis)***

Physical Properties:	
***Color:** **Part A:** Clear/Colorless **Part B:** Clear/Colorless	**Weight Loss:**
***Consistency:** Pourable Liquid	**@ 200°C:**
***Viscosity (@ 100 RPM/23°C):** 800 – 1,600 cPs	**@ 250°C:** 0.77%
Thixotropic Index: N/A	**@ 300°C:** 1.22%
***Glass Transition Temp.(Tg):** ≥ 55°C (Dynamic Cure 20—200°C /ISO 25 Min; Ramp -10—200°C @ 20°C/Min)	**Operating Temp:** **Continuous:** -55°C to 175°C
Coefficient of Thermal Expansion (CTE):	**Intermittent:** -55°C to 250°C
Below Tg: 56 x 10^{-6} in/in/°C	**Storage Modulus @ 23°C:** 251,532 psi
Above Tg: 193 x 10^{-6} in/in/°C	**Ions:** **Cl^-** 42 ppm
Shore D Hardness: 80	**Na^+** 10 ppm
Lap Shear Strength @ 23°C: > 2,000 psi	**NH_4^+** 1 ppm
Die Shear Strength @ 23°C: ≥ 10 Kg / 3,400 psi	**K^+** 4 ppm
Degradation Temp. (TGA): 351°C	***Particle Size:** N/A
Optical Properties @ 23°C:	
Refractive Index @ 23°C (uncured): 1.5446 @ 589 nm	**Spectral Transmission:** > 95% @ 460-1620 nm
Electrical & Thermal Properties:	
Thermal Conductivity: N/A	**Volume Resistivity @ 23°C:** ≥ 1 x 10^{13} Ohm-cm
Dielectric Constant (1KHz): 3.39	**Dissipation Factor (1KHz):** 0.0061

EPOXY TECHNOLOGY, INC.
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www.EPOTEK.com

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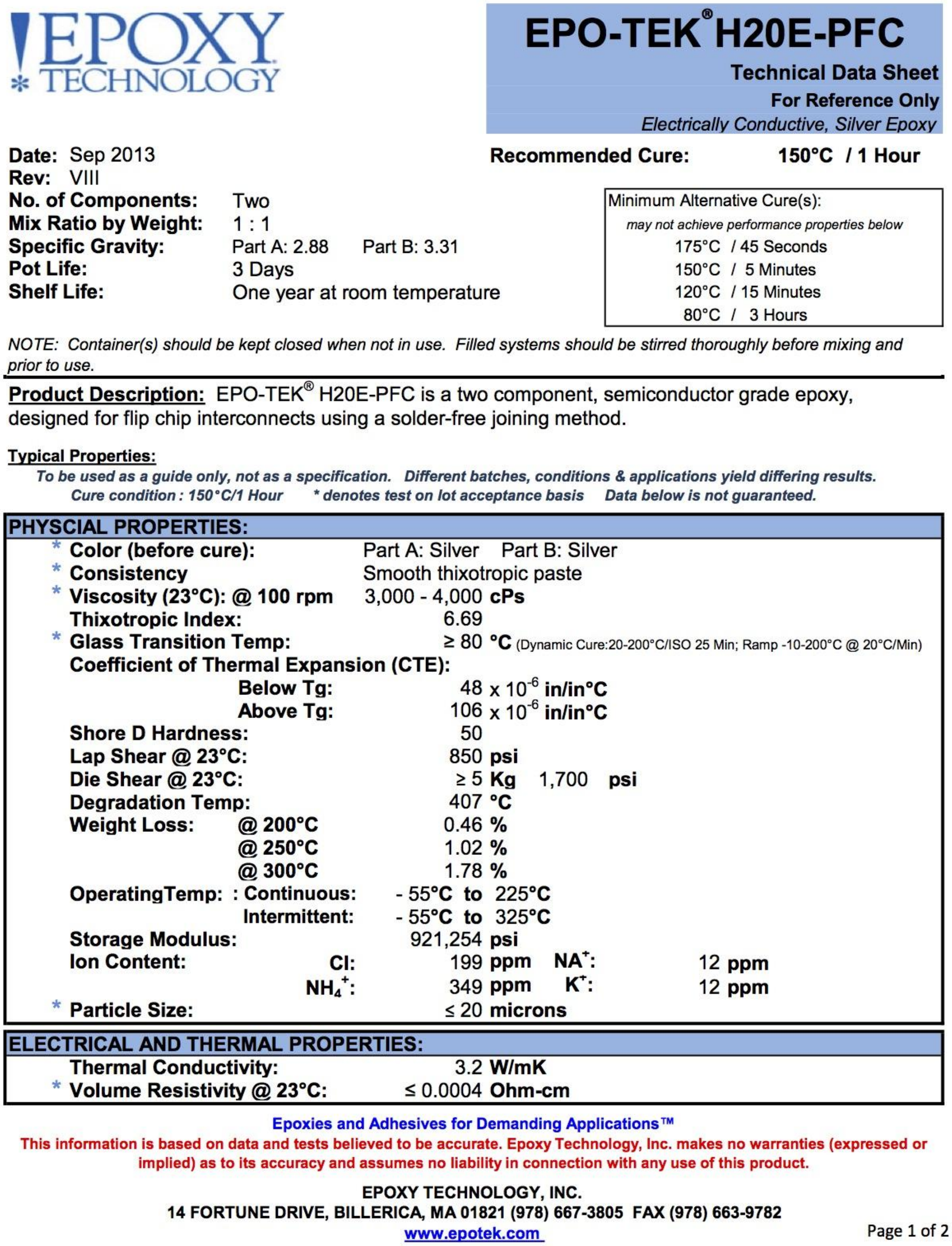
Rev. VIII
Apr 2010

EPO-TEK H20E-PFC



EPOXY TECHNOLOGY

EPO-TEK® H20E-PFC

Technical Data Sheet

For Reference Only

Electrically Conductive, Silver Epoxy

Date: Sep 2013
Rev: VIII

No. of Components:	Two
Mix Ratio by Weight:	1 : 1
Specific Gravity:	Part A: 2.88 Part B: 3.31
Pot Life:	3 Days
Shelf Life:	One year at room temperature

Recommended Cure: **150°C / 1 Hour**

Minimum Alternative Cure(s):
may not achieve performance properties below
175°C / 45 Seconds
150°C / 5 Minutes
120°C / 15 Minutes
80°C / 3 Hours

NOTE: Container(s) should be kept closed when not in use. Filled systems should be stirred thoroughly before mixing and prior to use.

Product Description: EPO-TEK® H20E-PFC is a two component, semiconductor grade epoxy, designed for flip chip interconnects using a solder-free joining method.

Typical Properties:

To be used as a guide only, not as a specification. Different batches, conditions & applications yield differing results.
*Cure condition : 150°C/1 Hour * denotes test on lot acceptance basis Data below is not guaranteed.*

PHYSCIAL PROPERTIES:			
* **Color (before cure):**	Part A: Silver Part B: Silver		
* **Consistency**	Smooth thixotropic paste		
* **Viscosity (23°C): @ 100 rpm**	3,000 - 4,000 **cPs**		
Thixotropic Index:	6.69		
* **Glass Transition Temp:**	≥ 80 **°C** (Dynamic Cure:20-200°C/ISO 25 Min; Ramp -10-200°C @ 20°C/Min)		
Coefficient of Thermal Expansion (CTE):			
Below Tg:	48 x 10^{-6} **in/in°C**		
Above Tg:	106 x 10^{-6} **in/in°C**		
Shore D Hardness:	50		
Lap Shear @ 23°C:	850 **psi**		
Die Shear @ 23°C:	≥ 5 **Kg** 1,700 **psi**		
Degradation Temp:	407 **°C**		
Weight Loss: @ 200°C	0.46 **%**		
@ 250°C	1.02 **%**		
@ 300°C	1.78 **%**		
OperatingTemp: : Continuous:	- 55**°C to** 225**°C**		
Intermittent:	- 55**°C to** 325**°C**		
Storage Modulus:	921,254 **psi**		
Ion Content: Cl:	199 **ppm**	**NA^+:**	12 **ppm**
NH_4^+:	349 **ppm**	**K^+:**	12 **ppm**
* **Particle Size:**	≤ 20 **microns**		

ELECTRICAL AND THERMAL PROPERTIES:	
Thermal Conductivity:	3.2 **W/mK**
* **Volume Resistivity @ 23°C:**	≤ 0.0004 **Ohm-cm**

Epoxies and Adhesives for Demanding Applications™

This information is based on data and tests believed to be accurate. Epoxy Technology, Inc. makes no warranties (expressed or implied) as to its accuracy and assumes no liability in connection with any use of this product.

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Page 1 of 2

Appendix B: Master Fabrication

#	Description
	Ordyl Alpha 850: negative dry resist with 50 µm thickness
1.	**Cleaning / Dehydration:** Cleaning: 5 min in HNO_3 20°C, rinse in H_2O, 5 min in HNO_3 100°C, rinse in H_2O 30 min @ 200 °C in oven
2.	**Lamination:** Parameter: Temperature: 105 – 125 °C Pressure: 2 – 3 kg/cm^2 Feed rate: 1 -2 m/min
3.	**Dwell time:** Min. 30 min, max. 5 days
4.	**Exposure:** Do not remove protection foil! Parameter: Proximity: 5 µm Dose, Constant Energy: 50 mJ/cm^2 (Cr-Mask) 100 mJ/cm^2 (Foilmask)
5.	**Dwell time:** Min. 10 min, max. 3 days
6.	**Develop:** Remove protection foil Developer: 1% Na_2CO_3-Solution Time: ca. 2 - 3 min

Appendix C: Speed Mixer Programs

Program #	Step #	RPM	Vacuum (kPa)	Time (s)
1	1	1000	96.6	30
	2	2000	96.6	60
	3	2000	30	60
2	1	600	96.6	30
	2	1250	96.6	60
	3	2000	96.6	60
	4	2000	96.6	20

Appendix D: Contact Angle of PMMA

	Test #	Theta(L) [deg]	Theta(R) [deg]	Theta(M) [deg]
PMMA before functionalization	1	75.3	74	74.6 ± 0.65
	2	68.1	69.4	68.7 ± 0.62
	3	71.8	72.8	72.3 ± 0.48
	Average:	71.7 ± 3.58	72.0 ± 2.39	71.9 ± 2.96
PMMA one week after functionalization	1	68.8	68	68.4 ± 0.43
	2	72.5	76.4	74.4 ± 1.97
	3	73.6	75.6	74.6 ± 1.01
	Average:	71.6 ± 2.49	73.3 ± 4.66	72.5 ± 3.53
PMMA after 15 min of functionalization	1	43.4	41.5	42.5 ± 0.93
	2	44.2	40	42.1 ± 2.15
	3	36.5	34.7	35.6 ± 0.91
	Average:	41.4 ± 4.26	38.7 ± 3.59	40.0 ± 3.88
PMMA after 20 min of functionalization	1	42.7	43	42.9 ± 0.15
	2	45.4	44.3	44.8 ± 0.56
	3	41.3	40.6	41.0 ± 0.31
	Average:	43.1 ± 2.10	42.6 ± 1.85	42.9 ± 1.94
PMMA after 35 of functionalization	1	44.7	48.8	46.7 ± 2.05
	2	46.8	42	44.4 ± 2.37
	3	48.8	50.2	49.5 ± 0.70
	Average:	46.7 ± 2.06	47.0 ± 4.37	46.9 ± 2.56
PMMA after 45 min of functionalization	1	63.8	64.5	64.1 ± 0.32
	2	64.1	73.3	68.7 ± 4.61
	3	51.9	60.8	56.3 ± 4.45
	Average:	59.9 ± 6.98	66.2 ± 6.43	63.0 ± 6.25
PMMA after 1 hours of	1	70.1	64.2	67.1 ± 2.94

functionalization	2	71.7	81	76.4 ± 4.63
	3	77.8	68.4	73.1 ± 4.73
	Average:	73.2 ± 4.09	71.2 ± 8.76	72.2 ± 4.69
PMMA after 1hrs 20 of functionalization	1	66.4	66.4	66.4
	2	63.9	61.5	62.7 ± 1.20
	3	64.8	69.3	67.0 ± 2.27
	Average:	65.0 ± 1.28	65.8 ± 3.93	65.4 ± 2.33
PMMA after 1 hrs 40 of functionalization	1	67.4	75.1	71.2 ± 3.89
	2	66.9	63.2	65.0 ± 1.85
	3	67.2	72.5	69.9 ± 2.64
	Average:	67.1 ± 0.25	70.3 ± 6.29	68.7 ± 3.27
PMMA after 120 min of functionalization	1	65.7	70.2	67.9 ± 2.26
	2	66.4	71.5	69.0 ± 2.55
	3	66.7	67.4	67.1 ± 0.34
	Average:	66.3 ± 0.56	69.7 ± 2.11	68.0 ± 0.97
PMMA after 3 hours of functionalization	1	69.8	75.4	72.6 ± 2.79
	2	63	61.7	62.4 ± 0.62
	3	69.9	69.2	69.5 ± 0.34
	Average:	67.5 ± 3.95	68.8 ± 6.82	68.2 ± 5.24

Appendix E: Contact Angle of PDMS

	Test #	Theta(L) [deg]	Theta(R) [deg]	Theta(M) [deg]
PDMS before functionalization	1	116.4	113	114.7 ± 1.74
	2	110.8	113.4	112.1 ± 1.31
	3	112.7	105.9	109.3 ± 3.45
	Average:	113.3 ± 2.86	110.7 ± 4.25	112.0 ± 2.70
PDMS after 15 min of functionalization	1	45.8	42.2	44.0 ± 1.83
	2	37.1	35	36.1 ± 1.06
	3	39.4	37.3	38.3 ± 1.02
	Average:	40.8 ± 4.51	38.2 ± 3.65	39.5 ± 4.08
PDMS after 30 of functionalization	1	72.3	70	71.2 ± 1.12
	2	73.9	74.2	74.0 ± 0.15
	3	76.1	71.6	73.9 ± 2.25
	Average:	74.1 ± 1.94	72.0 ± 2.09	73.0 ± 1.62
PDMS after 45 functionalization	1	80.9	81	80.9 ± 0.07
	2	86.9	78.5	82.7 ± 4.19
	3	85.9	87.2	86.6 ± 0.65
	Average:	84.6 ± 3.25	82.3 ± 4.47	83.4 ± 2.88
PDMS after 1 hr of functionalization	1	86.8	85.5	86.2 ± 0.66
	2	92.8	88.8	90.8 ± 1.99
	3	82	87.8	84.9 ± 2.88
	Average:	87.2 ± 5.40	87.4 ± 1.69	87.3 ± 3.12
PDMS after 1and half hour min of functionalization	1	103	100.5	101.8 ± 1.27
	2	93.9	82.5	88.2 ± 5.69
	3	88.2	89.8	89.0 ± 0.83
	Average:	95.0 ± 7.50	90.9 ± 9.04	93.0 ± 7.61
PDMS after 2 hours of functionalization	1	109	104.2	106.6 ± 2.40
	2	101.4	102	101.7 ± 0.32

	3	99.2	92.4	95.8 ± 3.41
	Average:	103.2 ± 5.13	99.5 ± 6.29	101.3 ± 5.41
PDMS after two weeks of functionalization	1	102.3	103.5	102.9 ± 0.61
	2	106.3	105.7	106.0 ± 0.30
	3	106.2	109	107.6 ± 1.38
	Average:	105.0 ± 2.30	106.1 ± 2.75	105.5 ± 2.39

Appendix F: Contact Angle of Glass

	Test #	Theta(L) [deg]	Theta(R) [deg]	Theta(M) [deg]
Glass cleaned by standard process	1	22	17.9	20.0 ± 2.04
	2	20.8	16.4	18.6 ± 2.23
	Average:	21.4 ± 0.83	17.1 ± 1.10	19.3 ± 0.96
Glass cleaned by hand	1	39	46	42.5 ± 3.50
	2	38.1	47.2	42.6 ± 4.53
	3	38.4	42.5	40.5 ± 2.07
	Average:	38.5 ± 0.48	45.3 ± 2.42	41.9 ± 1.23

Appendix G: Summary of Spin Coating Programs

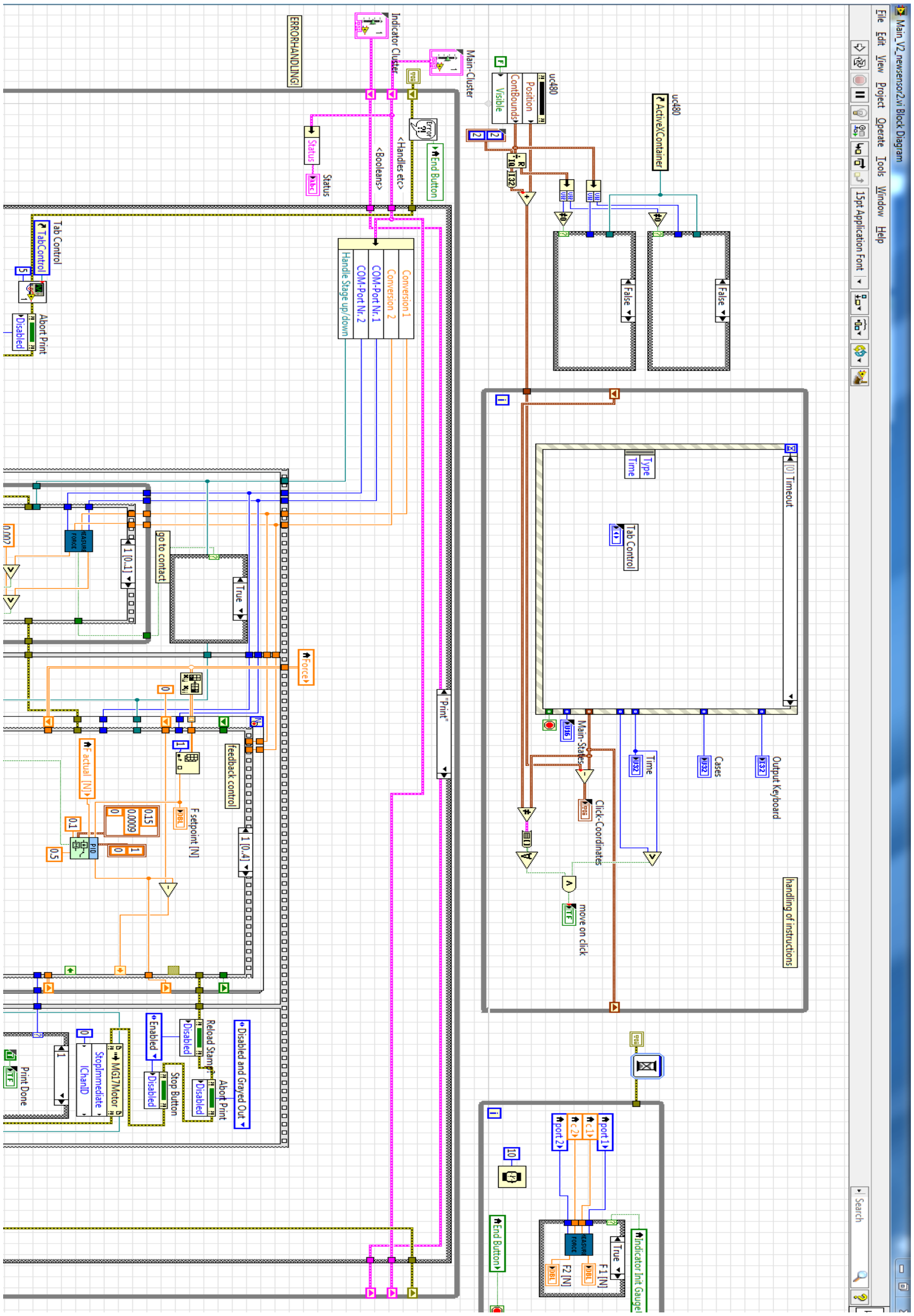
Program	Step #	RPM(*10)	Acceleration	Time (s)
Self-Def 1	1	10	1	20
Self-Def 2	1	10	1	40
Self-Def 3	1	10	1	60

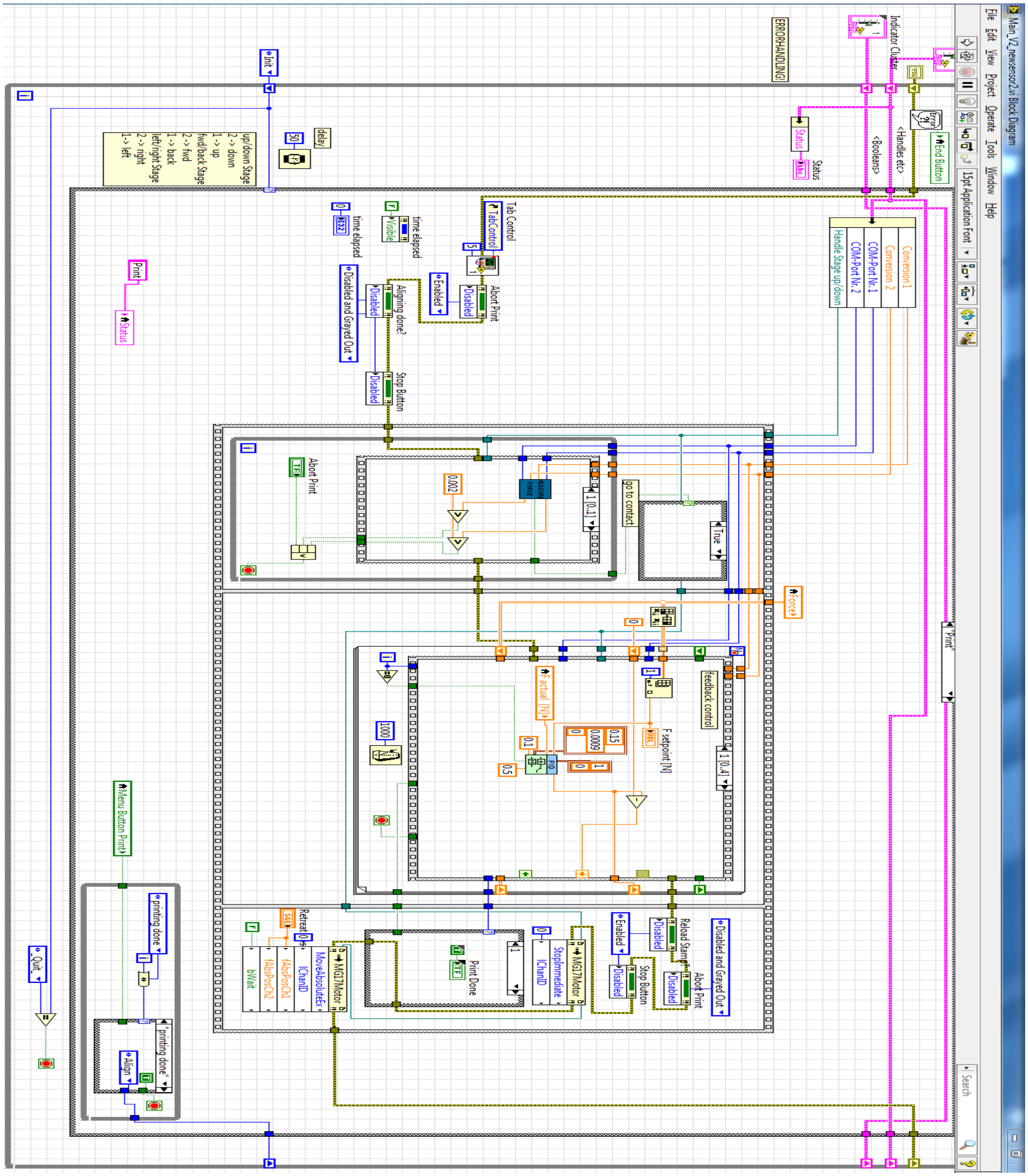
Program #	Step #	RPM(*10)	Acceleration	Time (s)
Self-Def 4	1	100	8	2
Self-Def 5	1	100	8	2
	2	50	1	10
Self-Def 6	1	100	8	8
	2	50	1	10
Self-Def 7	1	100	8	16
	2	50	1	10

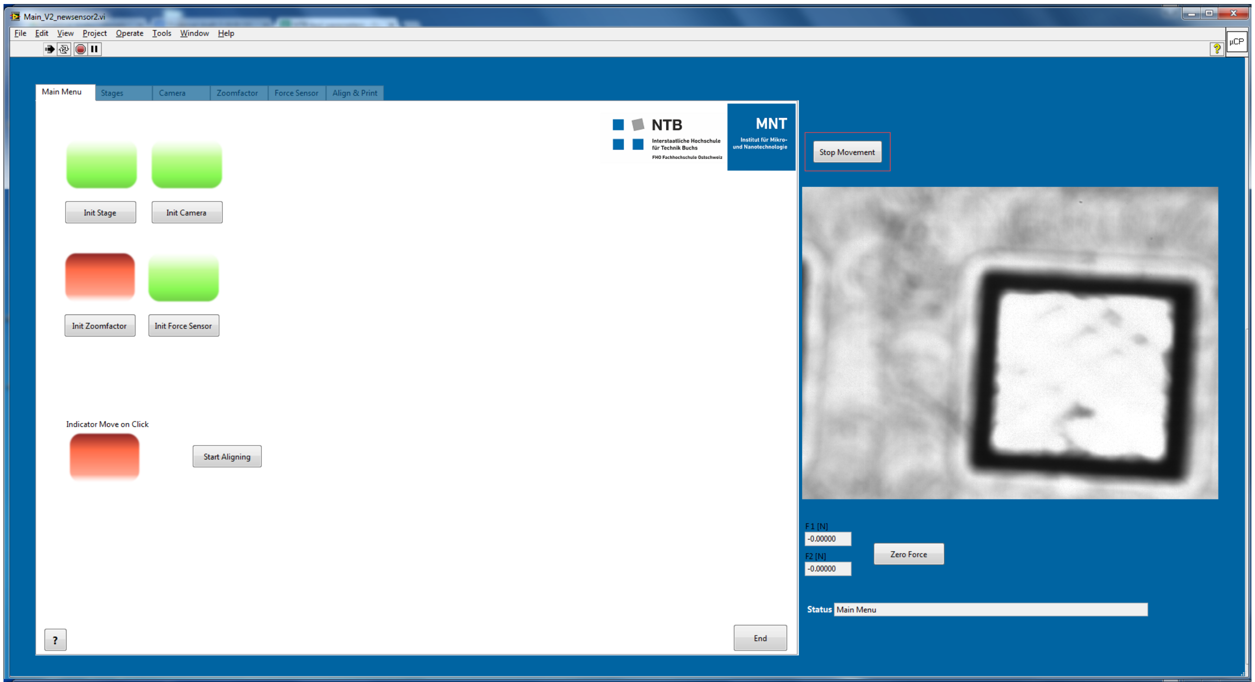
Program #	Step #	RPM(*10)	Acceleration	Time (s)
Self-Def 7	1	100	8	16
	2	50	1	10
Self-Def 8	1	70	8	16
	2	50	1	10
Self-Def 9	1	50	8	16
	2	50	1	10

Program #	Step #	RPM(*10)	Acceleration	Time (s)
4	1	250	8	5
	2	800	6	20
	3	2000	8	90
	4	2000	8	90
	5	100	6	5

Appendix H: LabVIEW Program



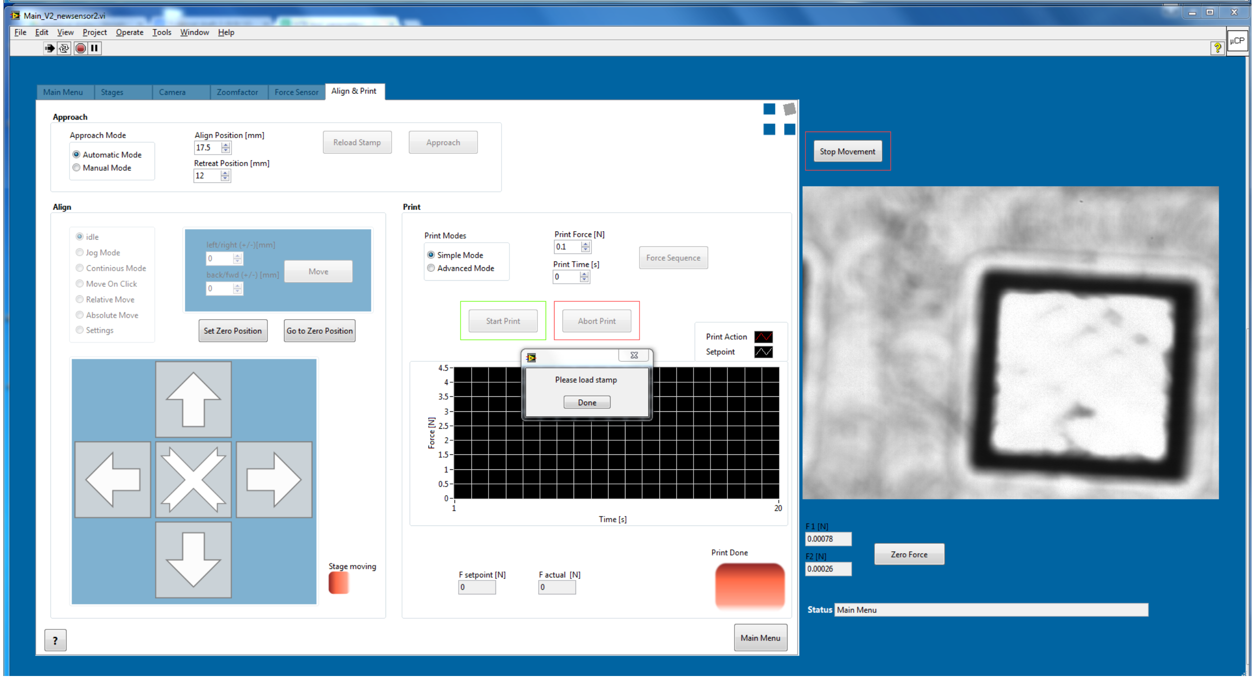

Main_V2_newsensor2.vi Block Diagram
File Edit View Project Operate Tools Window Help
15pt Application Font
Search
ERROR-HANDLING
Indicator Cluster
End Button
<Handles etc>
<Booleans>
Status
Conversion 1
Conversion 2
COM-Port Nr. 1
COM-Port Nr. 2
Handle Stage up/down
Tab Control
Abort Print
Disabled
Enabled
time elapsed
Visible
Aligning done?
Disabled and Grayed Out
Stop Button
delay
50
Init
up/down Stage
2-> down
1-> up
fwd/back Stage
2-> fwd
1-> back
left/right Stage
2-> right
1-> left
Print
Status
go to contact
True
0.002
1 [0..1]
Force
feedback control
F actual [N]
F setpoint [N]
0.15
0.0009
0.1
0.5
1000
1 [0..4]
Menu Button Print
"printing done"
Align
Quit
Retreat
MG17Motor
MoveAbsoluteEx
lChanID
fAbsPosCh1
fAbsPosCh2
bWait
StopImmediate
Print Done
Reload Stamp
"Print"



F1 [N] -0.00000

F2 [N] -0.00000

Status Main Menu



Approach Mode
● Automatic Mode
○ Manual Mode

Align Position [mm] 17.5

Retreat Position [mm] 12

● idle
○ Jog Mode
○ Continious Mode
○ Move On Click
○ Relative Move
○ Absolute Move
○ Settings

left/right (+/-) [mm] 0

back/fwd (+/-) [mm] 0

Print Modes
● Simple Mode
○ Advanced Mode

Print Force [N] 0.1

Print Time [s] 0

Please load stamp

F setpoint [N] 0

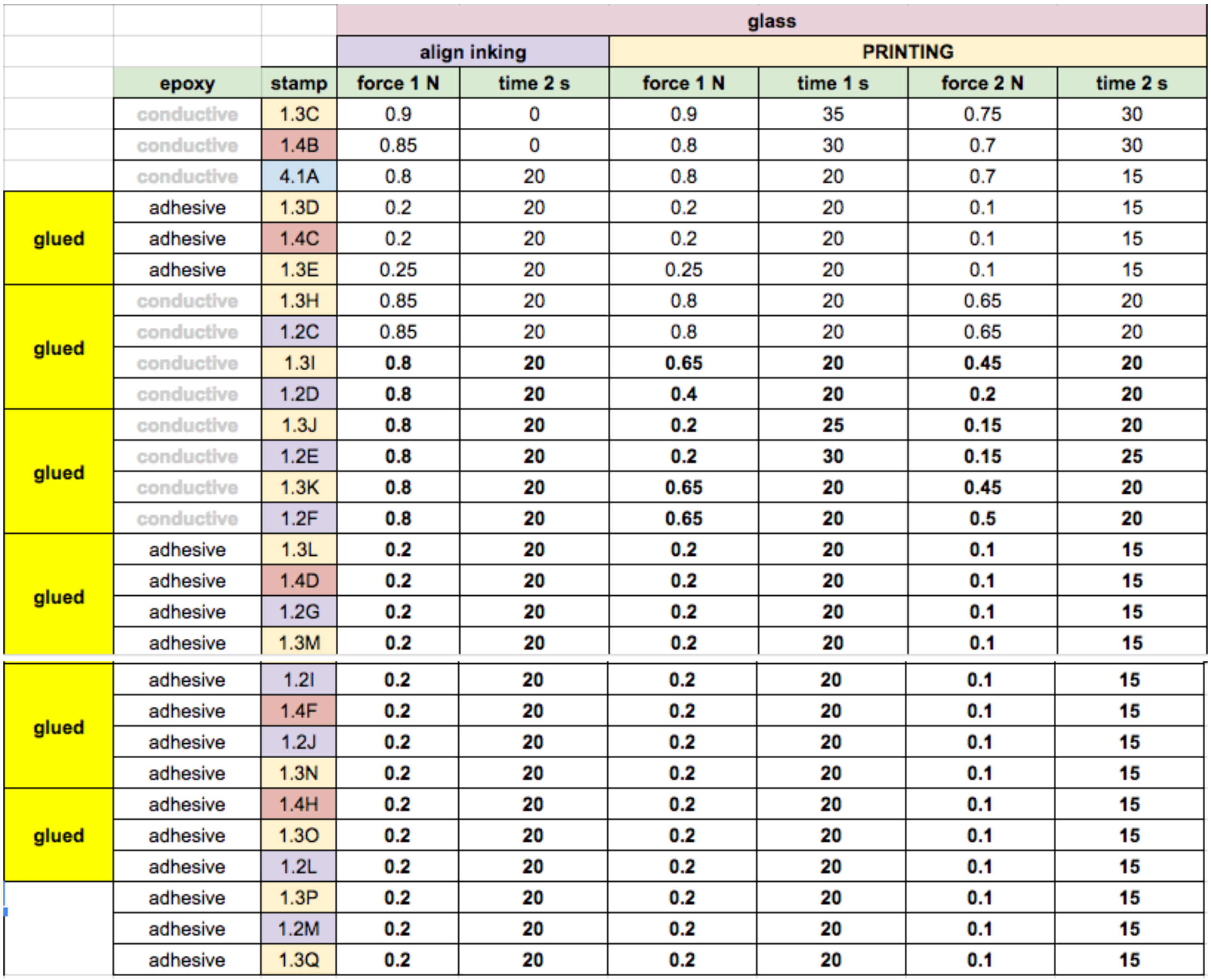
F actual [N] 0

F1 [N] 0.00078

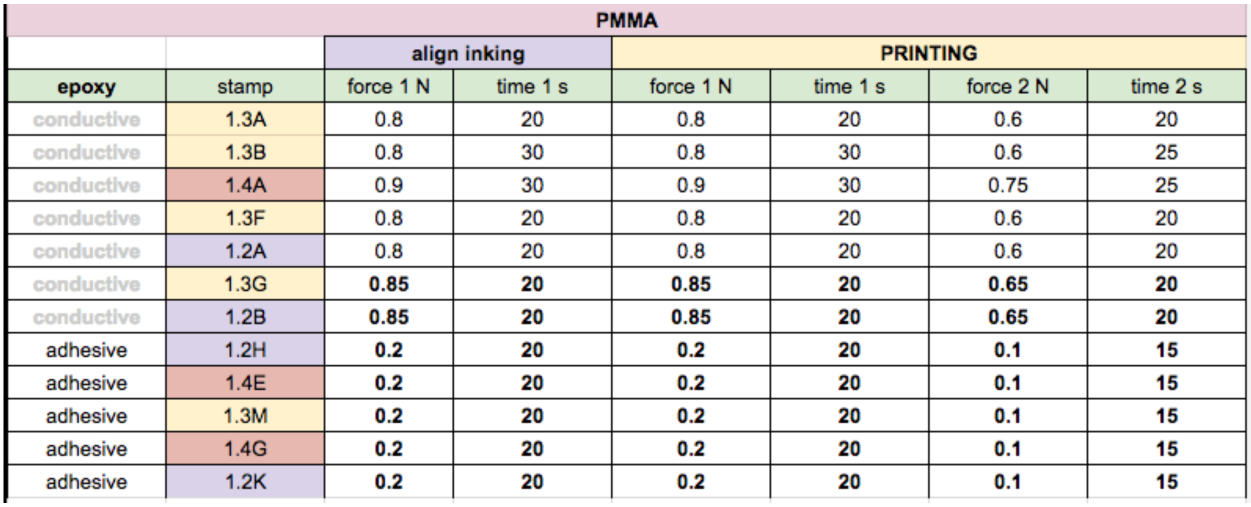
F2 [N] 0.00026

Status Main Menu

Appendix I: LabVIEW Input Parameter Trials

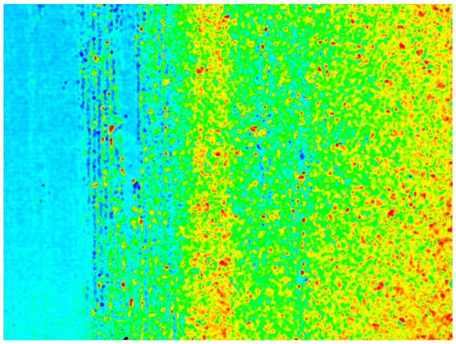
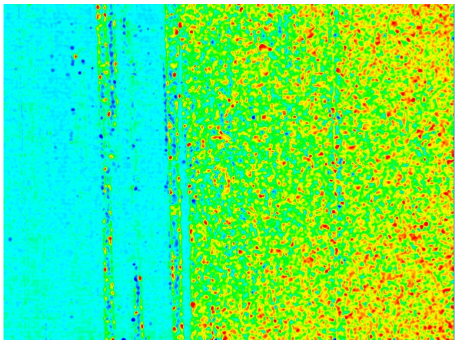
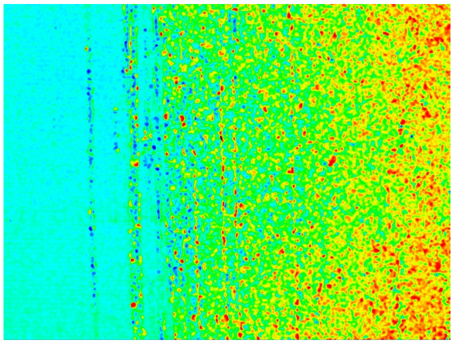


			glass					
			align inking		PRINTING			
	epoxy	stamp	force 1 N	time 2 s	force 1 N	time 1 s	force 2 N	time 2 s
	conductive	1.3C	0.9	0	0.9	35	0.75	30
	conductive	1.4B	0.85	0	0.8	30	0.7	30
	conductive	4.1A	0.8	20	0.8	20	0.7	15
glued	adhesive	1.3D	0.2	20	0.2	20	0.1	15
	adhesive	1.4C	0.2	20	0.2	20	0.1	15
	adhesive	1.3E	0.25	20	0.25	20	0.1	15
glued	conductive	1.3H	0.85	20	0.8	20	0.65	20
	conductive	1.2C	0.85	20	0.8	20	0.65	20
	conductive	1.3I	**0.8**	**20**	**0.65**	**20**	**0.45**	**20**
	conductive	1.2D	**0.8**	**20**	**0.4**	**20**	**0.2**	**20**
glued	conductive	1.3J	**0.8**	**20**	**0.2**	**25**	**0.15**	**20**
	conductive	1.2E	**0.8**	**20**	**0.2**	**30**	**0.15**	**25**
	conductive	1.3K	**0.8**	**20**	**0.65**	**20**	**0.45**	**20**
	conductive	1.2F	**0.8**	**20**	**0.65**	**20**	**0.5**	**20**
glued	adhesive	1.3L	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.4D	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.2G	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.3M	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
glued	adhesive	1.2I	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.4F	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.2J	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.3N	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
glued	adhesive	1.4H	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.3O	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.2L	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.3P	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.2M	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
	adhesive	1.3Q	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**

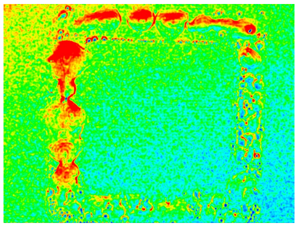
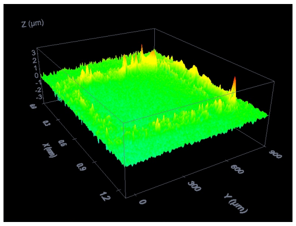
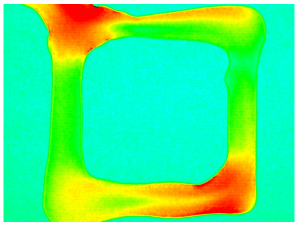
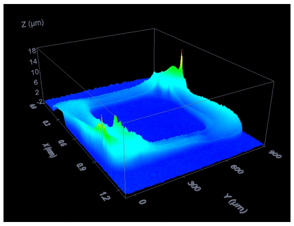
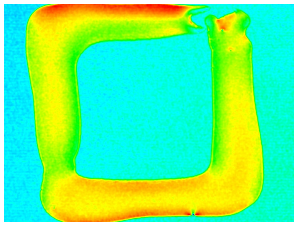
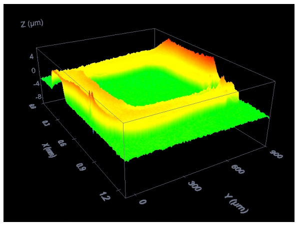
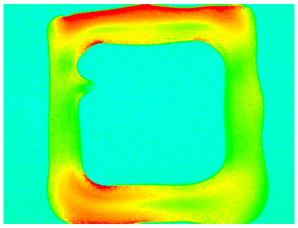
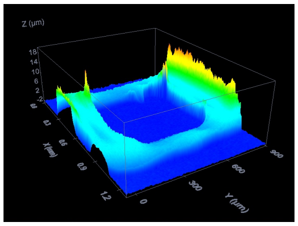
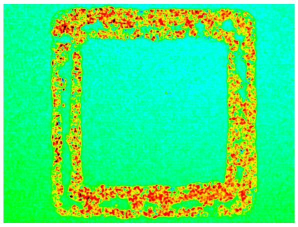
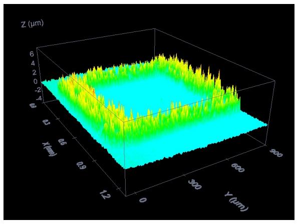


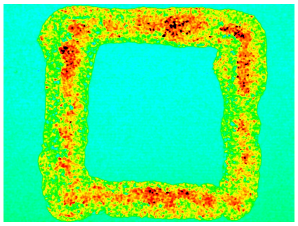
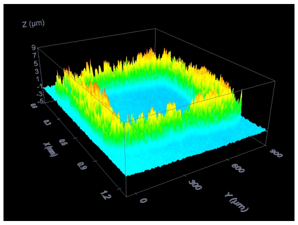
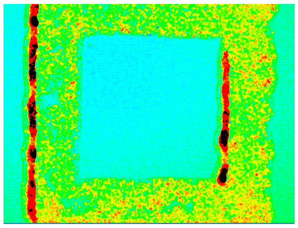
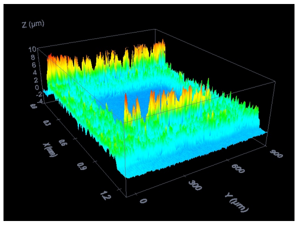
PMMA							
		align inking		PRINTING			
epoxy	stamp	force 1 N	time 1 s	force 1 N	time 1 s	force 2 N	time 2 s
conductive	1.3A	0.8	20	0.8	20	0.6	20
conductive	1.3B	0.8	30	0.8	30	0.6	25
conductive	1.4A	0.9	30	0.9	30	0.75	25
conductive	1.3F	0.8	20	0.8	20	0.6	20
conductive	1.2A	0.8	20	0.8	20	0.6	20
conductive	1.3G	**0.85**	**20**	**0.85**	**20**	**0.65**	**20**
conductive	1.2B	**0.85**	**20**	**0.85**	**20**	**0.65**	**20**
adhesive	1.2H	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
adhesive	1.4E	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
adhesive	1.3M	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
adhesive	1.4G	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**
adhesive	1.2K	**0.2**	**20**	**0.2**	**20**	**0.1**	**15**

Appendix J: White Light Interferometer Image Results (Conductive Epoxy Ink Pad)

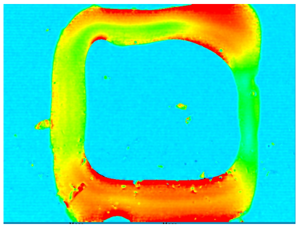
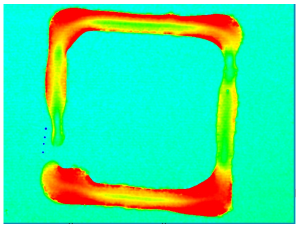
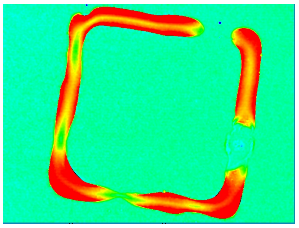
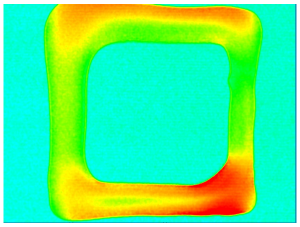
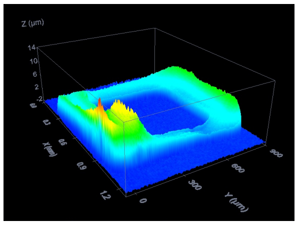
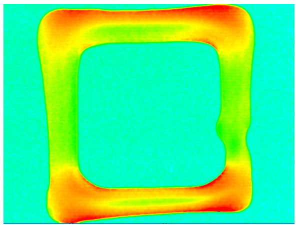
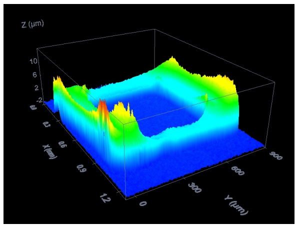
Micrometer Screw Value	Top View
15 µm	
17 µm	
20 µm	

Appendix K: White Light Interferometer Image Results (Conductive Epoxy Prints)

Print Number	Top View	Isometric View
1.2B		
1.2E		
1.3F		
1.3G		
1.3B		

1.3C		Z (µm) 9 7 5 3 1 -1 -3 -5 0.0 0.3 0.6 0.9 1.2 X (mm) 0 300 600 900 Y (µm)
1.3A		Z (µm) 10 8 6 4 2 0 -2 -4 0.0 0.3 0.6 0.9 1.2 X (mm) 0 300 600 900 Y (µm)

Appendix L: White Light Interferometer Image Results (Adhesive Epoxy Prints)

Print Number	Top View	Isometric View
1.3N		
1.4F		
1.2I		
1.3D		
1.3E		

Appendix M: Lateral Dimensions of the Final Prints

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<tr><th colspan="2">Glass Substrate</th><th>PMMA Substrate</th></tr>
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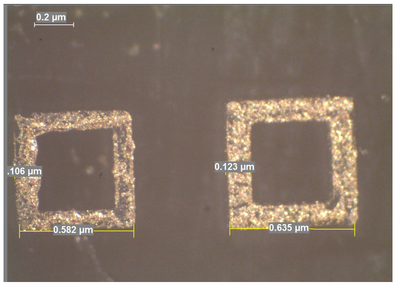
<td>
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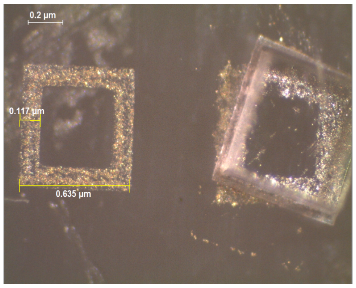
<td>
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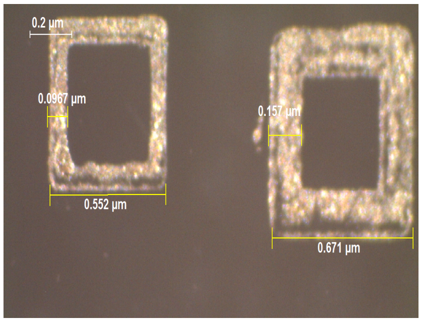
<td>
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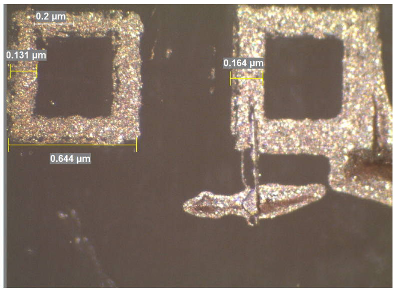
<td>
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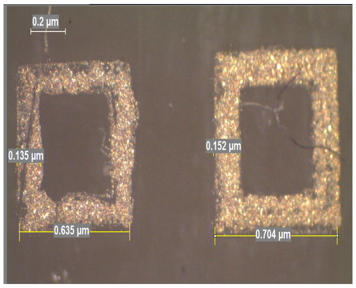
<td>
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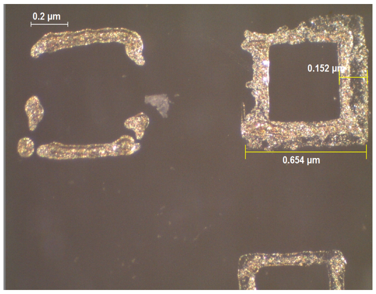
<td>
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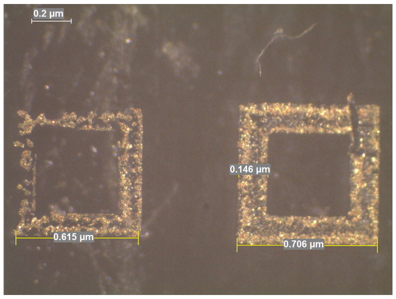
<td>
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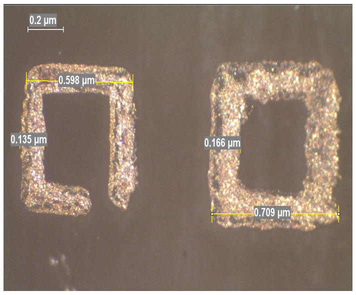
<td>
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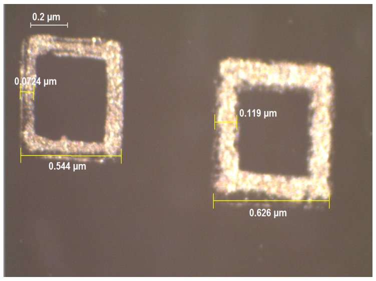
<td>
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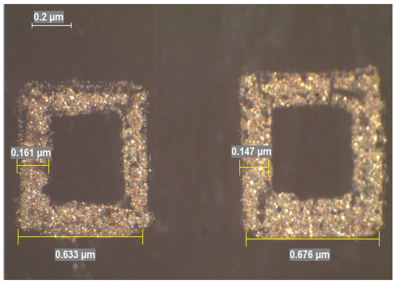
<td>
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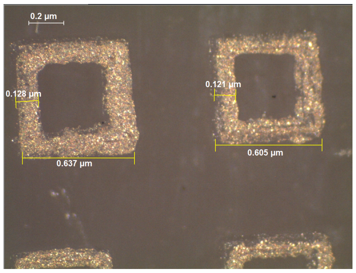
<td>
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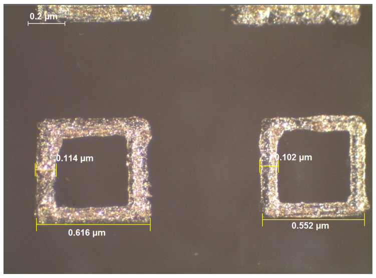
<td>
1.3 G</td>
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<tr>
<td colspan="3">Adhesive Epoxy</td>
</tr>
<tr>
<td colspan="2">Glass Substrate</td>
<td>PMMA Substrate</td>
</tr>
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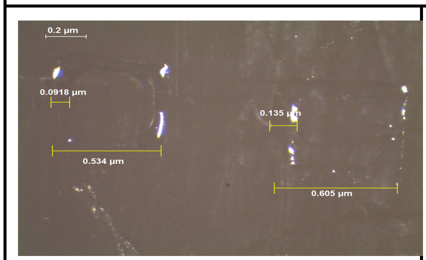
<td>
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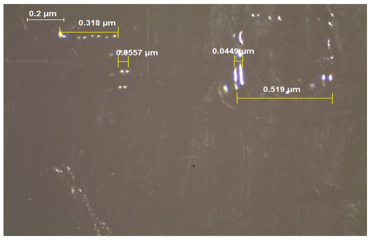
<td>
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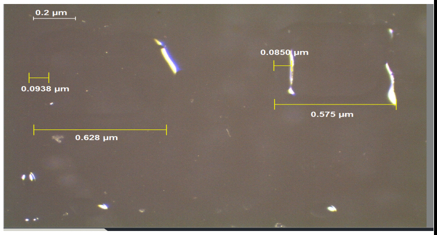
<td>
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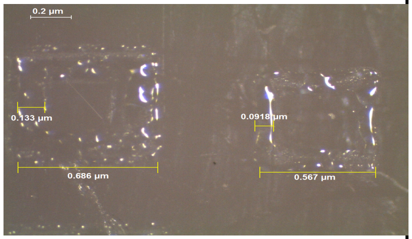
<td>
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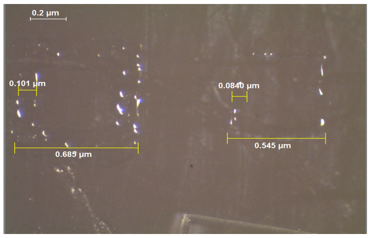
<td>
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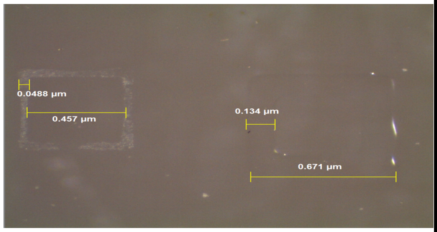
<td>
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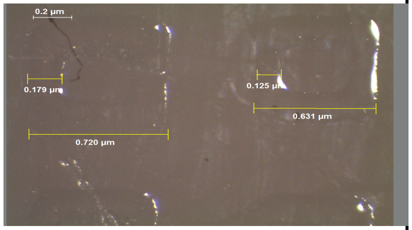
<td>
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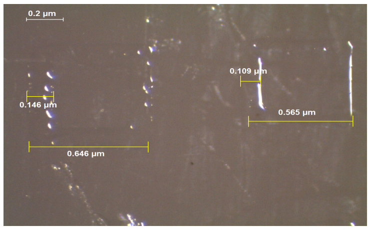
<td>
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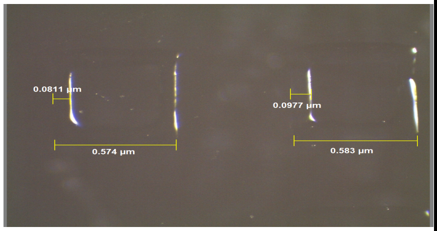
<td>
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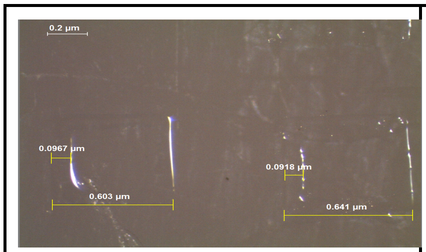
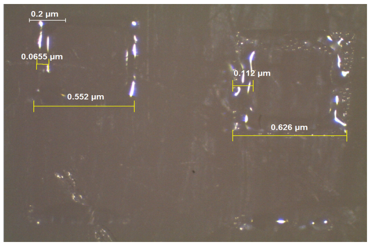


1.4 F



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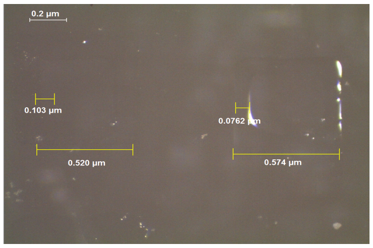
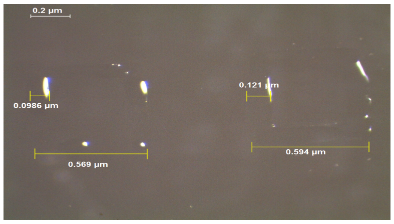


1.3 M

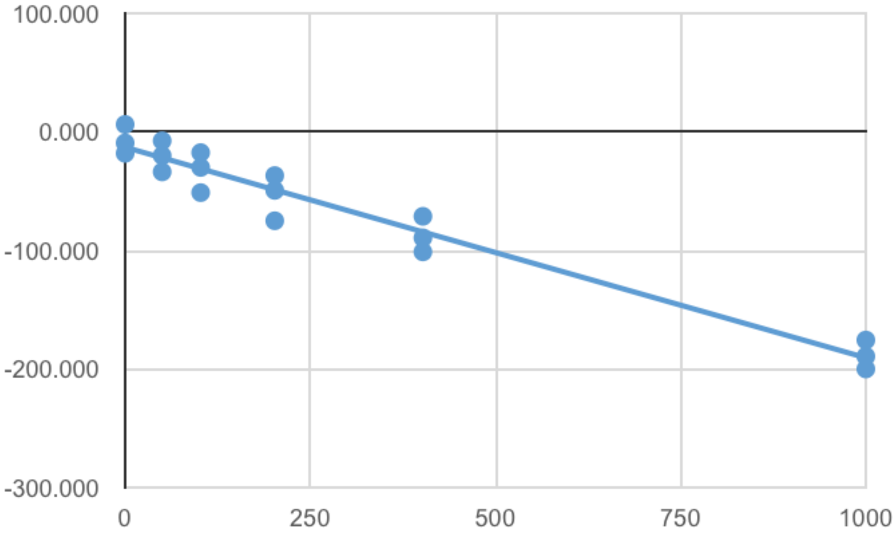


1.4 G

Appendix N: Mechanical Testing Calibration Data

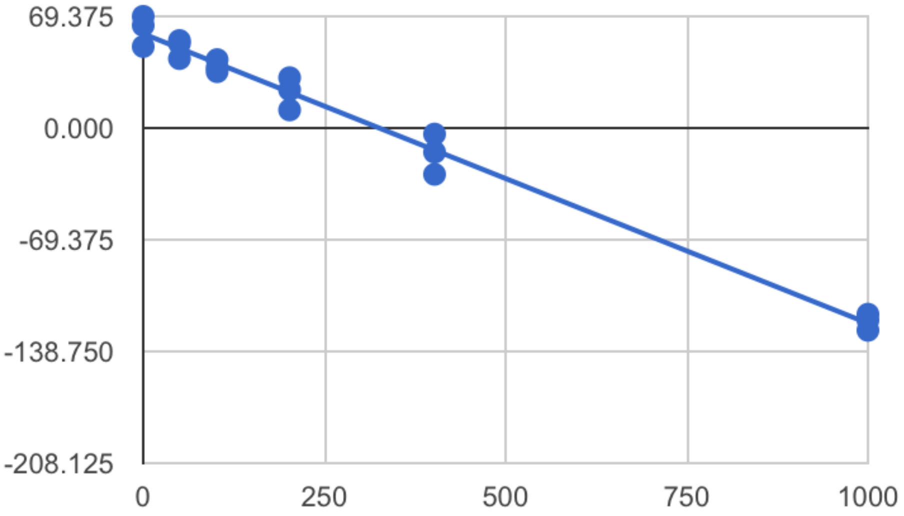
Trial One:

Force	Voltage
0	6.250
0	-9.375
0	-18.125
50	-7.500
50	-20.000
50	-33.750
102	-17.500
102	-30.000
102	-51.250
202	-36.875
202	-49.375
202	-75.000
402	-71.250
402	-89.375
402	-101.250
1000	-175.625
1000	-189.375
1000	-200.000



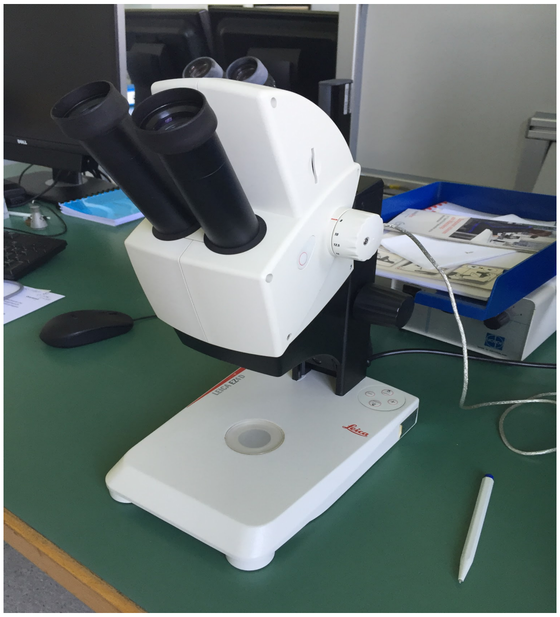
Trial Two:

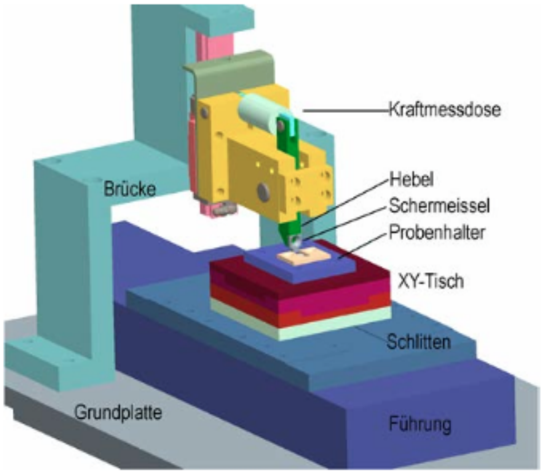
Force	Voltage
0	69.375
0	50.625
0	63.750
50	54.375
50	43.125
50	52.500
102	42.500
102	35.000
102	37.500
202	31.250
202	11.250
202	23.750
402	-15.000
402	-28.750
402	-3.750
1000	-125.625
1000	-119.375
1000	-115.625

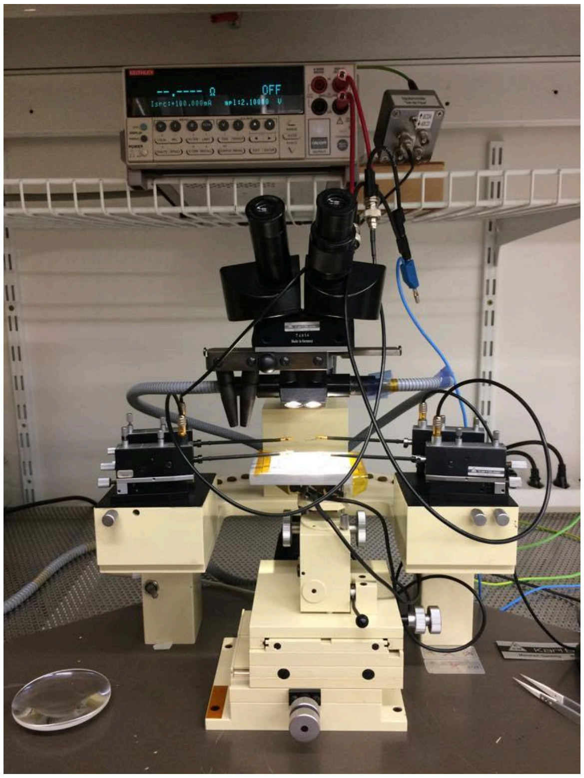


Appendix O: NTB Lab Equipment Images

Barrel Asher	
Spin Coater	

Curing Oven	
Optical Microscope	

White Light Interferometer	
Shear Tester	

Resistivity Tester	

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