DEVELOPMENT OF MOLDING FABRICATION TECHNIQUE FOR MEMS-BASED POLYVINYL ACETATE-NANOCOMPOSITE INTRACORTICAL PROBES

by

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# Table of Contents

List of Figures ..................................................................................................................... 6

List of Tables .................................................................................................................... 14

Acknowledgements ........................................................................................................... 15

Abstract ............................................................................................................................. 16

Chapter 1: Introduction .................................................................................................... 17

1.1 Introduction to Brain-Computer Interfaces ........................................................ 17

1.2 Functional Magnetic Resonance Imaging .......................................................... 18

1.3 Electroencephalography ..................................................................................... 19

1.4 Intracortical Probes ............................................................................................ 20

1.4.1 Silicon-Based Probe Designs .......................................................................... 20

1.4.1.1 Utah Intracortical Electrode Array (UIEA) ............................................. 21

1.4.1.2 Michigan Silicon Probe.............................................................................. 23

1.4.2 Primary Limitation of Silicon-Based Probes .................................................. 24

1.5 Flexible Probe Materials .................................................................................... 25

1.5.1 Inspiration: Sea Cucumber Dermis ................................................................. 26

1.5.2 Early Synthetic Materials with Dynamic Behavior ........................................ 27

1.5.3 Polyvinyl Acetate Nanocomposite ................................................................. 27

1.5.4 PVAc Nanocomposite Fabrication ................................................................. 29
1.5.5 Early Probe Production

1.5.6 Limitations of Early Fabrication Method

1.6 Objectives

Chapter 2: Methods

2.1 Proposal for Molding of Devices

2.2 Creating Device Molds and Stamps

2.2.1 Mask Fabrication

2.2.2 SU-8 Photoresist

2.2.3 Mold Fabrication

2.2.4 Stamp Fabrication

2.3 Device Fabrication

2.3.1 Sacrificial Layer

2.3.2 Neat PVAc Deposition Process Refinement

2.3.2.1 Problems with Excess Material

2.3.2.2 Neat PVAc Device Release

2.3.3 Fabrication with PVAc Nanocomposite

2.3.4 Problems with PVAc-NC Device Thickness and Surface Uniformity

2.3.5 Variations in the Fabrication Method

2.3.5.1 Thickening PVAc-NC Solution by Evaporating DMF

2.3.5.2 Acrylic Sidewalls with Single-Layer PVAc-NC

2.3.5.3 Acrylic Sidewalls with Multi-Layer PVAc-NC

2.3.5.4 Multi-Layer Acrylic Sidewalls
List of Figures

Figure 1: Intracortical probe shapes; (a) Single, implantable probe; (b) Dog-bone shaped test device used to test mechanical properties of beam structure .............. 31

Figure 2: Laser-cut PVAc-NC intracortical probe. Edges have notably nonuniform edges due to the laser cutting process. Micromolding should eliminate this nonuniformity. .................................................................................................. 32

Figure 3: Device Fabrication procedure. (a) Piranha-cleaned, silicon wafer base; (b) Spin-coat SU-8 layer on surface of wafer; (c) Expose and develop SU-8 layer to create mold wells; (d) Spin-coat sacrificial sucrose layer over the SU-8 mold; (e) Deposit PVAc-NC into mold wells, let dry; (f) Compress PVAc-NC down into molds with stamp; (g) Dissolve sacrificial layer in water, release devices. ............................................................................................................. 35

Figure 4: Mold mask layout produced in AutoCAD. Middle three columns contain devices with 50μm wide beams, columns to the right of the middle three columns contain devices with 150μm wide beams, and columns to the left contain devices with 250μm wide beams. Alignment markers are also included. ............................................................................................................. 38

Figure 5: Stamp Mask layout produced with AutoCAD. Although not discernable in this image, device shapes are reduced by 2.5μm on all sides in order to allow the resulting stamps to fit inside the molds. Alignment structures are left out.... 39

Figure 6: Probe structure with 50μm wide beam; (a) Intracortical probe structure; (b) dog-bone structure for tensile strength testing; (c) increased lateral dimensions for absorption tests during submersion. ................................................................. 40
Figure 7: Probe structure with 150µm wide beam; (a) Intracortical probe structure; (b) dog-bone structure for tensile strength testing; (c) increased lateral dimensions for absorption tests during submersion. ........................................................... 41

Figure 8: Probe structure with 250µm wide beam; (a) Intracortical probe structure; (b) dog-bone structure for tensile strength testing; (c) increased lateral dimensions for absorption tests during submersion. ........................................................... 42

Figure 9: Completed SU-8 device mold; (a) Roughness in the SU-8 layer is visible around the edges of the wafer; this roughness is the result of the wafer making contact with the mold mask during exposure, and the contact occurred because spin-coating left the SU-8 layer thicker around the edges of the wafer than in the center; (b) Some defects can also be seen on the surface as a result of bubbles that formed during SU-8 deposition prior to spin-coating. .................. 45

Figure 10: Close-up of raised structures on SU-8 device stamp wafer. The dimensions of the raised structures were consistently too large to fit in the complimenting molds, thereby rendering the stamps unusable in future device fabrication... 47

Figure 11: Second wafer with neat PVAc created with squeegeeing method. Picture was taken just after removal from being submerged in water overnight. A significant number of bubbles became apparent after submersion in water for several hours, such that none of the devices were usable. The excess material was also considerably thicker than expected. ......................................................... 52

Figure 12: Finished wafer using razor blade squeegeeing and vacuum chamber drying. The wafer was submerged in water for several hours after PVAc application.
The majority of excess material buildup occurs around the edges of the wafer.

Figure 13: PVAc-NC devices after deposition is complete and wafer has been submerged in water for several hours; (a) device molds with excess material visible around the edges; (b) after scraping across wafer surface with a razor blade, no excess material is apparent, and devices still appear in-tact.

Figure 14: PVAc nanocomposite device still in SU-8 mold after being subjected to ultrasonic vibrations. The devices began disintegrating shortly after the vibrations began and disintegration primarily began at the centers of the pads. Small, residual pieces of the material can be seen around the device.

Figure 15: Close-up of PVAc nanocomposite device pad after exposure to ultrasonic vibrations. The material appears to be too brittle to handle ultrasonic vibrations. In addition, the centers of the pads appear to be thinner as they are the first areas to be adversely affected.

Figure 16: PVAc-NC devices made from 37 consecutive layers, removed from the molds by hand with tweezers. Some fracturing is apparent on the pads and the connection between the pad and beam structures, which is where devices tended to break most upon extraction.

Figure 17: Profile of 37-layer PVAc-NC device pads; (a) Thickness at center of pad measured to be 21.8µm; (b) Thickness at edge of pad measured to be 96.4µm. The profile suggests the material forms a meniscus on the surface as it dries.
Figure 18: Profile of neat PVAc device pad; (a) Thickness at center measured to be 57.4µm; (b) Greatest measurable thickness at edge of pad measured at 115µm, though dips in graph around the 200µm and 1550µm marks indicate the thickest regions of the device are thicker than the profilometer’s measurement range. ............................................................................................................... 63

Figure 19: Profiles of device beams made using DEKTAK profilometer; (a) 37-layer PVAc-NC device; (b) 7-layer, neat PVAc device. Both profiles display consistent nonuniformity across the surfaces, meaning device thickness is not maintained. .................................................................................................................. 64

Figure 20: Profiles of PVAc-NC pads while devices are still in the SU-8 molds; Positions of reference markers R indicate where the pads begin, and the measurement markers M indicate the lowest point of each mold compared to the device edges. Red lines above graphs indicate location of the mold underneath the PVAc-NC material. ........................................................................................................ 67

Figure 21: PVAc-NC device made from 115 layers of solution after wafer was submerged for several hours in water. It is difficult to discern the device mold from the excess material because of the number of layers, and there is also visible unevenness across the surface of the device. ................................................. 69

Figure 22: PVAc-NC device made from 115 layers of solution after excess edge material was removed. Some excess material is still present, which can adversely affect test results. ................................................................. 70

Figure 23: PVAc-NC devices fabricated using thickened solution and squeegeeing method; (a) 15 layers; (b) 18 layers; (c) 35 layers; (d) 60 layers. These
devices do not present noticeable differences in appearance, though the thicker devices appeared more yellow (not visible in these images) and the larger devices were more difficult to extract and typically had more excess material stuck to them.

Figure 24: SU-8 device mold with acrylic side-wall extension. Residual, charred double-sided tape tended to stick out around the edges and often caused complete blockage of the narrow beam channels.

Figure 25: SU-8 device mold with adhered acrylic side-wall extension after charred material was scraped out of the beam channel. Some of the charred residue fell into the mold and stuck to the sucrose layer inside; this led to more rigorous attempts to clean the acrylic extensions prior to adhesion to the wafer.

Figure 26: Single-device acrylic side-wall extension. This individual acrylic block was created after it was determined that the rippled edges of the SU-8 mold prevented adequate adhesion of the acrylic to the SU-8 mold; the individual blocks could be better adhered to the flatter surface closer to the center of the wafer, and it also made alignment much easier. Applying double-sided tape after laser cutting the acrylic prevented charring.

Figure 27: Attempt to create devices using sidewall extensions and drying in a vacuum oven at 80ºC. PVAc-NC dried too quickly, so the material and air was trapped in the material inside the acrylic cavity.
Figure 28: Device created by drying in a vacuum at room temperature instead of in an oven. Attempts to remove the acrylic sidewalls caused the devices to fracture because excess material caused the molds to stick to the sidewalls. .......................... 79

Figure 29: Unreleased device created using sidewall extensions and a single application of PVAc-NC. These devices are too thin to pry out of the wells by hand, and also exhibit a lack of structural integrity, particularly at the centers of the pads. ................................................................................................................................................................................ 80

Figure 30: Attempt at using acrylic sidewall extension with multi-layer PVAc-NC deposition. The material got stuck in the acrylic, so the material that was in the mold got stuck to the acrylic. The complete imprint of the mold is visible in the dried PVAc-NC. ................................................................................................................ 81

Figure 31: Double-layer acrylic sidewall extension. The lack of focus of the laser due to the thickness of the material caused the cavity to be larger and less defined on one end of the acrylic compared to the other. (a) “Top” side of acrylic into which PVAc-NC is deposited; (b) “bottom” side of acrylic that adheres to SU-8; (c) side profile of mold that shows noticeable change in cavity size from one end to the other................................................................. 83

Figure 32: Result of using coconut oil sacrificial layer with PVAc-NC. This method proved more problematic than previous attempts, since it did not solve any previous issues and in addition, the nanocomposite apparently mixed with the oil, which rendered the material unusable. ........................................... 85

Figure 33: PVAc-NC devices (left) and their thickness profiles (right) displaying differences in uniformity. These devices were all from a single batch, which
means there is limited consistency in the devices molding and extraction processes. ................................................................. 88

Figure 34: PVAc-NC devices created with different methods; (a) laser-cut device; (b) micromolded device. Both devices have rough beam structures due to the limitations of each fabrication process. .................................................... 92

Figure 35: Wear on SU-8 molds after being used to make devices a few times; (a) device mold with fractured corners. This usually occurs in the process of extracting devices. (b) mold is completely peeled off of silicon wafer. Once liftoff of the SU-8 layers starts, it leads to larger breakage over time, as shown here. (c) beginning of SU-8 liftoff from silicon. Devices cannot be made with these molds because PVAc-NC solution dries underneath the SU-8.................. 97

Figure 36: Schematic of microtensile tester used for measuring force and displacement on the PVAc-NC devices, taken and modified from reference 23. .................. 99

Figure 37: Photo of microtensile testing apparatus. The setup is predominantly made of acrylic. Visible are the piezomotor, load cell, and the connection point of the motion indicator, as well as the sample located in between the fixed and mobile stages................................................................. 99

Figure 38: Schematic of microtensile tester used for wet testing, taken and modified from reference 23................................................................. 100

Figure 39: Microtensile test data of PVAc-NC device. The Young's Modulus is found by measuring the slope of the elastic region of the stress-strain curve. The fitted line created in this example using Origin 8.0 indicates a Young’s modulus of 434MPa with a certainty of 99%. ......................................................... 102
Figure 40: Stress-Strain curves obtained from wet-state and dry-state tensile tests. The saturated device did not break during the test, and the dry device fractured at a strain of approximately 0.03. ................................................................. 104

Figure 41: SEM image of beam with dimension measurements. Image shows significant nonuniformity in terms of thickness and curvature of the beam. ............... 108

Figure 42: SEM Image of a second PVAc-NC device. This device appears to have a more angled profile, though still a notable discrepancy between the thicknesses at the center compared to the sides. ................................. 109

Figure 43: Original Young’s Modulus data of (a) dry and (b) wet PVAc-NC devices. 111

Figure 44: Slope data for dry PVAc-NC devices after offsets are eliminated; (a) Stress vs. strain data; (b) Force vs. strain data. ................................................................. 111

Figure 45: Slope data for wet PVAc-NC devices after offsets are eliminated; (a) Stress vs. strain data; (b) Force vs. strain data. ................................................................. 112
List of Tables

Table 1: Width measurements made on PVAc-NC devices. Average widths of each device are given, as well as overall average and standard deviation. .................. 89

Table 2: Thickness measurements made on PVAc-NC devices. Average thickness of each device is given, as well as overall average and standard deviation. .......... 91

Table 3: Lateral swelling measurements of PVAc-NC; measurements made of dry devices and devices saturated with room temperature (20°C) deionized water. Percent changes and average percent change are given. ............................... 93

Table 4: Through plane swelling measurements for PVAc-NC devices. Average thickness measurements were made for four devices before and after submerging the devices in deionized water for an hour. ......................... 94

Table 5: Percent yield of 40-layer PVAc-NC device batches. Discrepancies in total devices are due to damage of the SU-8 layer that rendered some molds unusable on a given wafer. *The number of devices for one wafer was decreased because two of the 21 molds were too visibly damaged to be used. ............................... 96

Table 6: Young’s Modulus (E) recorded in MPa determined from tensile test results. Z-values were determined for each data point and outliers are identified with an asterisk (*) and were removed from the mean and standard deviation calculations listed at the bottom of the table. .................................................. 103

Table 7: Comparison of Z-values for Young's modulus (E) data vs. force (F) data; the similarities in the % error for both wet and dry devices indicates there is no significant difference in the overall variation when the area is removed from the data. ................................................................. 113
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Development of Molding Fabrication Technique For MEMS-Based Polyvinyl Acetate-Nanocomposite Intracortical Probes

Abstract

by

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This thesis presents the development of a novel micromolding fabrication technique for MEMS devices made from polyvinyl acetate nanocomposite (PVAc-NC)—a chemoresponsive material that exhibits changeable, reversible mechanical properties. PVAc-NC has previously demonstrated potential for use as a structural material for neural interfaces although fabrication of complex devices is limited by the laser micromachining technique used to pattern structures. The micromolding technique was tested and modified in a variety of ways in order to yield samples that could withstand material properties testing. Using this developed procedure, devices were created that demonstrated the anticipated dynamic behavior of the PVAc-NC and the micromolding method has been established as a potentially viable fabrication process for these devices, albeit with several significant issues that require further development.
1.1 Introduction to Brain-Computer Interfaces

The brain is comprised of a network of neurons that are connected to each other via their dendrites and axons and discharge electrical signals to each other in order to carry out various functions in the body—locomotion, thought processes, and subconscious behaviors, to name a few. These signals are caused by variations in electrical potential carried by ions in the neuronal membranes. In the process of firing, some of the electrical signal escapes the neuron pathways, and these escaped signals can be detected and measured by embedding electrodes into the brain tissue. When a patient thinks about performing a specific action, like grasping an object or walking, the potentials in the brain vary, and this variation can be programmed into a device in order to perform the specific action—a prosthetic limb can be designed to react to neural responses so that it behaves like a normal limb would, given the same commands from the brain.

Brain-computer interfaces (BCIs) or brain-computer machines (BCMIs) are important technological breakthroughs because they allow patients suffering from a wide range of maladies to regain various sensory abilities that they would not otherwise possess. A BCI or BCM is comprised of three main components: a sensor, a decoder, and an actuator. The sensor is the device that detects neural signals—methods of sensing include electroencephalography (EEG), functional magnetic resonance imaging (fMRI), and intracortical probing. The decoder analyzes the behavior of the sensor and translates it into a command that is then carried out by the actuator—a computer or mobility device,
for instance [1]. Together, these components allow individuals who have lost some or all of their physical functionality to regain the ability to perform otherwise difficult or even impossible tasks. BCIs have been developed for a wide range of functions; the devices in development include artificial limbs for amputees [2], cochlear implants [3], retinal implants [4], pain management treatment for individuals suffering from Parkinson’s disease [5], and a number of mobility and communication devices like motorized wheelchairs [6] and cursor control [7] for paraplegics.

1.2 Functional Magnetic Resonance Imaging

Functional MRI is useful in determining how patients can perform specified mental tasks by taking real-time images of the brain and monitoring changes in blood-oxygen levels. This type of monitoring is helpful in the process of developing our understanding of how the brain works, but response times of the patients can be quite slow. One experiment was performed in which patients were asked to perform four different mental tasks for the purpose of moving a cursor across a screen in four different directions, and the blood-oxygen level changes that resulted from those thought processes were classified accordingly. The effectiveness of moving the cursor across the screen was then evaluated when the patients performed the mental tasks again, and the fluctuations in blood-oxygen levels determined which direction the cursor would move. Although the patients were able to effectively perform this task, it took over two minutes for each cursor movement to be achieved, which is too slow for practical use [1]. In addition to the significantly slow response time, fMRI requires that the patient be
confined to an MRI magnet while the imaging process takes place; this does not make fMRI a viable option for allowing patients to regain motor functions in everyday life.

1.3 Electroencephelography

EEG involves the placement of several electrodes on the scalp of a patient to record signals. These signals are potential changes resulting from thousands of neurons firing close to the surface of the skull. The frequency of these emissions varies, typically in the range of 0.5Hz to 30Hz, and this range is divided into a set of four frequency bands [8]. To manipulate a frequency band, the patient is exposed to an external stimulus of sorts (such as an audible tone or visual display), and the appearance of the ‘correct’ stimulus would result in a change in the detected frequency at one or more electrode locations. The advantage of this method is that a patient is not required to learn any tasks, and can instead simply focus on a particular stimulus in order to elicit a specific response from the actuated device [1].

In principle this method is solid; however, there are still several significant limitations to the technology. In order to elicit desired responses with visual control, the system has to be calibrated for each patient before the control reaches an acceptable level of accuracy. The electrodes can damage the skin over time, which means the method cannot be used continuously, and the electrodes must also be placed very specifically on the scalp, which is time consuming and also requires that the head be shaved. EEG information transfer is quite slow, and the need to focus on individual stimuli does not allow patients with multiple locations of paralysis to regain function of all of those
regions simultaneously [1]. For these reasons, it is advantageous to seek out alternative technologies that have more long-term practical value.

1.4 Intracortical Probes

Intracortical probes are the sensor components of BCIs. An intracortical probe is a neural-activity sensing device that is directly implanted in the cortex of the brain, and mobile devices such as prosthetics or electric wheelchairs could be linked to these probes and controlled by neural activities [9]. The idea behind these probes is that the pattern of neural discharges is a direct representation of the movements a person wishes to perform. The discharge rate of individual cells is directly correlated with directions of motion, and these directions can be fairly well predicted when the discharges of multiple cells in a given region are recorded. These recordings are continuously fed into an extraction algorithm that translates the signals into a motion pattern [10]. The advantage of intracortical probes over other sensing techniques is that the device is directly interfaced with the brain tissue, which means signal-to-noise is greater than that of a sensor surface-mounted outside of the skull, and implants have greater potential for high speed sensing than other sensors—a quality that is ideal for such things as replicating natural motion.

1.4.1 Silicon-Based Probe Designs

The earliest form of intracortical electrodes were comprised of nanowires, for which the wires were tens of microns in diameter, and that were used either as independent probes [11] or were assembled manually into arrays [12, 13]. Early probes were made of fairly rigid materials including gold, tungsten, and silicon. The electrodes
are very thin wires, typically 20-50µm in diameter. Often, the devices contained on-board electronic components. Multiple electrodes are combined into arrays in order to increase the number of neurons whose signals can be detected [10], and these array devices range from 10 to approximately 100 µm on a side [14], which makes them large enough to collect stronger signals, but small enough to still have the capacity for targeting specific areas of the brain. The primary advantage of the multi-probe array over the single-electrode models is its ability to record ensemble activity of neurons. This is significant because complex human behaviors such as motion are the result of multi-neuronal activity, and accurately predicting movement parameters thus requires measurement of many neuronal signals at once [15]—something that single-electrode probes are unable to accomplish.

1.4.1.1 Utah Intracortical Electrode Array (UIEA)

The UIEA was a silicon multi-electrode device developed at the University of Utah in a response to the larger size of its predecessors. Previous electrode arrays designed for probing the visual cortex required milliampere currents to pass through them needed large surface areas—approximately 1mm². At the same time, they needed to be spaced at least 2mm apart in order to minimize coupling between adjacent electrodes. As a consequence, the arrays were very large, and because of the spacing, signal detection was fairly discontinuous across the brain tissue. For detecting signals in localized areas of the brain, this discontinuity is highly problematic, as it reduces the ability to directly correlate the signals with behaviors like motor functions. To improve the continuity of signal detection, it was proposed that the surface area of the probes be reduced, thereby
lowering the current necessary to pass through them and also reducing the required spacing, making local signal detection more effective [16].

To fabricate the UIEA, a silicon base is micromachined and acid-etched, resulting in a hundred probes in a 10x10 array configuration on top of a ~120µm platform. A 1.7mm n-type silicon wafer is p⁺-doped by means of thermomigration of aluminum on the surface of the wafer. In the thermomigration process, aluminum is deposited on the surface of the wafer and patterned into squares. Then, by creating a temperature gradient on one side of the wafer, the aluminum migrates across the surface towards the hotter side. This process results in a series of localized p⁺ trails that are electrically isolated from each other. The micromachining process cuts the trails into ten evenly spaced sections by dicing the wafer into a 10x10 array of columns; each of these resulting columns is approximately 1.5mm long. The columns are then refined via chemical etching, resulting in a needle shape that is tapered down from 90µm in diameter at the base to approximately 1µm at the tip. The needles are sputtered with gold then platinum and finally, the whole device except for the electrode tips is coated in polyimide for insulation [16].

Although the UIEA demonstrated a fairly high SNA of 6:1 [15]—substantially greater than its single-probe predecessors—the nature of the fabrication methods involved allows much room for error, which is not ideal for mass fabrication of the devices. UIEA fabrication takes a substantial number of steps, the most problematic of which is the thermomigration process. It is difficult to maintain orthogonality of the p⁺ trails, first, due to the difficulty of maintaining a temperature gradient and, second, controlling the tendency of the aluminum to perform “random walks” across the wafer.
due to surface defects. These inconsistencies in the p\(^+\) trails cause the probes to short out [16].

1.4.1.2 Michigan Silicon Probe

The fabrication of the Michigan probe begins with a p-type silicon wafer that is oxidized. The oxide layer is patterned such that the intended probe areas are defined, and the oxide is then doped with boron. Next, the oxide is removed, and a series of other materials is deposited: 300nm of thermal oxide, 300nm of silicon nitride, and 800nm of silicon dioxide. Then, tantalum and polysilicon are deposited and patterned, followed by a 50nm layer of nitride, and then a second series of thermal oxide, silicon-nitride and silicon dioxide are added in the same thicknesses as before. These upper layers are patterned via plasma etching to expose the underlying bonding pads and recording sites. Then a layer of gold is deposited into the exposed regions, field dielectrics outside these regions are removed with a plasma etch, and the back of the wafer is etched isotropically to thin it out. Finally, the individual probes are separated by etching in ethylene diamine-pyrocatechol [17].

The advantages of this probe were the high yield produced in batch fabrication (over 80%) and consistency of device dimensions using this fabrication method [18]—the dimensions can be controlled down to as little as 1µm. In addition, recording site placement and shape can be easily customized and on-board electronics can be easily integrated [19].
1.4.2 Primary Limitation of Silicon-Based Probes

The main limitation of early probe designs is a lack of longevity: their ability to detect the neuronal signals degrades significantly over time and cannot be guaranteed over long-term periods. The loss of signal detection is primarily due to the material properties of the probes. Although these previous devices were biocompatible enough to enable prolonged exposure of the device to brain tissue, the signal-detection capability of the devices made from rigid materials typically lasted no more than a number of months [20, 21]. For patients that suffer from permanent paralysis, such degradation of the devices does not lend itself well to being viable for clinical applications.

It has been found that cause of signal degradation in early probes is ultimately a consequence of trauma that the probe inflicts on surrounding tissues. It is theorized that this result is the consequence of the device being comprised of a rigid material; the rigid probe inflicts chronic trauma on the surrounding tissues through relative micromotion between the brain tissue and the probe [20], and the encapsulating shell, known as a ‘glial sheath,’ is an immune response to the strain that is caused by the differences in stiffness between the brain tissue and the device in an effort to reduce the trauma [14]. The brain tissue adapts to the presence of the device, and the probe eventually becomes encapsulated by the surrounding cells. This results in an overall reduction of the neural signals detected by the probe, because the glial sheath shields from probe from nearby neurons, thereby increasing the impedance between the neurons and the electrodes, and consequently diminishing the effective signal [20].
1.5 Flexible Probe Materials

Although it has been determined that probe size plays some role in determining how quickly the device becomes encapsulated [14], the material properties of the probes are believed to have a much greater effect. To eliminate the immune response, it was proposed that the devices be made from materials that would be rigid during implantation but would then soften post-insertion to more closely match the stiffness of the surrounding tissue [22]. More specifically, it was suggested that the Young’s modulus of the probe should, upon insertion be on the order of 1kPa to adequately match the brain tissue properties [20]. This way, the device would not be detected as a foreign body, would not cause scarring, and could be more effectively integrated into the brain tissue.

Researchers have turned to polymers for potential probe materials, because these materials exhibit considerable flexibility, high heat capacity, and are often substantially more biocompatible than their rigid counterparts [23]. A number of probes have been developed that use materials which exhibit the flexibility needed to better match the cortical tissue post implantation, such as polydimethylsiloxane (PDMS) [24], parylene [25-27] and polyimide [28, 29]. However, these materials do not exhibit any kind of mechanically dynamic behavior. That said, these flexible materials, once developed, cannot be made more rigid, and consequently implantation of the probes can be difficult, as they require incisions to be made in the brain tissue prior to insertion. To implant the devices into the cortex requires the devices be highly rigid prior to long-term exposure to biological fluid, and these flexible materials do not have such environmentally-dependent characteristics. In addition, some polymers like benzocyclobutene have a tendency to
absorb comparatively larger quantities of moisture [30] which can cause a change in the size of the probes which could damage the surrounding brain tissue.

1.5.1 Inspiration: Sea Cucumber Dermis

The nanocomposite material that was used in this thesis was inspired by the physiology of sea cucumbers. The sea cucumber dermis is unique in that its tensile properties can be substantially altered—the advantage of this transformation is so that the sea cucumber can increase the strength of its dermis from approximately 5MPa to around 50MPa when it detects the presence of an external threat [31]. The dermis can achieve this transformation as a consequence of its material makeup; it is a composite material made up of a viscoelastic substance combined with a network of rigid, whisker-like nanofibers. These structures are spindle-shaped and short—typically no longer than a millimeter in length [32] and have an aspect ratio on the order of 2000 [31]. The rigidity of the dermis is dependent on the hydrogen bonding interactions of these interspersed fibrils; the aggregation is the result of bonding specifically between surface hydroxyl groups. The fibril network becomes more rigid when neighboring fibrils form covalent bonds, and similarly the network rigidity lessens when these bonds are relaxed [33]. The sea cucumber secretes proteins called stiparin in order to trigger the bond formation. Then, the relaxation of the dermis and consequent breaking of these bonds occurs when stiparin-inhibitors are introduced [32]. An additional protein called tensilin also plays a role in increasing the stiffness of the dermis, but its effects are not fully understood [22].
1.5.2 Early Synthetic Materials with Dynamic Behavior

A number of attempts have been made to imitate the properties of the sea cucumber dermis, resulting in the creation of nanocomposite polymer materials. The first material developed that successfully imitated the tensile properties was a 1:1 mixture of ethyleneoxide and epichlorohydrin (EO-EPI) copolymer combined with cellulose fibrils that mimicked the sea-cucumber dermis’ nanofiber network. These cellulose structures were obtained from a variety of natural sources, including tunicates, wood, wheat straw, and cotton. The introduction of these whiskers to the neat solution has a substantial effect on the material properties. The tensile storage modulus (or Young’s modulus) of neat EO-EPI is 3.7MPa compared to around 800MPa with a tunicate-whisker content of approximately 19%. This material also exhibited a reversible change in material properties when exposed to water; for the same 19% whisker solution, the Young’s modulus decreased to about 20MPa in water, and regained its 800MPa modulus upon drying. Unfortunately, it was determined that this particular material that used tunicate whiskers was not stiff enough to be viable for an implantable cortical probe, and increasing the whisker concentration would merely cause the device to be too brittle, [22] so other solutions were later proposed.

1.5.3 Polyvinyl Acetate Nanocomposite

Polyvinyl acetate nanocomposite (PVAc-NC) is a synthetic material comprised of PVAc—a thermoplastic, synthetic polymer often used in multipurpose glues—and cotton-based cellulose nanofibers, and as with the earlier synthetic materials, PVAc-NC successfully mimics the behavior of the sea cucumber dermis when the external
environment is manipulated. Like earlier nanocomposite variations, its whiskers are also taken from natural sources. In air, the material is very stiff; a PVAc solution of 15% cotton-whiskers has a dry Young's modulus of about 2.7GPa. This Young's modulus is reduced substantially to approximately 4MPa when the device is submerged in water for about seven minutes. These numbers vary depending on the whisker content—a higher percentage of whiskers in the solution corresponds to a higher dry Young’s modulus. The same can be said for the device in a wet environment, though on a smaller scale. A study of 5% cotton-whisker solution compared to a 15% solution showed a difference in the dry-state Young’s modulus of 1GPa versus 2.7Gpa, respectively. In the wet state, the difference between the solutions is comparable but on a smaller scale—the 5% solution exhibited a modulus of 3.7MPa, and the 15% solution yielded 4.9MPa [34].

Given these material properties, PVAc-NC has a notable advantage as a material for intracortical probes over the previous materials used, as well as the EO-EPI solution. The high Young’s modulus of the dry-state device is ideal for the insertion process; it vastly exceeds the modulus of the EO-EPI solution in its dry state without being too brittle. Once it has been implanted, the device is exposed to fluids, and as a result, it softens to more closely match the mechanical characteristics of the surrounding tissue [33]. Consequently, an intracortical probe comprised of this material would have a lesser chance of causing trauma to the patient post-implantation than its rigid predecessors, which would mean the device would not become encapsulated and lose signal stability over time.
1.5.4 PVAc Nanocomposite Fabrication

Creating the PVAc-NC is a process that involves chemical solution deposition and a nanofiber template. Extraction of the cellulose nanofibers from their source (tunicates, for instance) requires acid hydrolysis using sulfuric acid. The fibers are then purified and redispersed in dimethyl formamide (DMF). Next, the fibers are mixed with a solution of PVAc polymer and DMF [20]. This solution maintains a fairly viscous and sticky texture when kept in a closed container. The composition of the solution used in my research consisted of 15% PVAc-NC in DMF, and 15% of the PVAc-NC weight was comprised of the cotton nanofibers.

1.5.5 Early Probe Production

In the early experiments, the nanocomposite was dried and pressed into sheets for the purpose of laser cutting the devices out of the bulk material. In these instances, the mixture is set and dried in a Teflon dish so that the DMF is removed, and the PVAc-NC is left over; to speed up the drying process, the nanocomposite was dried a vacuum oven at 65°C for one week, then the remaining material was compression molded in a press to create layers of the material. Once the material is completely dried, it is compressed down to a thin sheet. The earliest sheets were reported as ranging between 300 and 400μm thick [35] though in an effort to reduce the size of the structures, later specimens were produced that ranged in thickness from 50 to 150μm [31].

The early patterning process was designed with the limitations of PVAc-NC in mind. The material is very sensitive to temperature changes and chemical exposure.
PVAc-NC has a glass transition temperature of approximately 42ºC [23], which means the material would be subject to distortion if it were to undergo a standard soft-bake procedure in the process of photolithographic patterning (soft-bake temperatures are typically higher than 50ºC [36]). In addition exposure to the majority of acids, bases, and solvents would make the devices unsafe for implantation, as there would be a high risk of absorption of these chemicals into the device due to the tendency of PVAc to absorb moisture; this could be very damaging to the brain tissue when the device is implanted. Consequently, the intracortical probes were fabricated by means of laser cutting the devices out of a large sheet of material.

The laser cutting device used was a CO₂ laser, for which the power was 2.5W, the laser resolution was 600 pulses per inch, and the cutting speed was 560mm/s. The number of passes required in order to completely cut through the material was dependent on the material thickness, where a single pass would cut approximately 10µm; to free the devices therefore required up to about fifteen passes. Once released, the devices were removed from the wafer with tweezers [20].

Although intracortical probes normally have one end that is needle-like and tapered (Figure 1.a) for the purpose of insertion into the brain tissue, to test the mechanical properties of the probes, dog-bone shaped structures were created, as depicted in Figure 1.b. Two pads were located on either end of the device such that the tensile properties of the beam structure could be tested.
Figure 1: Intracortical probe shapes; (a) Single, implantable probe; (b) Dog-bone shaped test device used to test mechanical properties of beam structure.

The research done on these early PVAc-NC devices have shown that the probes do exhibit dynamic response when exposed to fluids as anticipated. Furthermore, devices that were implanted into a rat cortex exhibited consistent dynamic behavior, changing from rigid to flexible in under five minutes; the 15% cotton-whisker devices exhibited changes in Young’s modulus from ~2.3GPa when rigid to ~30MPa in water. In addition, PVAc-NC probes were effectively patterned with gold and parylene thin-films. The gold serves as a conductive pad for electronic compatibility, and the parylene acts as a protective layer for the metal layer. The thin-films did not delaminate when the devices were in air or exposed for short-term periods in a simulated biological environment [23].

1.5.6 Limitations of Early Fabrication Method

There are a number of factors that limit the effectiveness of the PVAc-NC based device when produced using the aforementioned fabrication method. The films from which the devices were laser cut were dried in a vacuum oven at 65°C for a week, so if the vacuum oven used in this process were not effectively cleaned, this could result in the PVAc-NC leeching contaminants, as was the case in some instances of film fabrication
In addition to this issue, there are issues with the laser cutting procedure; the first is that the nonuniformity of the devices along the beam structures. Laser cutting tends to leave the edges quite rough, as shown in Figure 2, which is not conducive to smooth entry into brain tissue. Another problem was that the thickness of the sheets of compressed PVAc-NC from which the devices are cut vary from one point to the next, so uniform thickness of the resulting probes is not guaranteed, which is not ideal for mass fabrication. In addition, the thicknesses of the bulk pieces (often hundreds of microns) are not ideal for intracortical probes, as the larger size may lend itself to a higher risk of trauma to the patient when the probe is inserted. Given the successful preliminary studies of PVAc-NC intracortical probes, it is advantageous, then, to seek out alternative fabrication methods of these devices for the purpose of creating improved devices.

Figure 2: Laser-cut PVAc-NC intracortical probe. Edges have notably nonuniform edges due to the laser cutting process. Micromolding should eliminate this nonuniformity.
1.6 Objectives

In response to the limitations of early methods of PVAc-NC probe fabrication, my thesis research centered around two primary objectives: (1) refine a procedure for fabricating PVAc-NC probes using a molding technique that is reproducible; (2) test the resulting structures comprised of both neat PVAc and PVAc-NC structures and compare the material properties of the two to determine if the molded nanocomposite devices display dynamic material properties compared to the neat PVAc. In addition, limitations of both the fabrication process and the resulting structures would be identified for potential improvement in future work.
Chapter 2: Methods

2.1 Proposal for Molding of Devices

My goal was to fabricate the dog-bone test devices by compression molding the PVAc-NC directly into the probe shape. The steps for creating the devices are illustrated in Figure 3. The process begins with a silicon wafer (Figure 3.a), on which a layer of SU-8 photoresist is spin-cast (Figure 1.b). Next, the SU-8 is exposed to UV radiation under a mask, and the SU-8 is developed, resulting in a series of device molds (Figure 3.c). A sacrificial layer of sucrose solution is next spin-cast over the surface (Figure 3.d), and PVAc-NC is deposited into the device molds (Figure 3.e). The devices are then compressed into the molds with a stamp in order to reduce the thickness and increase the density of the molded material (Figure 3.f). Finally, the sacrificial layer is dissolved away, and the devices are released (Figure 3.g).
Figure 3: Device Fabrication procedure. (a) Piranha-cleaned, silicon wafer base; (b) Spin-coat SU-8 layer on surface of wafer; (c) Expose and develop SU-8 layer to create mold wells; (d) Spin-coat sacrificial sucrose layer over the SU-8 mold; (e) Deposit PVAc-NC into mold wells, let dry; (f) Compress PVAc-NC down into molds with stamp; (g) Dissolve sacrificial layer in water, release devices.

Hypothetically, this fabrication technique should address the issues that arose in the laser cutting process. First, molding should offer more control over the thickness of the resulting devices; the devices thickness could be scaled to more appropriate sizes,
potentially down to a thickness of only 20 to 30 microns, compared to the several hundred micron-thick devices produced with the laser cutting method. This would address two issues: the devices would be more ideally sized for implantation, and also because the material used is not left in an oven for a week like the laser-cut films, the devices are not potentially subjected to contaminants for extended periods of time. Furthermore, the amount of the nanocomposite that is used to make each molded device could be controlled—the molds regulate the volume and the amount deposited could be fixed so that the error in device thickness from one device to the next could be vastly reduced compared to the laser-cut devices. Second, molding substantially reduces the amount of PVAc-NC that is wasted. A lot of material is left over as a consequence of cutting the devices out of a large sheet due to the shape of the devices. PVAc-NC is presently not one of the easiest materials to obtain, so it is beneficial to reduce the amount wasted. Molding would limit the amount used to the volume of the molds, which allows for one to produce many more devices with a smaller amount of the material. Finally, molding should eliminate the issue of rough device edges. Mold dimensions are very easy to regulate using highly controllable microfabrication techniques such as wet etching, so the resulting devices created in these molds would be much smoother and more even.

2.2 Creating Device Molds and Stamps

In order to fabricate the PVAc-NC test structures, molds in which to deposit the material, as well as stamps with which to compress the material into the molds, had to be developed. These stamps and molds would require very specific and ideally consistent
dimensions, so the molds were created by developing SU-8 photoresist. Due to
dimension discrepancies, the stamp wafers could not be used, so a second stamp was
attempted using PDMS.

### 2.2.1 Mask Fabrication

Two masks were created for fabricating the devices—one for the mold and one
for the compression stamp. The mask for the devices were created using AutoCAD; the
mold mask is shown in Figure 4 and the stamp mask is shown in Figure 5. The
dimensions of the devices were kept constant with the exception of beam widths: the
posts of the spindle shape were kept at 1500µm$^2$, the beam length was 300µm, and the
beam width was varied such that we had three variations: 50µm (Figure 6), 150µm
(Figure 7), and 250µm (Figure 8). The beams were also supported with rounded corners,
where the radius of curvature was 200µm. Devices with varying beam widths consisting
of were also created. These devices would be used for measuring changes in the lateral
dimensions of the devices from the dry to the wet state of the PVAc-NC.
Figure 4: Mold mask layout produced in AutoCAD. Middle three columns contain devices with 50µm wide beams, columns to the right of the middle three columns contain devices with 150µm wide beams, and columns to the left contain devices with 250µm wide beams. Alignment markers are also included.
Figure 5: Stamp Mask layout produced with AutoCAD. Although not discernable in this image, device shapes are reduced by 2.5µm on all sides in order to allow the resulting stamps to fit inside the molds. Alignment structures are left out.
Figure 6: Probe structure with 50µm wide beam; (a) Intracortical probe structure; (b) dog-bone structure for tensile strength testing; (c) increased lateral dimensions for absorption tests during submersion.
Figure 7: Probe structure with 150μm wide beam; (a) Intracortical probe structure; (b) dog-bone structure for tensile strength testing; (c) increased lateral dimensions for absorption tests during submersion.
Figure 8: Probe structure with 250µm wide beam; (a) Intracortical probe structure; (b) dog-bone structure for tensile strength testing; (c) increased lateral dimensions for absorption tests during submersion.

2.2.2 SU-8 Photoresist

SU-8 is a very thick, epoxy-based, negative photoresist that is often used in instances where a high aspect-ratio is desired, and it has also been used as a mold material for device fabrication. SU-8 tends to allow for high aspect-ratio development,
and this is due to its very low absorption rate of near-UV light during the development process. SU-8 is a popular material for MEMS fabrication for its versatility and cost-effectiveness, and has been used in applications such as piezoelectric motors [38] and stamps for high aspect-ratio microchannels [39]. In addition to its high aspect-ratio capabilities, SU-8 is a very rigid material once developed, and it adheres well to silicon wafers; these characteristics make it ideal for creating mold structures.

It was decided that the molds would be created using SU-8 2035 photoresist. The choice of SU-8 was due to the fact that the material lends itself well as a base mold material. The 2035 variety—which is 69.95% solids, has a viscosity of 7000cSt, and a density of 1.227g/ml—was chosen because although it has a lower viscosity than some of the other available types of SU-8 (such as SU-8 100), it is still possible to create substantially thick-enough layers with it. In addition, the 2000 varieties dry more quickly than the other types [36], which is helpful for expediting the fabrication process.

2.2.3 Mold Fabrication

The decision was made to create a mold that was approximately 100 microns thick. This thickness was chosen so that the mold would be deep enough that it could be filled with the nanocomposite material, but still thin enough that the device could be easily released once the device had been compressed to its final thickness. A thicker mold would mean it would need to be filled a fewer number of times, but this would make the release process considerably more difficult. Conversely, it would be very time consuming to repeatedly fill a very thin mold. Therefore, the 100 micron thickness was chosen as a compromise between these extremes. To create a 100 micron layer using
2035 photoresist requires a spin-coat speed of approximately 1200rpm [36]. Because we wanted to be sure the mold would be at least 100 microns thick after development of the photoresist, we made the SU-8 layer slightly thicker by using a reduced spin-coat speed of 1000rpm.

The fabrication of the molds is a multi-step process. First, silicon wafers were cleaned with a piranha wet etch; the wafers were set in a solution consisting of 0.65l of sulfuric acid and 2.6l of hydrogen peroxide for ten minutes, then rinsed with de-ionized water. Next, the SU-8 2035 was spin-coated onto the wafers. Approximately 4ml was dispensed on each wafer, and the spin coat speed was set at 500rpm for 10 seconds, followed by 1000rpm for 30 seconds. Following the spin-coating, the wafers were soft baked at 65ºC for 5 minutes, and then at 95ºC for 20 minutes. The subsequent step involved exposing the wafer to UV light through the mold and stamp masks. The wafers were exposed to 240mJ/cm² of radiation, initially for 37.5s, though this time was later reduced because we found our resulting feature dimensions for the mold were too small, and the dimensions for the stamp were too big (meaning the wafers were overexposed). Next, the wafers were baked again, this time at 65ºC for 5 minutes and then at 95ºC for 10 minutes. Once the baking was complete, the wafers were developed in SU-8 developer solution. The wafers were submerged in the solution for ten minutes and subjected to strong agitation in order to more effectively develop our high aspect-ratio, thick-film structures. Finally, the wafers were rinsed with isopropyl alcohol for ten seconds, and then blasted with pressurized air to dry. A finished device mold is presented in Figure 9.
Figure 9: Completed SU-8 device mold; (a) Roughness in the SU-8 layer is visible around the edges of the wafer; this roughness is the result of the wafer making contact with the mold mask during exposure, and the contact occurred because spin-coating left the SU-8 layer thicker around the edges of the wafer than in the center; (b) Some defects can also be seen on the surface as a result of bubbles that formed during SU-8 deposition prior to spin-coating.

2.2.4 Stamp Fabrication

My first attempt at fabricating the stamps was done using the same technique as the molds, but using the alternative stamp mask that resulted in inverse exposure of the
SU-8 and consequently ‘raised’ SU-8 structures that would, in theory, interlock with an underlying mold (fig. 9). However, it was found that the fabrication of the stamp yielded feature sizes too large to fit the features sizes of the molds. The initial parameters of the fabrication process of the molds were varied in an attempt to correct this but were unable to resolve the problem. The soft-bake timing was the first parameter to be adjusted; the photoresist around the edges of the wafer were notably thicker than the center as a consequence of the spin-coat procedure, so the SU-8 near the edges did not dry completely. As a consequence, the wafer stuck to the mask near the edges during the subsequent exposure step, though it was fairly easy to dislodge the wafer from the mask with tweezers. It was thought that this lack of contact in the center might have been the cause of the feature size discrepancy—that the mask was scattering light and therefore causing the resulting features to be smaller than desired. We attempted to correct this by increasing our soft-bake time such that the edges were completely dry (27.5 minutes at 95°C); however this caused the dimensions of devices on the drier wafers to be smaller even than the dimensions of the original mold. We decided to continue using the sticky-wafers, so we went back to baking for 20 minutes at 95°C, and instead attempted to vary the exposure times. Unfortunately, this did not achieve the desired effect either; wafers were both overexposed up to 45 seconds and underexposed down to 15 seconds, and neither extreme case caused significant variation in the feature sizes. The contact mode was also changed from soft contact to hard contact to see if this made any difference, but this did not seem to positively affect the resulting devices, either. Ultimately, it was determined that the discrepancy in feature sizes between the stamp and mold masks was too great for these stamps to be useable in the device fabrication process.
Figure 10: Close-up of raised structures on SU-8 device stamp wafer. The dimensions of the raised structures were consistently too large to fit in the complimenting molds, thereby rendering the stamps unusable in future device fabrication.

A second attempt at creating a viable stamp was made, this time using PDMS. In order to fabricate a stamp, PDMS was coated over a finished SU-8 device mold and then dried. Because PDMS is a fairly malleable substance, it could be easily peeled off the wafer once dried. Furthermore, the dried material is still rigid enough to maintain a molded shape. This would allow for the stamp to exactly match the features of the underlying mold, and would theoretically be a viable solution for the compression step of the device fabrication.

PDMS was first produced using a 10:1 ratio of base polymer to curing agent (Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 were used in this case).
The base polymer and curing agent in their respective masses were first mixed together, and the mixture was then set in a vacuum chamber for an hour to remove any gas that had been added during the mixing process. Once finished, the viscous PDMS was deposited on one of the SU-8 molds, and then set in an oven at 70ºC for 30 minutes. Initially, the PDMS was spin-coated on the wafer at 500rpm, but after baking, it was found that the layer was very thin, and it was difficult to peel the layer off without tearing. In a second attempt, the spin-coat step was eliminated, and a large quantity of the PDMS was instead deposited over the wafer and held in place during the baking stage with a piece of acrylic that was laser-cut to fit the wafer. The result was a thicker layer that did not tear when it was peeled away from the mold.

This attempted stamp proved unusable as well. Because of the elastic nature of PDMS, realigning the stamp with the mold wafer after device fabrication was too problematic. Attempts to align the entire stamp up with the mold did not work; because the material is sticky, it was too difficult to get the stamp to move in a desirable manner to make adjustments to its positioning. Cutting out small pieces of the mold in order to align fewer of the devices also did not work. The discrepancy between the features of the mold and the stamp was enough that, because of the malleable nature of PDMS, any applied force would consequently not be isolated to the area of the mold.

2.3 Device Fabrication

Once several device molds had been created, the process for fabricating the dog-bone structures was developed. This process consisted of coating the molds with a sacrificial layer, depositing the PVAc nanocomposite into the wells, and releasing the
devices by dissolving the sacrificial layer. Although the theoretical process was fairly straightforward, a number of challenges arose that required revising and refining the procedures and methods involved.

2.3.1 Sacrificial Layer

To fabricate a probe, the SU-8 mold was first filled with a thin, sacrificial sucrose layer; this way, the PVAc would not be stuck to the wafers upon drying, and when the sucrose layer is dissolved in water, the devices would more easily dislodge from their respective molds. To apply this layer of sucrose, the wafers were first made hydrophobic by placing them in a vacuum chamber, and then exposing them to pure oxygen gas. Once this was finished, the wafers were mounted on a spin-coating table, and a small amount of 90% sucrose solution was deposited on top. In order to make the sucrose film very thin, the solution was spin-coated onto the wafers at 500rpm for 10 seconds, then 3000rpm for 30 seconds. Next, the wafers were baked at 95ºC for two minutes, followed by a bake at 120ºC for several hours to ensure that the sucrose layer would dry completely.

2.3.2 Neat PVAc Deposition Process Refinement

Once the sucrose layer was dried, several attempts were made to refine the PVAc deposition process. A neat PVAc solution was used, which was comprised of 15% PVAc in dimethylformamide (DMF); this was done in order to prevent wasting any of the nanocomposite solution until an adequate fabrication process had been developed. The primary challenge with PVAc deposition was filling the molds and not having excess
material build up on the rest of the wafer, as too much material would be difficult to remove from the devices upon release.

2.3.2.1 Problems with Excess Material

The first attempt at depositing the solution involved manually dropping the PVAc in the molds, then baking the wafer at 80°C for 30 minutes to evaporate away the DMF. This process was then repeated several times in order to fill the molds with a sufficient amount of material. Then, the wafer was set in water overnight in order to dissolve the sucrose layer and to let the devices become malleable enough to peel out of the mold wells. Using this method, releasable devices were created, but there were some significant issues with the method that needed improvement. First, the volume dropped into each well was not uniform from one well to the next because the excess material would overflow around the edges of the mold. Furthermore, the excess material around the edges was dried along with the material in the mold, and without a viable compression step, the excess material would stick to the mold structures; this made the smallest feature sizes (namely, the 50µm beam structures) nearly impossible to discern from the built-up material around the edges. Although it was possible to cut away most of the excess material from the 150µm and 250µm beam devices after the PVAc had been submerged in water for several hours, because of the small size of the structures it was not easy to remove the excess material evenly or exactly.
Figure 10: First attempt at PVAc deposition; picture taken after moderately successful attempts to remove some devices from the molds. Lots of excess material is visible around the edges of the devices, and none of the 50um beam structures could be differentiated from the surrounding PVAc.

The second attempt at filling the mold involved pouring PVAc on the wafer, and then squeegeeing excess material off the wafer with a flat block of acrylic so that excess material around the molds was minimized. The wafer was baked in the 80°C oven for 30 minutes, and the application/baking process was repeated several times. Unfortunately, the squeegeeing process left the PVAc considerably aerated, and because the wells were
refilled and dried several times, the number of bubbles that were created increased with every repetition. This left the devices completely unusable, and most of them were not discernable from the rest of the material (Figure 11). It appeared that in addition to the issue of bubbles, there was still considerable excess material, so a more finely-edged scraping device was necessary to adequately scrape excess material off the wafer.

Figure 11: Second wafer with neat PVAc created with squeegeeing method. Picture was taken just after removal from being submerged in water overnight. A significant number of bubbles became apparent after submersion in water for several hours, such that none of the devices were usable. The excess material was also considerably thicker than expected.
The process was further refined in several ways. First the baking process was switched from a regular atmospheric oven to a vacuum oven in order to eliminate the bubbles that resulted in the squeegeeing process. This oven was set at 80°C for 30 minutes, but it seemed that this temperature was too high, as the wafer dried before all of the bubbles could be completely removed from the PVAc. The temperature was reduced further to 40°C; this wafer was slightly more successful, as there were significantly fewer bubbles than the previous one and the excess material around the molds was minimal. However, as there was no control over the locations of the bubbles, it would seem that using room temperature would be the most effective when also utilizing the squeegeeing technique. In a subsequent trial, the process was repeated, but instead of using a vacuum oven, the wafer was placed in a vacuum chamber and let it dry at room temperature for an hour in between depositing the layers of PVAc. This procedure was repeated six times before submerging the wafer in water overnight. This method worked significantly better; the majority of devices were retrieved only from the 250µm side of the wafer, though the 150µm beams tended to break. In later trials, the same procedure was repeated as before except this time seven subsequent layers of the neat PVAc were deposited before submersion as opposed to six, and substantially more of the 150µm devices were retrievable because of the extra layer.

2.3.2.2 Neat PVAc Device Release

Although creating the devices was, in itself, a problem, the release of the devices was somewhat difficult as well. The first issue was the excess material that tended to
stick to the edges of the devices. By soaking the wafers in water for several hours, this excess material would typically be loose enough to cut or peel away from the edges without causing any damage to the material left in the molds. Excess material was removed as much as possible before attempting to pry devices out of the molds, and this seemed to work quite well, even for the smaller 150µm devices. Using the squeegeeing method with the razor blade, most of the wafer remained fairly clear of the excess material (Figure 12); the majority of buildup occurred around the edges of the wafers where the SU-8 layer was uneven.

![ Finished wafer using razor blade squeegeeing and vacuum chamber drying.](image)

Figure 12: Finished wafer using razor blade squeegeeing and vacuum chamber drying. The wafer was submerged in water for several hours after PVAc application. The majority of excess material buildup occurs around the edges of the wafer.
Another issue was that the devices tended to remain fairly situated in the device molds, even after the sacrificial layer was dissolved. Although the devices could be fairly easily pried out of the molds with tweezers, this tended to cause the beam structures to stretch somewhat, and during material properties testing, this change in device dimensions would substantially skew the results. To rectify this problem, a sonic bath was used to let the devices self-release from the wafers. The wafers were prepared using the same deposition method as before, and then it was set in an ultrasonic bath overnight. The devices had all been released from the mold successfully; however, they had clumped together in the process, and because the water had gradually heated, the devices had melted together and were rendered quite useless. On a subsequent trial, the devices were removed as they released, which proved more effective. However, the 50µm and 150µm devices could not withstand the vibrations, however, and the pads tended to break off from the beam structures. Because of the consistently low yield from the sections of the wafers containing the 50µm and 150µm devices, and given the even more brittle nature of the PVAc nanocomposite, application of the neat PVAc to wafer was henceforth limited to the side containing 250µm devices.

### 2.3.3 Fabrication with PVAc Nanocomposite

There were issues when the neat PVAc was substituted by the PVAc nanocomposite due to the significantly reduced viscosity of the nanocomposite over the neat PVAc. The amount of DMF in the PVAc-NC solution was significantly higher, which made the material much more fluid; the number of layers that needed to be deposited was approximately threefold, since there was about 5% of the solid material in
this solution compared to 15% in the neat PVAc. More problematic was the fact that squeegeeing the material across the wafer no longer worked. The nanocomposite tended not to remain inside the molds when scraping the razor blade across the wafer, and there was no way to successfully squeegee excess material off from the edges; these effects are likely due to increased surface tension. For this reason, the fabrication procedure for this new material needed to be redefined.

Because squeegeeing proved ineffective, the solution was instead deposited in the wells by hand with a syringe. The drying process was also modified; because of the solution composition and the length of time required to deposit the solution into the molds, the drying time in the vacuum chamber was to 20 minutes. Depositing the material by hand resulted in a notable amount of buildup of the material around the edges, even with my best attempts to minimize the amount of material deposited; however, after the wafer was submerged in water for a few hours, this excess material was surprisingly easy to remove by means of scraping across the surface of the wafer with a razor blade—the material crumbled in a way that the neat PVAc did not, likely due to the presence of nanowhiskers. This excess nanocomposite was removed from the sides without causing any damage to the material in the molds. Figure 13 shows molds before (Figure 13.a) and after (Figure 13.b) the excess material is removed in this fashion. Using this modified process, devices of varying thicknesses were created, and ultimately further process refinement was needed in order to obtain a high enough yield in order to adequately test the material properties of these molded PVAc-NC devices.
Figure 13: PVAc-NC devices after deposition is complete and wafer has been submerged in water for several hours; (a) device molds with excess material visible around the edges; (b) after scraping across wafer surface with a razor blade, no excess material is apparent, and devices still appear in-tact.

2.3.4 Problems with PVAc-NC Device Thickness and Surface Uniformity

The first wafer of devices was made by applying 21 layers of PVAc-NC, then soaking in water for several hours to dissolve the sacrificial sucrose layer. The 21 layer devices were too thin to pry out by hand with tweezers; furthermore, when attempting to remove the devices in the ultrasonic bath, the devices started to disintegrate due to the vibrations. Figure 14 and Figure 15 show the effects of the ultrasonic bath; Figure 14
shows a device after a few minutes of being subjected to the vibrations, and Figure 15 shows a close-up of one of the pads. It is apparent that the centers of the device pads are thinner than the edges, as these areas were the first to break apart when subjected to the ultrasonic vibrations.

Figure 14: PVAc nanocomposite device still in SU-8 mold after being subjected to ultrasonic vibrations. The devices began disintegrating shortly after the vibrations began and disintegration primarily began at the centers of the pads. Small, residual pieces of the material can be seen around the device.
Figure 15: Close-up of PVAc nanocomposite device pad after exposure to ultrasonic vibrations. The material appears to be too brittle to handle ultrasonic vibrations. In addition, the centers of the pads appear to be thinner as they are the first areas to be adversely affected.

Devices were then created by applying 37 subsequent layers of PVAc-NC; this number was arrived at because the resulting devices were thicker than the previous ones, and at 37 it appeared that the wells had been fairly substantially filled with the nanocomposite. It also seemed that at that stage, the amount of excess material that was starting to accumulate on the sides. After submersion in water, the excess material was still removable by means of scraping, and the devices were releasable with tweezers; a
couple of these devices are shown in Figure 16. However, when the remaining devices were submerged in the ultrasonic bath, these, too, began breaking apart like the thinner devices had.

Figure 16: PVAc-NC devices made from 37 consecutive layers, removed from the molds by hand with tweezers. Some fracturing is apparent on the pads and the connection between the pad and beam structures, which is where devices tended to break most upon extraction.

Because a couple of the devices were retrieved prior to the ultrasonic bath, a Sloan DEKTAK 3030ST profilometer was used to obtain the profiles of the device pads to determine the extent of the thickness variation. The profilometer drags a stylus across
the device to measure variation in vertical displacement and provides a thickness measurement down to 50Å. The profilometer was set to measure across the centers of the PVAc-NC device pads. The results of one scan are given in Figure 17. It is evident from the profile analyses that the devices are substantially thinner across the center compared to the edges—for the device shown, the difference in thickness from the edge of the pad to the center is approximately 75µm. Comparing the profiles of the nanocomposite devices to those of the neat PVAc devices (an example profile is shown in Figure 18) it is apparent that the profiles were similar in shape, but that the difference in thickness from the edge to the center was less for the neat PVAc devices. For the specific device shown in Figure 18, the difference in thickness from the edge to the center of the pad was approximately 58µm. It should be noted that this value is very approximate because the actual thickness at the edges was not determinable using the profilometer, so the difference in thickness is probably a few micrometers greater.
Figure 17: Profile of 37-layer PVAc-NC device pads; (a) Thickness at center of pad measured to be 21.8µm; (b) Thickness at edge of pad measured to be 96.4µm. The profile suggests the material forms a meniscus on the surface as it dries.
Figure 18: Profile of neat PVAc device pad; (a) Thickness at center measured to be 57.4µm; (b) Greatest measurable thickness at edge of pad measured at 115µm, though dips in graph around the 200µm and 1550µm marks indicate the thickest regions of the device are thicker than the profilometer’s measurement range.
The profile of the beam structures of both neat PVAc and PVAc-NC devices were also measured, and these scans also showed considerable nonuniformity across the surface. Examples of each are given in Figure 19, the devices for which were again the 7-layer neat PVAc and the 37-layer PVAc-NC devices. There seems to be a suggestion of a meniscus forming, though the shape is not quite as parabolic. This is perhaps the result of narrowness of the beams or the nature of the nanocomposite while drying.

Figure 19: Profiles of device beams made using DEKTAK profilometer; (a) 37-layer PVAc-NC device; (b) 7-layer, neat PVAc device. Both profiles display consistent nonuniformity across the surfaces, meaning device thickness is not maintained.
These profiles indicate that the material does not dry uniformly everywhere in the mold. There are two possible explanations for this. The first is that, given that the viscosity of the nanocomposite is extremely low, the unevenness of the material could be the consequence of surface tension; as the material dries in those larger areas, it tends to adhere to the SU-8 and a concave meniscus develops, making the material build up more the edges than in the centers of the pads. There seems to be less of this problem in the neat PVAc because the material has a significantly lower viscosity, so the surface tension is lower during the drying process. Another possibility is that the nonuniformity is the result of the underlying sacrificial layer not being evenly distributed in the wells. Although the spin-coating process is done to minimize the variation across the surface, it still does not guarantee exact thickness uniformity.

To correct the issues with the profile, the molds were filled with a substantially greater number of PVAc-NC layers such that the mold would be completely filled with the material. This was done, first, in the hopes that the devices would be thicker and hence more robust than their predecessors, and second, so that the thickness may be more consistent across the device, thereby eliminating the concave profile that otherwise occurs due to surface tension. For my first trial, 115 layers of the PVAc-NC solution were applied before it seemed that the material filled up the molds.

The adjustments made to the process did not help very much. Profiles were obtained of several devices across the pads and beams while the devices were still in the molds; this was done to see if there was any improvement in the shape, and also to see if there was consistency from one device to the next. From the profiles obtained, this was not the case. Figure 20 shows profiles obtained for three of the device pads. There was
no apparent consistency from one mold to the next. The reference markers labeled ‘R’ indicate where the mold edge begins and the red lines above the graphs shows the span of the mold under the PVAc-NC. Most of the molds were overfilled with material, as evidenced by the general elevation of the material in the mold regions compared to the elevation outside the molds. In addition to a lack of consistency from one device to the next, there was a suggestion of a meniscus shape, as the edges seemed to be consistently more elevated than the centers.
Figure 20: Profiles of PVAc-NC pads while devices are still in the SU-8 molds; Positions of reference markers R indicate where the pads begin, and the measurement markers M indicate the lowest point of each mold compared to the device edges. Red lines above graphs indicate location of the mold underneath the PVAc-NC material.
The next problem with the 115 layer devices was removing the devices from the wafer. After the wafer was soaked overnight in water, the material had expanded considerably, especially in the vertical direction, and because of the many number of layers, there was a lot of excess material around the edges (Figure 21) that was much more difficult to remove completely than the extra material from the 37 layer device wafer. This material could not be scraped away, but rather had to be carefully cut away. Figure 22 shows a device in the SU-8 mold after the excess material had been removed. Ultimately, no devices were successfully extracted without fracturing. The deposition process with 95 and 70 layers with a similar lack of success in terms of yield; only 1 out of 21 of the 95-layer structures and 2 out of 21 of the 70-layer devices were extracted intact, and all of these whole devices broke after drying and attempting to transfer them to a storage container.
Figure 21: PVAc-NC device made from 115 layers of solution after wafer was submerged for several hours in water. It is difficult to discern the device mold from the excess material because of the number of layers, and there is also visible unevenness across the surface of the device.
2.3.5 Variations in the Fabrication Method

When fabricating devices using manual deposition of the PVAc-NC into the individual molds, there are two major concerns. The first is that the nonuniform profile resulting from the initial attempts at fabrication is problematic for testing. The profile of thinner devices appears to be more uniform than the thicker devices, but the thinner centers of the pads are weak, which is not ideal for testing. Conversely, the thicker devices are more robust but have extremely nonuniform profiles that result from drying.
It would be ideal to create devices that would be uniform or at least thicker overall in order to increase the chances of the device surviving the testing process. The second issue is that the process is very lengthy; because the individual molds are filled by hand, the substantial number of layers due to the higher ratio of DMF to PVAc-NC in the solution, and because each subsequent layer takes 20 minutes to dry, the total time required to create these devices is quite substantial, more so if even thicker devices are attempted. Consequently, alternative methods of fabrication were sought in an attempt to yield more testable devices.

2.3.5.1 Thickening PVAc-NC Solution by Evaporating DMF

Since the viscosity of the PVAc-NC was significantly higher than that of the neat PVAc, and because the manual deposition of the nanocomposite with a syringe was a very lengthy process, attempts were made to reduce the number of layer applications needed and increased the viscosity by evaporating away some of the DMF in the solution—the weight of the material was measured before and after evaporation, and it was determined that the weight percent of solution remaining was 25%.

There were some concerns with doing this; the reason for having such a high ratio of DMF to PVAc-NC was so that the whiskers would be adequately dispersed. In the process of thickening the solution, the whiskers tended to clump together somewhat as the material dried. Although mixing seemed to help re-disperse the whiskers a bit, there was some apparent clustering. The material was effectively deposited into the device molds, though it is possible that the clustering of the whiskers might adversely affect the material properties of the resulting devices.
As before, devices were created by applying varying numbers of layers—fewer than had been attempted previously. A few of these devices were successfully extracted from the molds, but the yield was comparatively lower than the devices made using the unevaporated PVAc-NC solution. The devices were created by applying 15, 18, 35, and 60 subsequent layers of the thickened PVAc-NC solution. Examples of the devices procured are given in Figure 23. The devices made with 35 and 60 layers had a lot of excess material around the edges that was very difficult to remove; for this reason the number of layers was scaled back. Some excess material tends to stick to these thicker devices; the examples in Figure 23 show excess material still stuck to the devices, giving them rough, uneven edges. After all the trials attempted to create thicker devices, it was clear that the increased thickness made the devices substantially more brittle and prone to fracturing, even in the wet state, and that to be able to mass-fabricate testable devices, they would have to be substantially thinner.
Figure 23: PVAc-NC devices fabricated using thickened solution and squeegeeing method; (a) 15 layers; (b) 18 layers; (c) 35 layers; (d) 60 layers. These devices do not present noticeable differences in appearance, though the thicker devices appeared more yellow (not visible in these images) and the larger devices were more difficult to extract and typically had more excess material stuck to them.

Extracting the devices that were made from fewer layers was still difficult and the yield was not as good as that of the 40-layer devices made from the unevaporated PVAc-NC solution. The pads tended to break apart very easily, particularly at the center of the pad as a consequence of those areas being the thinnest, and more often than not the pads that did remain whole snapped off at the point where the pads and beams connect. More
of the 18 layer devices could be retrieved than of the 15 layer ones, but it is clear that the material properties of the thickened solution is different enough from the normal solution that without a viable self-release method, it is optimal to stick with the original fabrication procedure.

2.3.5.2 Acrylic Sidewalls with Single-Layer PVAc-NC

Because of the excessive number of layers that needed to be deposited into the molds, and because this might be contributing somewhat to the brittleness of early PVAc-NC devices, it seemed that a more effective approach to molding would be to reduce the number of layer depositions. To do this, removable sidewall extensions were created by laser-cutting pieces of 2.5mm-thick acrylic. On one side of the sidewall extensions, double-sided tape was applied so that one surface could be adhered to the SU-8 mold.

First, several mold shapes were cut out of a block of acrylic, and the shapes in the acrylic were lined up with the wafer; this proved difficult, though it was achieved to a certain level of accuracy; unfortunately, there were still several problems with this method. First, double-sided tape had been applied prior to laser-cutting the shapes, and this resulted in a fair amount of charred tape around the edges of the openings that blocked much of the cavity, particularly along the beam structure (Figure 24), and attempting to remove the excess material after the block was stuck to the wafer caused a lot of it to get stuck inside the mold (Figure 25). More problematic was the fact that the block covered part of the edge of the wafer where the SU-8 was uneven; this likely caused the double-sided tape to not adhere properly to the wafer, because in the attempts to fill the molds, the PVAc nanocomposite leaked out from under the acrylic on all sides.
Both problems from the first attempt were corrected by creating smaller sections of acrylic that had individual molds carved out. This made alignment much easier. In addition, the double-sided tape was applied after laser cutting the acrylic so that there was no charred material, and cut out the holes by hand with a razor blade. Because the acrylic could be confined to single devices closer to the center of the wafer, the edges of the wafer were no longer an issue and the tape stuck much more effectively to the SU-8. The wells could therefore be filled with PVAc-NC without the solution leaking out.
Figure 25: SU-8 device mold with adhered acrylic side-wall extension after charred material was scraped out of the beam channel. Some of the charred residue fell into the mold and stuck to the sucrose layer inside; this led to more rigorous attempts to clean the acrylic extensions prior to adhesion to the wafer.
Figure 26: Single-device acrylic side-wall extension. This individual acrylic block was created after it was determined that the rippled edges of the SU-8 mold prevented adequate adhesion of the acrylic to the SU-8 mold; the individual blocks could be better adhered to the flatter surface closer to the center of the wafer, and it also made alignment much easier. Applying double-sided tape after laser cutting the acrylic prevented charring.

Drying the PVAc-NC presented the same issues as without the sidewalls. The devices were first dried in a vacuum oven; as with the earliest attempts using neat PVAc, this caused the material to dry too quickly, and air and material was trapped inside the acrylic pieces (Figure 27). The oven was replaced with a room-temperature vacuum
chamber, but drying in this way took several hours. Although some of the PVAc-NC ended up in the wells as hoped, removing the sidewalls caused some amount of fracturing because the material was still stuck to the acrylic, and a whole device could not be procured (Figure 28).

Figure 27: Attempt to create devices using sidewall extensions and drying in a vacuum oven at 80°C. PVAc-NC dried too quickly, so the material and air was trapped in the material inside the acrylic cavity.
Figure 28: Device created by drying in a vacuum at room temperature instead of in an oven. Attempts to remove the acrylic sidewalls caused the devices to fracture because excess material caused the molds to stick to the sidewalls.

To solve the issue of fracturing, the next wafer with the sidewall extension was submerged in water for several hours in order to loosen the material up better. This proved much more effective; all the excess material could be removed and sidewalls while leaving the devices in the molds; Figure 29 shows a device that resulted from this process. Although the device is largely intact, it is evidently still quite thin, as some cracks in the center of the pads are evident. Because of the feebleness of the structure, the devices could not be removed by hand, and they certainly did not hold up in an
Two alternative methods of PVAc-NC deposition were consequently attempted.

Figure 29: Unreleased device created using sidewall extensions and a single application of PVAc-NC. These devices are too thin to pry out of the wells by hand, and also exhibit a lack of structural integrity, particularly at the centers of the pads.

2.3.5.3 Acrylic Sidewalls with Multi-Layer PVAc-NC

Still using the sidewall extensions, more layers of solution were applied. Because the amount of material deposited with each layer was significantly greater than without the sidewalls, the number of layers should be vastly reduced. Unfortunately, this method did not yield any positive results. Every device with two or more applied layers could not be retrieved; the material got lodged in the acrylic pieces, as shown in Figure 30. The material that was deposited in the mold is clearly visible within the confines of the
sidewall cavity, but attempts to cut out devices from this excess material were unsuccessful.

Figure 30: Attempt at using acrylic sidewall extension with multi-layer PVAc-NC deposition. The material got stuck in the acrylic, so the material that was in the mold got stuck to the acrylic. The complete imprint of the mold is visible in the dried PVAc-NC.

2.3.5.4 Multi-Layer Acrylic Sidewalls

The next attempt at improving the sidewall extension method was to increase the thickness of the acrylic so that more material could be deposited at once. Two pieces of acrylic of the same thickness as before were glued together with acetone. The same shape as before was cut, except the beam section was made slightly wider to allow more
room for error in lining up the acrylic pieces with the molds. Because of the thickness of the acrylic, the laser did not cut through evenly, and the resulting shape is shown in Figure 31; this shape still made deposition possible as the more defined side of the acrylic could be stuck to the SU-8. There were similar problems with this method as there has been with applying multiple layers of PVAc-NC in the thinner sidewall extensions. The solution tended to stick to the sidewalls as it dried, and because there was substantially more of the solution in these raised sidewalls, it dried inside the cavity as well as in the device mold, so the devices were not extractable.
Figure 31: Double-layer acrylic sidewall extension. The lack of focus of the laser due to the thickness of the material caused the cavity to be larger and less defined on one end of the acrylic compared to the other. (a) “Top” side of acrylic into which PVAe-NC is deposited; (b) “bottom” side of acrylic that adheres to SU-8; (c) side profile of mold that shows noticeable change in cavity size from one end to the other.
2.3.5.5 Sidewall Extensions with Oil Sacrificial Layer

To eliminate the problem of the material sticking to the sidewalls, an attempt was made to coat the sides in a layer of hydrophobic material—in this case, coconut oil was used because it has a melting temperature just above room temperature (about 25°C) and lower than the glass transition temperature of PVAc. The inside walls of the cavity in the acrylic were coated by melting the oil on a hot plate, dropping small amounts of the oil into the acrylic with a syringe and blowing pressurized air from the same side to remove as much excess oil as possible. The oil was deposited from the side with the double-sided tape prior to removing the protective layer of plastic to avoid rendering its adhesive power useless. Unfortunately the results of this method were not desirable; apparently the PVAc mixed with the oil, because the resulting material was still stuck in the acrylic, and it was a cloudy-white color (Figure 32).
Figure 32: Result of using coconut oil sacrificial layer with PVAc-NC. This method proved more problematic than previous attempts, since it did not solve any previous issues and in addition, the nanocomposite apparently mixed with the oil, which rendered the material unusable.

2.3.6 Final Method of Fabrication

Ultimately, the fabrication process used to make the devices was a deposition of 40 consecutive layers of the PVAc-NC solution into the SU-8 molds by hand. The solution was deposited into the molds with a syringe. In between depositing layers, the wafers were dried in a vacuum for 20 minutes, and after all 40 layers were deposited, the wafers were placed in an oven at 65°C as an added measure to completely eliminate all
possible remaining DMF. The wafers were then submerged in room-temperature deionized water overnight to dissolve the sacrificial layer, and extraction occurred while the devices were in their saturated state due to heightened flexibility of the wet-state material. The extraction was done by using blade to lift the devices off the underlying silicon carefully, starting at the outmost edges of the pads and working inwards from both sides. Once the device was completely loosened from the mold, tweezers could be used to remove the device from the wafer. At this stage a device was typically bent or curled and still malleable from saturation, and before it dried it would be placed on an empty silicon wafer, flattened with the side of a razor blade, and reshaped into its dog bone structure with tweezers.
Chapter 3: Device Testing and Results

There are a few primary considerations when measuring the material properties of the probes. Regarding the fabrication procedure, it was important to determine the effectiveness of the process in terms of device dimension consistency—particularly thickness—and reproducibility of the fabrication process. In addition, measurements were made of the changes of lateral dimensions of the devices from the dry to the wet state to determine whether the effects of these changes may have impacted device fabrication. In terms of determining the effectiveness of the devices, the goal was to demonstrate the dynamic behavior of the devices to prove that the micro-molding technique, though still in its early stages, is at least a viable procedure for making devices that exhibit the anticipated material properties of PVAc-NC.

3.1 Device Thickness and Dimension Consistency

Although it was hypothesized that the micro-molding technique would result in more consistency in device dimensions and thickness uniformity, this did not appear to be the case. In the process of testing the neat PVAc and PVAc-NC devices, a variety of device widths were measured and it was determined that the measurements were fairly varied, both from one device to the next and also from one point to another on a single beam. These differences on individual beams are probably the result to stretching of the beam structures caused by extraction with tweezers, as well as a lack of definition of the beam structures due to the presence of excess material. To measure the dimensions, each individual device was measured in multiple locations along the beam structures, and this
was done on several devices. The average was calculated by considering all the obtained measurements (three or four measurements from each device). Figure 33 shows three devices extracted from a single wafer and their corresponding side profiles that were used to measure their thicknesses. There are noticeable, superficial differences between the images; device (a) is observably smoother and has a fairly uniform thickness compared to the other two, and device (c) is the most nonuniform in its thickness.

Figure 33: PVAc-NC devices (left) and their thickness profiles (right) displaying differences in uniformity. These devices were all from a single batch, which means there is limited consistency in the devices molding and extraction processes.
All of the devices used for testing purposes were originally designed to be 250µm wide, but due to SU-8 processing variations, the device molds turned out smaller, and the sacrificial layer should have added an additional reduction in the dimensions. The average width was 205±33µm for the neat PVAc devices and 240±13µm for PVAc-NC. The measurement data for the nanocomposite devices are shown in Table 1. It seemed that the neat PVAc devices were thinner because they were generally stretched more during extraction; the same set of molds and same extraction technique was used for both sets of devices but the neat devices evidently turned out thinner. Also, there is a bit more variation in the widths, as indicated by the larger standard deviation; these dimension variations are likely due to a lack of extraction technique.

<table>
<thead>
<tr>
<th>PVAc-NC Device Width Measurements (µm)</th>
<th>Device Average (µm)</th>
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<td>246.5 238 242 243.5</td>
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</table>

| Overall Average: 240±13µm |

Table 1: Width measurements made on PVAc-NC devices. Average widths of each device are given, as well as overall average and standard deviation.
The thicknesses of the devices were also measured prior to testing, and these values, too, were inconsistent from one device to the next, but more importantly, the thickness of a single device was widely varied from one point on the probe to the next. The average thickness for neat PVAc and PVAc-NC devices were 118.7±24µm and 123±29µm, respectively, though the ranges for a single PVAc-NC were from 7.5µm up to 59µm. The measurement data for the nanocomposite devices are given in Table 2. There are a few reasons for the variation in these values. First, because the fabrication process lacks a compression step, there is no way to guarantee thickness consistency from one point to the next since the material does not necessarily dry in a completely uniform manner. Another issue is the method of extraction—pulling out with tweezers—sometimes causes the material to stretch, and such deformation is not desirable for tensile measurements.
<table>
<thead>
<tr>
<th>PVAc-NC Device Thickness Measurements (µm)</th>
<th>Device Average (µm)</th>
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| Overall Average Thickness: 123± 29µm |

Table 2: Thickness measurements made on PVAc-NC devices. Average thickness of each device is given, as well as overall average and standard deviation.

It should also be noted that, although one goal of microfabrication was to create more uniformity in the beam structure, the nonuniformity issue remained as a consequence of the excess material that built up along the edges. Figure 34 shows devices made from laser-cutting and micromolding. The laser-cut device looks arguably
better in these images, as the excess material built up on the micromolded device is considerable. However, the excess material on the micromolding process can be eliminated with process refinement, whereas the laser-cut device is limited by the resolution of the laser printer.

Figure 34: PVAc-NC devices created with different methods; (a) laser-cut device; (b) micromolded device. Both devices have rough beam structures due to the limitations of each fabrication process.

3.2 Swelling Measurements

Although the dimensions of all tested devices were measured in the dry-state, it was important to know the average through-plane and lateral swelling of the devices for the wet-state testing, since the devices swell upon submersion in water and the dimension measurements are made prior to loading the devices into the microtensile tester. Thus, the thicknesses and widths of devices were measured before and after submersion in water for an hour. For the lateral dimensions, changes in the widths of the PVAc-NC devices were measured using the wide-beam devices that were specially molded for this purpose. The pads of the devices were secured between pieces of tape fixed to an acrylic frame so that the devices were fixed but the beam structures were left open in the middle. Because of the significant variation in the beams from one point to the next in previous
dimension measurements, the beams were measured at each end of the wide beam sections, first, so that two measurements from each device could be obtained, and second, so that there would be greater consistency in the wet-to-dry measurements because the end-points of the wide beams were the most easily identifiable positions under a microscope. The results of this test are listed in Table 3, below.

<table>
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<th>Wet-State (µm)</th>
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<td><strong>Average</strong></td>
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<td><strong>4.5±2.3</strong></td>
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Table 3: Lateral swelling measurements of PVAc-NC; measurements made of dry devices and devices saturated with room temperature (20°C) deionized water. Percent changes and average percent change are given.

The amount of lateral swelling is small but consistently evident. Assuming a mold beam width of 250µm, the resulting device beam would be slightly less. Given the average dry-state device beam dimensions of 240µm, if the devices expand 4.5%, then the dimensions when saturated would be 250.9µm. This exceeds the dimensions of an ideal mold, which would imply that an average device might expand into its mold while the wafer is submerged in water during the release process. This may explain some of the difficulty with the extraction method. Given this finding, it is possible that the reason the sacrificial layer did not allow self-release was the consequence of the devices
saturating and expanding into their molds quicker than the sucrose layer dissolved. To resolve this issue, a thicker or non-water-soluble sacrificial layer may be necessary.

For the through-plane swelling measurements, the devices were oriented vertically in acrylic jigs to hold the pads in place and leave the beam section free so that the thickness could be measured before and after submerging in deionized water. Average measurements of the wet- and dry-state thicknesses were taken, since there was no way to ensure measuring the same spot twice. Measurements were made along each beam in five different, random places prior to and after submersion. The results of these tests are listed in Table 4, below. The average percent change in thickness upon submersion was 15.9±3.6%, which suggests the material expands in the through plane more than in the lateral plane. This was not an expected result; devices made from laser-cutting were created from bulk material that had been compressed, so it was logical to expect some amount of greater swelling in the through plane than in the lateral plane. However, here we see a similar occurrence, though the difference is less extreme. For the compressed PVAc-NC, the lateral expansion was about an eighth of the through-plane expansion, whereas here we see the lateral expansion is about a fourth.

<table>
<thead>
<tr>
<th>Dry-State (µm)</th>
<th>Wet-State (µm)</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>138</td>
<td>162.8</td>
<td>18</td>
</tr>
<tr>
<td>121.8</td>
<td>145.8</td>
<td>19.7</td>
</tr>
<tr>
<td>148.1</td>
<td>165.9</td>
<td>12</td>
</tr>
<tr>
<td>106.5</td>
<td>121.3</td>
<td>13.9</td>
</tr>
</tbody>
</table>

Average % Change: 15.9 ± 3.6%

Table 4: Through plane swelling measurements for PVAc-NC devices. Average thickness measurements were made for four devices before and after submerging the devices in deionized water for an hour.
3.3 Batch Yield

The yield of the PVAc-NC batches over the course of this investigation were tracked. The device molds had cavities for a total of 43 possible 250µm-wide test structures, 21 of which were the straight-beam devices that would be used for tensile testing, and the remaining molds were for the wide-lateral beam structures. The straight-beams were the most difficult to extract and these were the ones most likely to break during testing, so production of these devices was the focus, and thus the yield of these devices was also recorded.

Of the fabrication methods that yielded any devices, those that required less material ultimately proved to have substantially higher yields of the test structures. The yield was substantially higher; from the batches of thicker devices, only a few of these devices could ever be extracted—three at most per batch. The batches defined as ‘thick’ included the ones where 70 or more layers of the regular PVAc-NC solution was used, or batches that used 35 or more layers of the thickened, partially-evaporated PVAc-NC solution. These thicker devices that were extracted also tended to break if any attempts to move them were made upon drying, so very few made it to the testing stage. In the case of the thinner devices, which used 40 layers of the regular PVAc-NC solution, many more of the devices per wafer could be extracted; after repeating the fabrication process five times, the yield was an average of 71.3%. The details of the yield success are given in Table 5.
Table 5: Percent yield of 40-layer PVAc-NC device batches. Discrepancies in total devices are due to damage of the SU-8 layer that rendered some molds unusable on a given wafer. *The number of devices for one wafer was decreased because two of the 21 molds were too visibly damaged to be used.

The numbers of devices extracted from the wafers were fairly consistent, with the exception of the last one with a yield of 47.6%. The quality of the molds progressively degraded after being used multiple times, which would account for the decrease in yield success. The SU-8 layers became scratched and worn; some examples of the damage done to the molds are shown in Figure 35. The molds that appeared to be in good condition were used multiple times, but it is likely that a number of these molds had residue from previous batches or other damage not immediately apparent that would have caused the devices to stick to the molds. These factors would have made subsequent devices more prone to breaking upon extraction.
Figure 35: Wear on SU-8 molds after being used to make devices a few times; (a) device mold with fractured corners. This usually occurs in the process of extracting devices. (b) mold is completely peeled off of silicon wafer. Once liftoff of the SU-8 layers starts, it leads to larger breakage over time, as shown here. (c) beginning of SU-8 liftoff from silicon. Devices cannot be made with these molds because PVAc-NC solution dries underneath the SU-8.

3.4 Tensile Testing Procedure

To test the dynamic behavior of the devices created using micromolding, the Young’s modulus of devices were measured in both the wet and dry states. The Young’s modulus is the ratio of the stress and strain, and consequently dependent on the force
required to deform the material (F) on the cross-sectional area (A), and the initial length (L₀) and change in length (ΔL):

\[ E = \frac{FL_0}{A\Delta L} \]

Therefore the width and thickness of each device beam were measured prior to testing.

The microtensile tester was the same that was built for testing the laser-cut probes that had established PVAc-NC as a viable material for intracortical probes. A schematic of the setup is given in shown in Figure 36. The apparatus consists of two stages on which each pad of the test device is clamped. One stage remains fixed, and the other is attached to a beam which is motion-controlled by a piezomotor with a stroke resolution down to 20nm. An indicator is attached to the mobile side as well, and it measures displacement of the mobile end, and these measurements are precise to 0.5µm and can record as far as 30mm. The load cell measures the forces applied to the sample in the process of elongation with a precision of 49µN and a range of 111N. The clamps were made from acrylic, as were a number of stability features added to the setup (visible in the photograph in Figure 37). The load cell, motor, and indicator were interfaced with a computer using the program DAQFactory, in which programs were designed to control data acquisition and motor functions while collecting data from the load cell and indicator [23].
Figure 36: Schematic of microtensile tester used for measuring force and displacement on the PVAc-NC devices, taken and modified from reference 23.

Figure 37: Photo of microtensile testing apparatus. The setup is predominantly made of acrylic. Visible are the piezomotor, load cell, and the connection point of the motion indicator, as well as the sample located in between the fixed and mobile stages.
For the wet-state tests, a reservoir was added to the microtensile test setup. The reservoir was made of acrylic and reinforced with PDMS to prevent leakage, and was designed to encapsulate the stages that held the sample in place while still allowing the full range of motion. The reservoir was also made deep enough such that the device would be submerged during testing. For these tests, the samples are loaded into the clamps in their dry, rigid state, and then room-temperature, deionized water is added to the reservoir after the device is fixed in place. This is done because the malleable nature of the wet-state devices makes loading them exceedingly difficult. Saturation of the devices is ensured by letting the devices sit in the To compensate for the material swelling that occurs, the width value is multiplied by 1.045 to account for the 4.5% lateral swelling, and the thickness value is multiplied by 1.159 to account for the 15.9% through-plane swelling.

Figure 38: Schematic of microtensile tester used for wet testing, taken and modified from reference 23.
The Young’s modulus was determined by fitting a linear model to the straight region of data points of the stress-strain curve obtained during the tensile test, as shown in Figure 39. At first pass, the data falls into a fairly large range for both neat and nanocomposite devices, the Grubbs’ test was performed to identify any outliers [40]. First, the Z-value was calculated for each data point, wherein the Z-value is determined by finding the difference between the data point \(x_i\) and the mean \(\bar{x}\), and dividing that result by the standard deviation \(\sigma\):

\[
Z = \frac{|(x_i - \bar{x})|}{\sigma}
\]

Then, the Z values were compared to the critical Z-values for 5% significance (determined using the method described in source 40), and outliers were identified as those data points whose Z-values were greater than the critical Z values.
Figure 39: Microtensile test data of PVAc-NC device. The Young's Modulus is found by measuring the slope of the elastic region of the stress-strain curve. The fitted line created in this example using Origin 8.0 indicates a Young’s modulus of 434MPa with a certainty of 99%.

3.4.1 Dry versus Saturated (Wet) PVAc-NC Devices

To validate the micromolding method of fabrication, it was necessary to show that the method effectively yielded devices with dynamic behavior. For this reason, devices were tested in both the wet and the dry states and the Young’s modulus was measured in each case. There was an obvious qualitative difference in the behavior of the material when observing the devices during the tensile tests; the wet devices exhibited
nonreversible, plastic behavior and often did not break for the duration of the tests, whereas the dry devices tended to break quickly, and often too early for data collection. Several devices were tested for both wet and dry states, and the results of every device are given in Table 6. A comparison of the data acquired for the wet and dry-state devices are shown in Figure 40.

<table>
<thead>
<tr>
<th>Dry-State</th>
<th>Wet-State</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (MPa)</td>
<td>E (MPa)</td>
</tr>
<tr>
<td>Z-value</td>
<td>Z-value</td>
</tr>
<tr>
<td>578.04</td>
<td>13.668</td>
</tr>
<tr>
<td>0.54</td>
<td>0.22</td>
</tr>
<tr>
<td>433.57</td>
<td>12.274</td>
</tr>
<tr>
<td>0.75</td>
<td>0.03</td>
</tr>
<tr>
<td>515.27</td>
<td>16.404</td>
</tr>
<tr>
<td>0.63</td>
<td>0.71</td>
</tr>
<tr>
<td>1281.1</td>
<td>19.897</td>
</tr>
<tr>
<td>0.48</td>
<td>1.33</td>
</tr>
<tr>
<td>816.2</td>
<td>14.294</td>
</tr>
<tr>
<td>0.19</td>
<td>0.33</td>
</tr>
<tr>
<td>461.73</td>
<td>7.391</td>
</tr>
<tr>
<td>0.71</td>
<td>0.90</td>
</tr>
<tr>
<td>610.31</td>
<td>3.0883</td>
</tr>
<tr>
<td>0.50</td>
<td>1.66</td>
</tr>
<tr>
<td>2592.2*</td>
<td>2.40</td>
</tr>
<tr>
<td>658.5</td>
<td>0.43</td>
</tr>
<tr>
<td>Critical Z: 2.29</td>
<td>Critical Z: 2.02</td>
</tr>
<tr>
<td>Mean: 766.76</td>
<td>Mean: 12.43</td>
</tr>
<tr>
<td>St. Dev: 389.47</td>
<td>St. Dev: 5.62</td>
</tr>
</tbody>
</table>

Table 6: Young’s Modulus (E) recorded in MPa determined from tensile test results. Z-values were determined for each data point and outliers are identified with an asterisk (*) and were removed from the mean and standard deviation calculations listed at the bottom of the table.
Figure 40: Stress-Strain curves obtained from wet-state and dry-state tensile tests. The saturated device did not break during the test, and the dry device fractured at a strain of approximately 0.03.

The Z-values for each data point are given, as well as the critical Z-values for each set of data. For the wet and dry-state devices, the critical Z-values are 2.02 (N=7) and 2.29 (N=10), respectively. These numbers were used to determine the presence of outliers in the data, of which one was found for the dry-state devices. After outliers were identified, the mean and standard deviations were determined for each group of data. For the dry-state devices, the average Young’s modulus was 767±389MPa, and for the wet-state devices, the average Young’s modulus was 12.4±5.6MPa. Although the standard
deviations indicate a fairly large range of variation in the devices, there is an evident
difference in the behavior of the PVAc-NC from the wet to the dry state, indicating that
dynamic behavior is achievable when these devices are created with the micromolding
technique. However, the quality of the devices remains an issue, as there is an obvious
lack of consistency in the measured Young’s modulus from one device from the next.

There are a few reasons for why the devices exhibited significantly varied
Young’s moduli; namely, the thickness and width measurements of the devices used in
the calculations were averages for each device. The point of fracture of a given device
may have had a substantially smaller cross-sectional area than its average dimensions
would have suggested. Although it would be possible to use the thinnest measurements
for thickness and width for each device rather than an average, because width and
thicknesses were measured separately there was no way to determine the true cross-
sectional area of a device at any given point. Thus, it seemed that an average would be a
better representation. In spite of this, the results were still quite inconsistent, which
suggests that the variation in the dimensions contributes to the variation in the measured
Young’s moduli.

It is likely that the dimensions of the anomalistic outlier with the Young’s
modulus of 2.59GPa may have been erroneously measured. The width of this device had
an average value of 141µm, which is uncharacteristically thin for a device made with a
250µm device mold. It is likely that the magnification on the microscope used for
measuring width may have been too great. It seemed that the two faces of the beam
structure were different widths, one being smaller than the other; if the smaller side were
face-up under the microscope, and the resolution were too high, then the device would
appear to only be as wide as that thinner side. To examine this further, the thickness and width of the device were changed to match the average device dimensions obtained earlier (240µm wide and 123µm thick) and adjusted the stress data to include new cross-sectional area. The resulting Young’s modulus was 1326MPa, and this value would have a Z-value that is acceptable under the constraints of the Grubbs’ test.

Another reason for the variation in moduli is the tendency of the devices to not be straight upon extraction from the molds. When the devices were pulled from their molds, they were still wet and consequently malleable, so they were laid on a silicon wafer surface to dry. Best attempts were made to flatten the structures and straighten them back into their prescribed orientation. This method was only marginally effective, and the resulting shapes were not necessarily ideal. Slight skewing of the device’s shape could have caused variation in the tensile test, as the beams were more difficult to align and the slight bends in the beams may have caused strain or stress within the material upon drying, which would have affected how the beams fractured during the tensile test.

3.4.2 Causes of Uncertainty in Young’s Modulus

It seems that dimensional uncertainty is the greatest source of error in the determination of Young’s modulus; the error from the tensile testing setup is negligible due to the high precision and resolution of the sensors involved. The dimension measurements of the beams, particularly the thickness, indicated a considerable amount of variability across individual devices. It is most likely that the dimension measurements did not accurately describe each device at the point of breaking during the
testing process, thereby causing the resulting Young’s modulus to be different from one device to the next.

Images of the cross-section of three device beams were taken using a scanning electron microscope (SEM). The images showed a notable nonuniformity in the profile that suggests the measured cross-sectional areas would not have accurately represented the real cross-sectional areas, and this would have skewed the final results. One of the cross-sections is shown in Figure 41, which depicts a rectangular profile that is folded on the sides; this folded material is excess material; the devices are too thin to completely fill the device mold—the one pictured is 43µm at its center—and some material sticks to the sidewalls and dries, resulting in the non-rectangular shape. Because the device is thinner than the depth of the well, this excess material cannot be scraped away from the device as can be done with the excess material that sticks around the edges of the SU-8 molds. The severity of the angles of the excess material varies from one device to the next; Figure 42 shows a device whose side walls are angled inwards. This variation in the angles could be the result of a few issues with the extraction process, namely scraping away excess material around the edges of the molds, twisting of the beams during extraction, and the need for prying the device out of the mold as opposed to a self-release method.
Figure 41: SEM image of beam with dimension measurements. Image shows significant nonuniformity in terms of thickness and curvature of the beam.
Figure 42: SEM Image of a second PVAc-NC device. This device appears to have a more angled profile, though still a notable discrepancy between the thicknesses at the center compared to the sides.

The difference in the profile from this device compared to the measurements made with the optical microscope is considerable. Because the thicknesses were measured by observing the devices from the side, the actual thicknesses were misrepresented by the height of the excess material built up on the sidewalls—the device
in Figure 41, for instance, is nearly 99µm on the side where the excess material has built up, but only 43µm at the center. The actual thickness of this device, then, is variable. It should also be noted that the width measurement in the image is not exact, as the device has an observable curvature, and the given width value of 193µm is thus smaller than it should be. If it is assumed that the width of the beam in Figure 41 is the average width of 240µm, then the actual width is approximately 20% greater than the measured width. Estimating the area of the two wings to be about 1800µm² each, the actual cross sectional area of the device would be roughly 13900µm². The measured cross-sectional area, on the other hand, would be around 19100µm²; this value is 37% greater than the actual area. Figure 42 shows a device where the sidewall features have a smaller angle of about 38º, which makes the wings appear shorter from a side view. However, the discrepancy in cross-sectional area from what would be measured on an optical microscope and what would be measured using the SEM image is still quite large; the estimated areas are 21200µm² and 13400µm², respectively, meaning the cross-sectional area used in calculations that would be 58% too large. It is apparent that the measurement method used to determine the beam dimensions was not accurate and that process refinement is necessary to make the beam structures more uniform.

3.4.3 Side-By-Side Comaprisson of Data Plots

In an effort to see if uncertainties in cross-sectional area was the only factor that caused the large variation in the Young’s modulus, all of the tests done on both wet and dry devices were directly compared(Figure 43). The offsets from all stress data were then subtracted to make all the y-intercepts converge at zero so that the spread of slopes would
be more apparent. Then, the stress data for each device was multiplied by its corresponding cross-sectional area, thereby making the graphs a comparison of force vs. strain instead of stress vs. strain. The graphs of the dry devices are shown in Figure 44 and the graphs of the wet devices are shown in Figure 45.

Figure 43: Original Young’s Modulus data of (a) dry and (b) wet PVAc-NC devices.

Figure 44: Slope data for dry PVAc-NC devices after offsets are eliminated; (a) Stress vs. strain data; (b) Force vs. strain data.
Figure 45: Slope data for wet PVAc-NC devices after offsets are eliminated; (a) Stress vs. strain data; (b) Force vs. strain data.

Unfortunately the spread of slopes for the force data did not fall into a narrower band than that for the strain data. The Grubb’s test was performed on these data to identify any outliers and to compare $Z$ with the stress-strain data. This information is listed in Table 7.
<table>
<thead>
<tr>
<th>Young's Modulus Data</th>
<th>Force Data</th>
<th>Young's Modulus Data</th>
<th>Force Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (MPa)</td>
<td>Z</td>
<td>F (N)</td>
<td>Z</td>
</tr>
<tr>
<td>2592.23</td>
<td>2.40</td>
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<td>0.85</td>
</tr>
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<td>1.39E-05</td>
<td>0.76</td>
</tr>
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<td>433.57</td>
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<td>658.50</td>
<td>0.43</td>
<td>1.96E-05</td>
<td>0.40</td>
</tr>
<tr>
<td>Average E: 949.31</td>
<td>Average F: 2.58E-05</td>
<td>Average E: 12.43</td>
<td>Average F: 3.24E-07</td>
</tr>
<tr>
<td>St. Dev: 684.15</td>
<td>St. Dev: 1.56E-05</td>
<td>St. Dev: 5.62</td>
<td>St. Dev: 1.43E-07</td>
</tr>
<tr>
<td>% error: 72.07</td>
<td>% error: 60.68</td>
<td>% error: 45.18</td>
<td>% error: 44.19</td>
</tr>
</tbody>
</table>

Table 7: Comparison of Z-values for Young's modulus (E) data vs. force (F) data; the similarities in the % error for both wet and dry devices indicates there is no significant difference in the overall variation when the area is removed from the data.

As is seen in Table 7, there are no apparent trends that can be used to characterize the data. The dry PVAc-NC device that had been at outlier with a E = 2.59GPa and a Z of 2.40 became acceptable when factoring out cross-sectional area, with a Z of 0.85. Meanwhile, other devices became notably more distant from the mean, such as the device with E = 1.281GPa, which went from having a Z of 0.48 to a Z of 1.39. Overall, the standard deviations of both wet and dry data sets did not substantially improve. If all Young’s modulus data is taken into account, including the outliers, the error for the dry devices is 72.1%, whereas the error for the force data is 60.1%. For the wet devices, the overall error changes from 45.1% to 44.1% with the removal of the area.

Evidently there is something else in addition to area that causes the wide range of values for the Young’s modulus. The factors other than the cross-sectional area that
would likely have contributed to the variation are the method of extracting devices and
the process of loading the devices in the test apparatus. To extract the devices, the molds
were submerged in water for the purpose of dissolving the sacrificial layer. However,
this submersion causes the devices to lose their rigidity, and the process of removing the
devices from the molds involves handling the devices such that the dog-bone structure
does not keep its flat, straight shape. Although it is attempted to straighten out the
devices by placing them on the flat surface of a silicon wafer, this process is not ideal.
The material has a sort of memory characteristic that causes it to maintain whatever shape
it dries in, so if the device does not dry perfectly flat, and if there are slight bends and
curves in the beam structure, then these defects carry through the drying process and the
resulting device is not ideal for aligning in the testing apparatus. Furthermore, the testing
apparatus does not have a stage designed to fix devices in the same place during every
test—it is up to the person performing the test to attempt to align the devices as straight
as possible on the stages. Although significant effort was made to keep the devices as
straight as possible, the devices were often too irregular to line them up adequately, and
therefore this process likely contributed to the spread of slopes in the force vs. strain
plots.
Chapter 4: Conclusions

A number of conclusions can be made from the development of the molding procedure and the results obtained from the devices made using the process. The collective data indicates that micromolding is a viable option for creating PVAc-NC intracortical probes that exhibit dynamic behavior from the dry to wet states. Though the process used to create the devices yields a great amount of inconsistencies in device dimensions and shapes, there is evidence that the method can be used to create functional probes. There is much room for improvement in the process; the numerical results suggest that a compression step is necessary. Compression would likely allow for more evenness in the device dimensions, as the deposition process without compression results in highly nonuniform surface features.

The deposition method used in the micromolding process could also be improved. The material was deposited in the molds by hand, and this typically resulted in overfilling and is likely the cause for the variation in thickness from one device to the next. There was limited regulation on the volume of material deposited in each well because the volume of a well is so small (less than a cubic millimeter) and the devices used for depositing the PVAc-NC could not dispense in small enough quantities. With each repetition of filling the wells, the volume of the well is decreased slightly due to the presence of dried material (tests indicated less than 2% of the original weight is left after the DMF is completely evaporated). In addition, each well is not necessary of the same thickness since the SU-8 layer is thicker near the edges than in the center as a result of spin-coating—because attempts were made to fill the wells up to the top, the thicker
wells would hold more material and would thus yield thicker devices. A precise volume deposition method would eliminate the overfilling problem, and could also allow for more consistency in the thicknesses of all devices, as equal volumes could be deposited in each well regardless of the well’s size.

Although the sucrose layer appeared to be effective enough to prevent the devices from getting stuck to the underlying silicon wafer, it seemed there were some problems with using sucrose as the sacrificial material. Instances were observed when the sucrose layer that had been baked onto a wafer would become more fluid-like after having the PVAc-NC squeegeed across the surface and left to dry in a vacuum. Although it was initially thought that this may be the result of a defective vacuum system, testing showed that sucrose crystals dissolve over time into DMF. Moreover, sucrose tended to dissolve when exposed to PVAc-NC solution, which also contains DMF. It seems, then, that some amount of the sacrificial sucrose layer would get redistributed when it comes in contact with the nanocomposite solution during device fabrication, and it is very likely that this sucrose becomes integrated into the device as the DMF is evaporated away. It was not possible to determine how much of the sucrose layer gets integrated into the polymer, as it is dependent on the ratio of DMF to sucrose, the behavior of the sucrose in the form of the sacrificial layer as opposed to the granules used in my test, flow rates, and the rate at which the DMF evaporation occurs and how that interplays with the dissolving of the sucrose. However, it is likely that at least some the sucrose becomes interspersed in the PVAc-NC material, and it could be impacting the material properties of the resulting devices. Furthermore, because the sucrose does not remain solid, it does not act like a
release layer and consequently may be the reason the devices do not release on their own in water.

Even if we assume that the sucrose sacrificial layer does work properly, it is a cause of other issues in the fabrication process, and the problems with it would be corrected with the use of an alternative sacrificial layer. Because the sucrose requires submersion in water, the devices are released in their wet form, which makes testing the material properties more difficult because the released devices are not guaranteed to be as flat and straight as they were in the molds. An alternative sacrificial layer would be preferred—one that does not require water to be released. Some kind of electroplating would be ideal, as it would ensure that the sacrificial layer is uniform everywhere, which would improve the uniformity, and the dry-state release would not allow the devices to shape-shift in the process.

The Young’s modulus of the PVAc-NC devices created using the micromolding technique is not immediately apparent, as the range of error for all of the devices is 46% or greater, depending on methods of analysis. Although the Young’s Modulus data for the dry devices yields the lowest error of 46% when outliers are eliminated, removing the cross-sectional area from consideration causes the outlying data to no longer lie outside the range of consideration, and therefore the Young’s modulus data cannot fairly represent an average device without the inclusion of all data sets, which brings the error up to 72.1%. When area is eliminated from the equation, the error becomes 60.1%, which is still too large to make any solid conclusions about the exact modulus value; however, the data does indicate that the dry devices exhibit a Young’s modulus at least one order of magnitude greater than the saturated devices. The cause of the wide range
of measured Young’s moduli is the variation in device dimensions, particularly the thickness, which cannot be easily measured without a high resolution method such as SEM imaging. Assumptions are made about the device dimensions that do not accurately match the profile of the beam structures in reality; the cross section is assumed to be rectangular, but because of the limitations on deposition and extraction, and because there is no compression in the molding process, the resulting cross section shapes are not rectangular and have decidedly smaller cross sections than the optical microscope measurements suggest. It is very likely that the material properties of PVAc-NC are entirely retained in micromolding as opposed to laser-cutting, but the limitations of the probes do now allow for accurate testing. Although microfabrication is definitely worth pursuing for creating intracortical probes, a more refined process is necessary in order to create more ideal test structures.
References


