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Improving Template-Based Nanomanufacturing of Carbon Nanotube Arrays Via Polishing Wet Etching Method

by
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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

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Abstract

Multifunctional carbon nanotubes (CNTs) enable novel ways of interacting with complex biological fluid environments, such as single living cells and tissues. It has been shown that vertically aligned carbon nanotube arrays can be utilized to deliver genes into cells with high efficiency. These arrays were produced through template-based nanomanufacturing, where chemical vapor deposition forms carbon nanotubes inside the pores and oxygen plasma and reactive ion etching (RIE) expose the tubes by selective etching. The same devices could be produced faster and cheaper by replacing oxygen plasma and RIE with mechanical polishing and wet etching. However, the biomedical utilization of CNT-based technology has been hindered by inconsistencies in fabrication of effective CNT arrays which can facilitate fluid transport and gene transfer. In this research, the polishing process of CNT arrays was examined to identify the source of variability in results and developing solutions to overcome the issues. To this end, the capabilities and limitations of the current polishing step was tested using multiple characterization techniques, different variables were investigated, several alternative techniques were developed and explored and the best solutions considering the current restrictions were proposed. The results of this study will contribute to building the platform for a consistent scaled up technology for probing multiple cells in parallel and providing substrates for wearable or implantable biological sensors.

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1.0 Introduction

All diseases and medical conditions except for trauma, have a genetic component [1]. In many cases, a true cure which can actually stop the disease does not exist. Currently available therapies usually just slow down the progress of the disease with so many side effects and extend the life span of the patients while reducing the quality of their lives. Also, every person has genetic mutations and perfect genome does not exist. Some gene mutations cause serious health conditions.

In this situation, gene therapy can be suggested as a comprehensive cure for most of these diseases [2]. Gene therapy is the transplantation of a normal gene in place of the mutated or defective gene in a patient's cell to correct genetic disorders. There are several approaches to gene therapy: a corrected copy of the mutated gene will be substituted; the mutated gene is deactivated; a new gene is introduced to patient's body to fight the disease. Due to the risky nature of gene therapy, it is still being studied to obtain the U.S. Food and Drug Administration (FDA) approvals to be introduced to the market. FDA scientists examine the product in terms of risks and efficacy and determine if the benefits can overshadow the side effects. FDA has approved three methods of gene therapy since August 2017 [2,3]. Two of these novel techniques train T-cells to attack the cancer cells. The third method is called Luxturna and is used to cure an inherited kind of vision loss resulted by mutation in a specific gene. Luxturna is the first FDA approved technique that is purely directed by gene therapy in which a normal copy of the gene (RPE65) is delivered to retinal cells.

The effectiveness of gene therapy is mainly dependent on the quality of techniques that are used for delivering gene into target cells in terms of safety and efficiency [4]. There are different

methods for gene transfection with their own advantages and disadvantages. Toxic, time consuming, costly and labor-intensive processes, accompanied with inconsistent efficiency have resulted in developing aligned nanostructures [5]. They can deliver biomolecules which are located on one end to the other end where the cultured cells are located through the lumens of carbon nanotubes. This method can ensure cell viability; however, long incubation time is still required, and the efficiency is not considerable yet. In order to increase the efficiency, assistive techniques such as electroporation need to be applied.

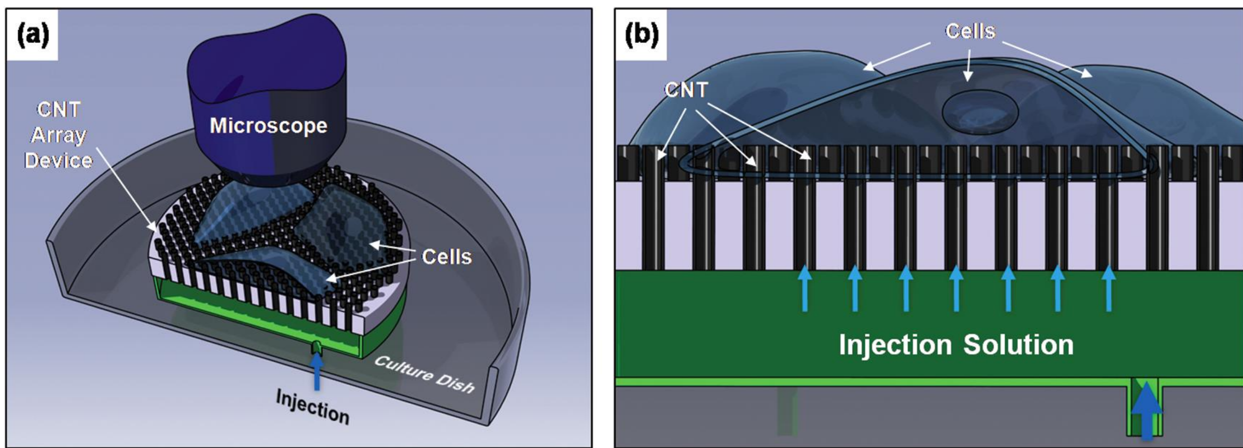

Figure 1: Schematic illustration of carbon nanotube array device for transfection of multiple cells in parallel (a) Top view (b) Side view [6].

A novel high efficiency version of this method was proposed by Golshadi et al. In this method, as shown in Figure 1, an aligned array of nano-structured tubes can transfect many cells at a time which results in increased efficiency with no need for assistive techniques [5]. Moreover, many issues such as lack of control on the transfected cargo, limitations on size and type of the cargo, toxicity and cost efficiency have been solved. Using Whatman anodized aluminum oxide membranes (Whatman Anodisc 13) with their porous structure, make it possible to form carbon nanotubes inside pores in a less complicated way. As indicated in Figure 2, making these nanostructured devices requires four main steps: annealing, chemical vapor

deposition (CVD), oxygen plasma, and reactive ion etching (RIE). Annealing and oxygen plasma are considered as a pre-step for their following processes. Annealing is done in order to make membranes stronger to avoid curling and deformation. Next, CVD forms a thin layer of carbon on the walls of the pores and builds a nanostructure similar to a carbon nanotube. By selectively removing carbon from the surface during oxygen plasma, membranes get prepared for the last step, RIE that selectively removes the template and exposes a specific length of the carbon nanotubes. These nanotubes make simultaneous transfection of different types of cargo such as macromolecules, DNA and nanoparticles into tens of thousands of cells. However, this method is limited due to dependency of products characteristics on physical parameters of settings and equipment, high cost and required time, especially time needed for RIE which inhibits the commercialization and hinders further research to be done on a larger scale [5].

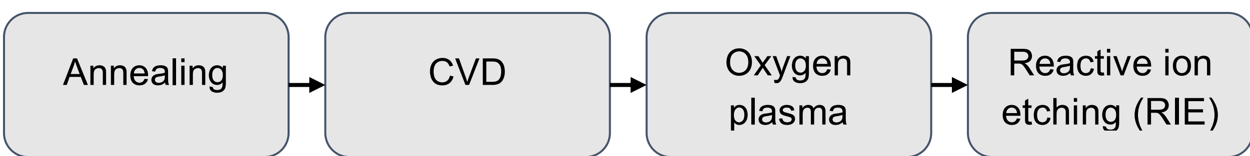

Figure 2: Nanomanufacturing steps of aligned CNT arrays using dry etching.

To overcome the limitations regarding time and cost-efficiency, an alternative method for manufacturing the CNT array was developed by substituting oxygen plasma and RIE with mechanical polishing and wet etching (PWE) to expose the tips of the CNTs [5,6]. Here, the coated carbon on the surface of the membrane and the top layer of AAO, known as the “Lattice

Layer" are removed by mechanical polishing, and the tips of the nanotubes are exposed by wet etching the template selectively.

The entire PWE manufacturing process can be summarized in 4 main steps (Figure 3): annealing, deposition, polishing and etching [6].

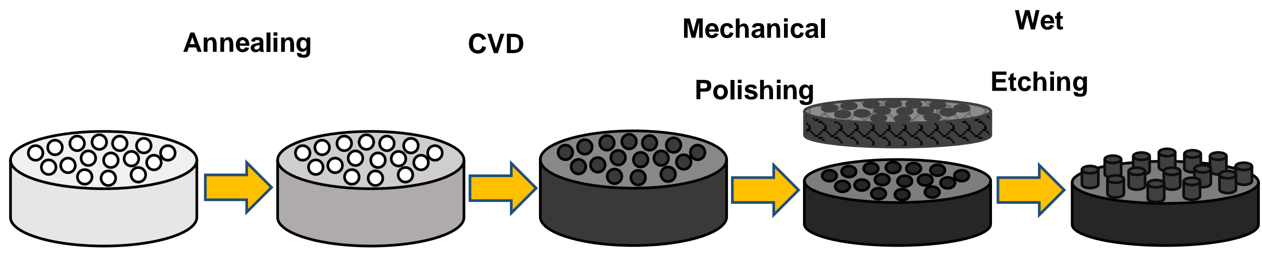

Figure 3: Schematic of fabrication process using PWE process.

The proposed method has proved to be effective in many cases; however, a major problem is the inconsistency and unpredictability of the results [6]. Comparing oxygen plasma-RIE and PWE methods, it is concluded that the first two steps of annealing and deposition cannot be the source of variability. Among the two remaining steps of polishing and wet etching, it has been observed that the irregularity in results mainly appears during and after the polishing process. Therefore, this research is focused on studying obstacles of consistency in the polishing procedures and provide solutions for an ideal manufacturing process.

2.0 Literature Review

2.1 Gene Therapy

To define in a few words, gene therapy is introducing a flawless copy of the gene into the necessitating cells [7,8]. In contrast with its simple definition, the technical issues especially associated with the sufficiency of number of correct genes in cells to fix the phenotype has made the progress of gene replacement therapy very slow. The phenotype of an organism depends on which genes are dominant and on the interaction between genes and environment.

Nowadays, with available information of genome structure, characterizing the origin of genetic disorders has become much simpler. Most of genetic disorders originate from single gene mutations and there are several hundred thousand of potential genetic disorders that can be potentially cured by gene therapy [8]. Gene therapy can provide us with treatments for many serious diseases such as Parkinson's disease, infections, and cancer. It can also help with application of viral vectors in vaccination. Most reliable methods in terms of repeatability of manufacturing and identified composition include synthetic components such as lipids or polymers to transport the DNA [9]. Inadequate efficacy together with viability uncertainty are considered as big challenges in these kinds of methods. Therefore, most methods that are considered useful for clinical applications have used viral vectors [8–10]. Viral vector method is used in 2 different ways: introducing the viral vector directly to the tissue or modifying the cells in culture then injection of the cell into the body. In this method, viruses incorporate their genome into the host cell and this way transfect the integrated genome to the daughter cell.

The key factor to a successful gene therapy process is improving gene delivery methods [4]. Gene therapy using viral vectors has caused problems such as immune issues [11]. Using non-viral vectors proved to show advantages in simplicity and higher possibility of mass production and eliminating undesirable immune responses. Non-viral method is generally divided in two main groups: first group involve physical processes by using naked DNA delivery, for example electroporation and gene gun and second group exploit a chemical delivery system like a cationic polymer or lipid.

Naked DNA is the DNA that is not protected by any molecules like lipids, proteins, etc. it is also known as unprotected DNA [4,11]. Using naked DNA has found popularity because it is the safest method. Naked DNA can either be injected directly to the tissues like skeletal muscles, liver, heart muscles, skin or tumor, etc. or be injected through the vessels for gene administration purposes. To solve the problems associated with low efficacy, such as low expression level and limited area after injection, several methods such as electroporation, gene gun (bio-ballistic), ultrasound and hydrodynamic (high pressure) injection can be proposed.

Electroporation is manipulating electric fields in order to increase gene absorbance after DNA injection through raising cell penetrability in this method electric field is applied for a very short time to create a cavity [4,12]. Electroporation can successfully be used in a wide variety of tissues and be used for immunization against different diseases like AIDS, Hepatitis B and tumor growth. Too much electric field strength may cause cell damage [4,13]. Moreover, local injection is not guaranteed to provide a uniform delivery system. Using syringe electrodes can use lower electric fields with acceptable efficiency and reduce the tissue damage considerably.

Bio-ballistic or gene gun exploits gold particles to diffuse cells directly through the cell membrane and has immunological applications [4]. However, the low permeability of DNA is considered as a disadvantage in this method.

Ultrasound is a safe method that can increase penetration of macromolecules in cells [4]. Combining ultrasound with microbubble can contribute to increase in gene expression efficacy due to the fact that ultrasound energy can decrease the energy needed for cavitation [4,14,15]. Therefore, it can be a good option for gene transfection to muscles and vascular cells [4,16].

Hydrodynamic injection is injecting high volume of cargo into cell in a short time and at a high pressure [4]. It can provide us with high rates of gene transfer in internal organs, especially liver which has high flexibility and special DNA receptors that can absorb DNA from solution before mixing with blood due to the hydrostatic pressure [4,17].

Chemical gene carriers, such as lipids or polymers, develop efficient methods for high gene expressions and are divided into four major groups: the first group protect the DNA against blood components by forming a complex shield around the DNA [8]. The second group are used to aim certain tissues to deliver cargo, the other group's goal is raise the delivery rate to nucleus and cytoplasm and the last group of these chemical carriers are responsible for DNA delivery in the tissue to obtain a controlled gene expression [4,8].

Vertical nanostructure arrays have recently found popularity in fields of biology, bio and chemical sensing and drug delivery [18,19]. The system consists of a vertical array of nano straws that is connected to a microfluidic device on one end and uses nano-electroporation to enable nondestructive transfection of plasmids and dye molecules with high efficiency [20]. Moreover, the intimate contact provided by nano-straws contributes to reducing the required

voltage and possibility of cell damage. However, a 24-hour interval is required for incubation and transfection yield is still low and for higher efficiencies, utilizing assistive techniques becomes necessary.

A novel CNT device was proposed that has the ability to support cell growth while providing highly efficient transfection in short periods of time [5]. This method is very efficient without using any complementary technique and can deliver a variety of materials such as macromolecules, DNA and nanoparticles to tens of thousands of cells instantaneously while ensuring their viability. Devices are manufactured using commercially available anodized aluminum oxide membranes (Whatman Anodisc 13, nominal pore diameter and thickness: 200 nm and 60 μm). Membranes are annealed to become resistant to high temperature deformation and then, carbon is deposited in the pores and on the surface of the membrane using chemical vapor deposition. Next, the carbon deposited on a side of the membrane that is intended to be used for cell culture is removed using oxygen plasma and then, by selectively etching the aluminum oxide template, tip of the CNT's was exposed to provide a suitable platform for cell culture. Moreover, this method has higher chances to be commercialized compared to conventional methods, since it can be done with common cell culture consumables and protocols. Fabricating 7 devices using this method, takes about 4 days to get higher quantities it is necessary to do process parallelization in large scale equipment, which makes the process even more expensive [5,6]. Moreover, the product characteristics are considerably dependent on physical parameters of the equipment such as size, voltage, etc. therefore, it is impossible to simply transfer the fabrication parameters to a larger scale equipment and obtain the same results.

To improve the process, the alternative method for etching can be replacing oxygen plasma-RIE with mechanical polishing and wet etching [5,6]. The alternative method suggests a significant reduction in the required time for etching step (6 to 12 hours reduced to 10 to 40 minutes (up to 98%)), eliminates the need for clean room facilities and reduces the cost and the dependency of results to physical parameters.

The current manufacturing process is done in four steps:

Step 1: Annealing

Commercially available anodized aluminum oxide membranes (Whatman Anodisc 13, nominal pore diameter and thickness: 200 nm and 60 μm) used as templates to form CNT arrays. In order to prevent curling and other deformation during subsequent processing, membranes are annealed in a high temperature furnace [6]. Membranes are sandwiched between two quartz plates and placed in tube furnace at 730 °C for 4 hours. The tube is open to atmosphere during the slow ramp-up, 4-hour annealing and slow ramp-down periods. Figure 4 shows heating and cooling cycles of the annealing.

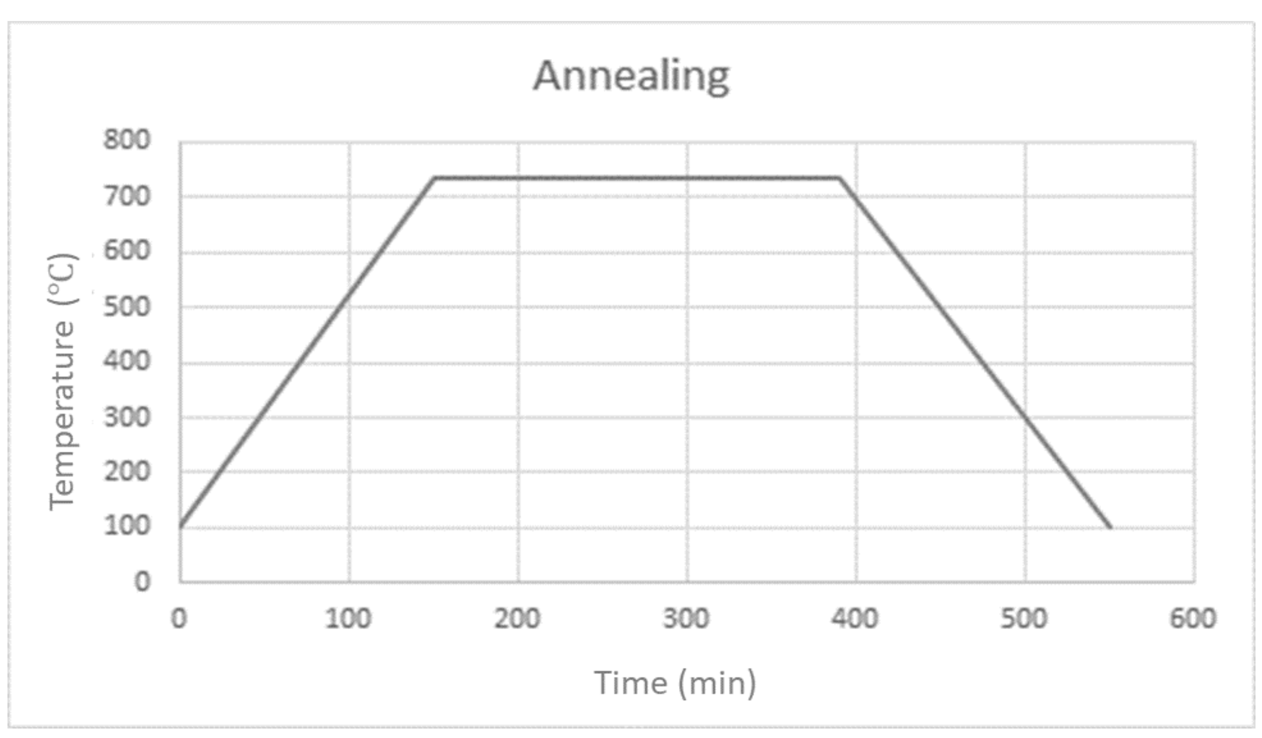

Figure 4: Stages of the annealing process.

Step 2: Deposition

Carbon is deposited on all surfaces of the membrane, including the pore surfaces during CVD. Seven annealed membranes are placed on the center of a CVD boat and the boat is put in the middle of a closed-tube furnace as shown in Figure 5 [6]. The closed furnace is heated up to 705 °C under flow of argon gas. The temperature is held constant for 5 hours under flow of ethylene gas, where the ethylene gas thermally decomposes and carbon deposits on the surface and inside the pores. After 5 hours, the membranes cool down under the flow of argon gas.

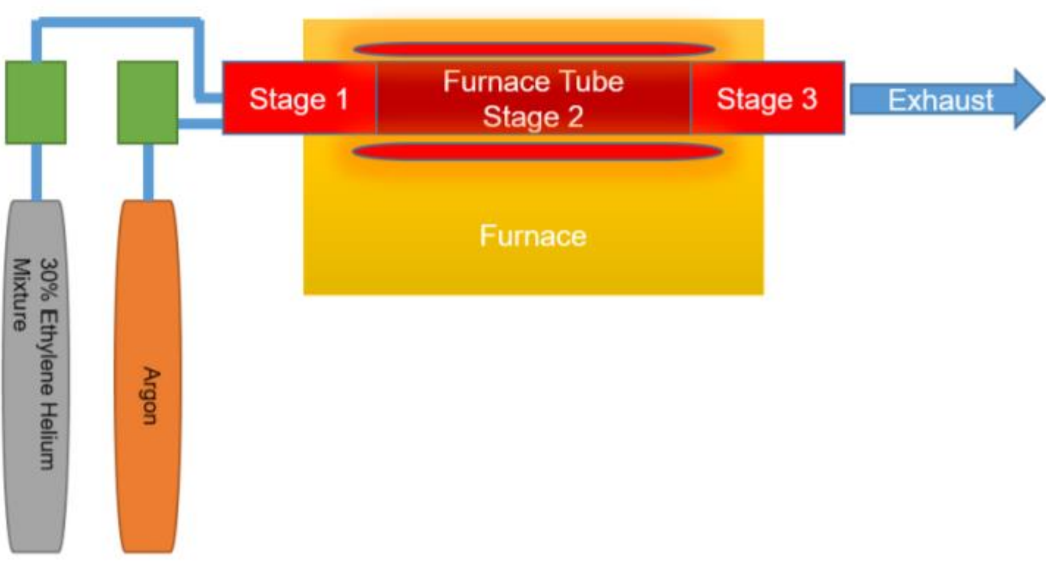

Figure 5: Schematic of CVD setup [6].

Step 3: Polishing

Mechanical polishing is used to selectively remove the carbon and lattice layer from top side of the carbon coated AAO membranes which is supposed to be utilized for cell culture [6]. First, the carbon-coated membranes are temporarily fastened to aluminum polishing stubs. Stubs are placed on a standard hotplate (Presider, 946 C) and heated up to 170 °C. Solid wax (J.H. Young Company Inc, 7036.61 Blanchard Wax) is applied on the stub by rubbing the wax bar on the hot stub. The membrane is then placed on the hot wax and tapped by tweezers to sit as evenly as possible on the stub. Subsequently, the stub with membrane is placed in water and at room temperature to cool down and temporarily attach the membrane to the stub.

Next, the top surface needs to be polished for removing the carbon on the surface and the lattice layer [6]. The polishing stubs with membranes mounted on them are placed in a commercial mechanical polishing machine (Struers, Tegrapol15) and are polished for 5 minutes

at 30 N and 150 rpm by using 250nm diamond slurry (Struers, DiaPro-Nap ¼). 4-5 droplets of slurry are dispensed consistently throughout the process. The polishing process often results in membrane damage (crushed or broken) or loss (being dislodged from the stub surface). The remaining uncrushed membranes are then unmounted from the stub surface using acetone, which dissolves the wax and breaks the bond to take the membrane off the stub. Membranes are then placed in acetone for 5 minutes to remove excess wax. A general schematic of the polishing process can be seen in Figure 6.

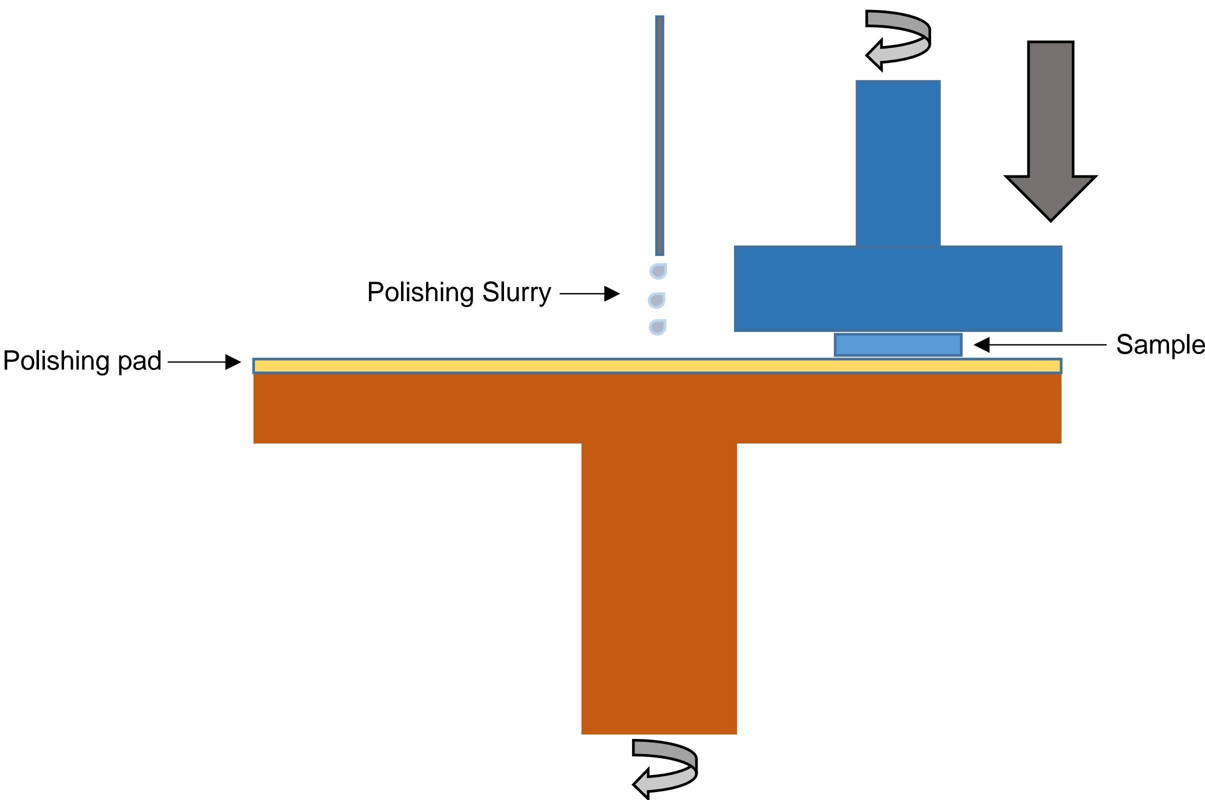

Figure 6: Schematic of the Mechanical Polishing.

Step 4: Etching

To expose the tips of the carbon nanotubes embedded in the AAO membranes, the polished surface is submerged in 1M sodium hydroxide for 5 minutes [6]. After 5 minutes, membranes are washed with DI water to stop the etching and remove residual sodium hydroxide. Scanning electron microscopy is then used to check the quality of the tubes and surface. The PWE method is simple, cheap and efficient and shown to be less time-consuming compared to using oxygen plasma and RIE. However, making every device work consistently has been a serious issue as many of CNT arrays manufactured this way were clogged which results in problems in microfluidic transport of cargo. Unfortunately, these issues hinder effective transfection through devices and endanger the viability of the cells.

2.2 Anodized Aluminum Oxide Membranes

2.2.1 Manufacturing

Using self-organizing methods for fabricating nanostructures has become popular due to inexpensive high production rate they can provide with no need for complex techniques such as electron exposure beams [21]. Highly ordered porous structure in aluminum oxide, known as "Alumite", can be produced using electrochemical anodic oxidation of aluminum. This material contains holes that grow vertical to its surface. These nano-holes which range from tens to several nanometers can be used as a template to make nanostructures [21,22]. These ordered nanostructures can be applied to many fields, for example, chemical sensors, electronics, functional biochemical membranes, etc.

Two types of oxide can be produced depending on the pH of the anodization solutions [23]. While solutions with pH values smaller than 5 create a uniformly insulating layer with no pores called "barrier-type film" (BTF), acidic solutions are able to produce a porous structure known as "pore-type film (PTF).

A well-arranged array of pores can be achieved with two steps of anodic oxidation of high purity aluminum [21]. Orderliness of the holes increases proportionally with the thickness of the oxide layer. After formation of the oxide layer, it is wet etched selectively with a mixture of H_3PO_4 and CrO_3 [22]. The phosphoric acid used in wet etching causes the enlargement of the holes. The bottom of the holes may get closed by a barrier-film of aluminum. The barrier layer is a hemispherical layer that is formed during anodization process with an even thickness and must be removed in most of the applications in order to get open pores. Among the proposed removal methods such as wet chemical etching, plasma etching and ion milling, wet etching has been known for being one of the hardest techniques to control for obtaining intact pores. However, due to the costly and slow process for small processable areas at a certain period, wet etching has started to get more attention since it is cheap, fast, easy and usable for large samples.

The size and geometry of the holes are dependent on the acids that were used in the self-organization process [21]. The regularity of the holes increases with time and acid concentration during the oxidation process. The size of the pores increases linearly with voltage. Moreover, the voltage that can provide the highest regularity in the arrays is determined based on the acid that is being used. Under a certain voltage, different acids can result in different pore sizes.

Another method to control the regularity of pores is using a silicon carbide mold with periodic high spots that form a pattern of ordered depressions [21]. The intervals between the indentation and the applied voltage are the controlling parameters in this approach.

There are several methods to exploit the porous alumina template to fabricate a nanostructure [21]. In semiconductors, selective etching is possible by using the porous alumina as a mask, using chemical vapor deposition (CVD), electroplating and sol gel to deposit functional materials in the holes and simulating patterns using the arranged pores as a template.

To deposit carbon in the pores of porous alumina template, the main concern is how much of the hole can be deposited using this method due to high aspect ratio of the holes [21]. It is suggested that for a reasonable deposition profile CVD can be done under a supercritical fluid which is a material above its critical point at which the gas and liquid phase are indistinguishable.

Depositing carbon on the pores, leads to manufacturing carbon nanotubes [21]. It is common to use catalysis for thermal disintegration of the precursor gases for producing CNT arrays using CVD of porous alumina.

Pore diameter and pore to pore distance can be determined by composition and concentration of the electrolyte, applied potential during the anodization process [22]. While, the distance between the pores and the thickness of the oxide barrier layer are mainly a function of the applied potential, electrolyte pH becomes responsible for pore diameter by influencing the dissolution rate of aluminum oxide.

2.2.2 Characterization

Uniformity and flatness of the aluminum oxide membranes are the key characteristics that influence the final product significantly. Achieving a uniformly polished surface consistently with a certain set of process parameters needs initial uniformity and consistency. To test the flatness of the membrane, optical profilometer was used to define the approximate thickness, curvature and surface roughness.

2.2.2.1 3D Profilometer

Characterizing the surface of samples is a crucial step to determine the effectiveness of the devices [24]. The initial technique to study the surface topography involved moving a cone spherical stylus with a diamond tip along the surface and measuring the vertical movements to understand surface variations. Non-contact optical methods presented relatively faster computations while avoiding possible damages to the surface due to the contacts. Measurements either can be done across a line which reports height parameters while moving laterally (surface profile measurement), or across a plane that height parameters of a plane are reported (areal surface measurement). Areal measurements are more accurate for the fact that they are able to capture more features of the surface and obtain a more detailed representation of the surface topography.

Chromatic confocal microscope studies every point on the sample using a confocal probe with lateral motion which allows profile and areal measurements by turning the extracted data to height and light intensity [24]. Chromatic confocal microscope data are not affected by external (environment) light and reflections from the sample; therefore, it has the advantage of fixed head

(vertically) over traditional confocal microscopes which used an internal source of vibration to produce vertical movements to measure the height parameters.

On a traditional confocal probe, the sample is placed on a vertical scanning system and intensity is measured based on where the focal point is located [24]. If the focal point is not on the surface, the reflected light does not reach the detector and intensity is perceived as zero; however, for the focal points that are located exactly on the surface the reflected light is received by photodetector and forms intensity peaks and by monitoring the vertical motions of the stage, the intensity can be related to height of the surface. By replacing the objective lens with a chromatic objective lens and the photodetector with a spectrometer the need for vertical scanning is eliminated.

Chromatic aberration is a property that causes the lights with different wavelengths to be focused at different spots which results in blurry images [24]. This property is usually tried to be avoided in most of optical applications. However, axial chromatism is used in chromatic confocal probe to create a relationship between every wavelength and each focal point on the vertical optical axis and subsequently the surface height parameters. Shorter wavelengths focus at a closer distance than longer wavelengths. The distance between the shortest and longest focal points is called “vertical range”. Higher vertical ranges can be obtained by decreasing frequency since more light reach the detector at lower frequencies.

The white light breaks into different wavelength along the optical axis through chromatic dispersion [24]. The wavelength that is in focus on the surface can reach the detector and produce intensity peaks. The wavelengths that are not in focus are either below or above the surface and cannot reach the detector. The spectrometer is responsible to recognize the

wavelength at which the maximum intensity can be captured for every measured point and the maximum intensity can be attributed to the height via calibrations. The highest intensity can be measured with different methods. For high frequency systems, the maximum of the curve can be considered as the highest intensity; however, the accuracy may not be sufficient. To increase the accuracy, a mathematical model can be fitted to the curve and the maximum of the model should be calculated to provide high accuracy (sub-pixel). Commercial probes might not be able to provide such an accuracy; therefore, for an optimized accuracy, centroid of the peak area can be calculated which still is able to provide high accuracy without needing special probes.

Calibration and Preparation for Measurement

Detectors are constantly receiving signals even when no light is reaching them through objective lens [24]. These signals come from the internal components of the microscope such as reflective lights from optical interfaces or noises of electronic parts including the detector itself. These signals are known as "dark level signals" and are included in every measurement and depend on the ambient temperature and internal temperature of the components which is a function of their clock rate. Therefore, it is crucial to measure and calibrate the dark level signal before any measurements in order to be able to subtract it from the acquired data.

Before data acquisition, probe should be focused on the sample, frequency should be adjusted to avoid too much, or little light and the probe should be in a certain position depending on the sample geometry and scan direction [24].

Prior to analyzing the data, the local defects in measurements need to be removed by eliminating the outliers using morphological filtering (remove form and levelling) and the non-measured points have to be compensated by filling in them (micro-roughness filtering) [24].

Method Limitations

Based on the calculations from the intensity curve the measured point can be a non-measured data, a correct data or an outlier [24]. The non-measured data includes the points that cannot be calculated using the spectrometers curve, the correct data is obtained from the curves that have distinguished intensity peaks which are sufficiently higher than the noise level and outliers are any data points that are neither a correct data point nor a non-measured point.

For a photodetector to work efficiently, the light intensity should not be below the noise level in order to get identified and not too bright to saturate the detector and make an outlier [24]. A flat mirror-like surface can cause the light to reflect outside the detector and the point cannot be measured. The material can either make the light intensity too low or it can be too shiny to saturate the detector and result in a non-measured point or an outlier. However, these issues can be addressed by changing the measurement frequency as it influences the light intensity that is received by the detector inversely. Processing the data after measurements are necessary to eliminate non-measured data. Although, too many of these points indicate that the probe was off the sample area.

A noise level which is well higher than the limit may yield to a misread peak [24]. The peak calculations may also get manipulated by a false reflection or other types of aberrations. Multiple peaks can be produced due to interferences or transparent samples. Moreover, inherent curvatures in the samples lead to unoriginal peaks due to ghost reflections.

Transparent samples with significantly smaller thickness than the probe range may result in interference between upper and lower surfaces which creates a falsely modified data point [24].

For surfaces that are locally spherical, a virtual focal point might be created for which a mirror-like surface will result in outliers that are known as ghost foci.

2.2.2.2 Scanning Electron Microscopy

Scanning electron microscope uses an electron beam to study the structure of bulk specimens on or near their surface [25]. Electrons interact differently with various features of the specimen. When the primary electron enters the specimen, it can be scattered elastically or inelastically. Elastic scattering happens when the electron does not lose energy significantly, although its direction might change. Inelastic scattering causes the initial electron to lose energy. Increasing the thickness will cause more than one inelastic interaction to happen which either result in stopping the electron due to energy loss or leaving the sample because of backscattering.

Secondary electrons are the initial electrons which have not lost all their energy and are able to find their way out of the sample with their small remaining energy [25]. If the consumed energy is not as high as the energy used by secondary electrons, the escaping electron is known as a backscattered electron. Backscattered electrons are not as frequent as secondary electrons as they conserve higher energies.

Scanning electron microscope uses all the different types of electron interactions with the sample to produce contrast in the image and obtain information on the specimen [25]. The volume in sample that an electron can diffuse is called “the interaction volume” and only the electrons that are able to leave this volume after entering it get detected. SEM images can provide us information on surface topography and composition of the sample. While secondary electron coefficient (number of secondary electrons from an incident electron beam) is more sensitive to electronic properties of the surface the backscattered coefficient (number of

backscattered electrons emitted from an incident beam) shows more sensitivity due to changes in atomic number.

2.3 CNT Array Manufacturing Method

In this section the steps of proposed method for manufacturing CNT arrays using mechanical polishing and wet etching is studied to obtain a better understanding of each process and its effect on the final product. Variables and their influence for each processing step has been studied to provide us with the tools for experiment design.

2.3.1 Annealing

Annealing is the first step to prepare our membranes for further processes [5,6]. Annealing is a heat treatment process in which the material is heated to an elevated temperature and cooled down slowly [26]. During this process, microstructure of the material reforms, the internal residual stresses relieve, and the material becomes more workable by increased toughness and ductility. Due to specific changes which are mostly microstructural, the mechanical properties alter.

Each annealing heat treatment consists of 3 main stages: (1) heating up the material to a specific temperature, (2) keeping the material on that temperature and (3) cooling down to room temperature [26]. During annealing, a gradient of temperature is created between external and internal part of the material and the magnitude of this gradient is dependent on size and geometry. Therefore, the rate at which the temperature is ramping up becomes a key factor, because if the rate is too high, the growth in the internal stresses and magnitude of the temperature may cause warp and nucleation of a crack in the piece. Moreover, sufficiently long

time is needed to complete any transformation. Because of the diffusional nature of the annealing process, temperature plays an important role in it.

2.3.2 Chemical Vapor Deposition

Chemical vapor deposition is widely used in materials processing and its main application is in depositing thin films on surface of materials [27]. Moreover, it is used to produce high purity bulk materials or powders. Chemical vapor deposition is done by heating pieces and flowing precursor gas which goes into reaction near the hot surface and deposit a thin film on that. Then, by-products and unreacted gases are exhausted out of the chamber. The temperature varies usually from 200 to 1600 °C. Chemical vapor deposition has some advantages over other thin film deposition methods such as forming conformal films, high purity, relatively high rates of deposition, and it also does not require high vacuum like physical vapor deposition processes.

By using proper templates, chemical vapor deposition can produce carbon nanotubes [28]. In template-based CVD, carbon is deposited on a sacrificial surface which is the template by breaking the precursor gas into carbon. The product properties are dictated either by process parameters or template parameters. Length and outer diameter of the nanotubes are determined by template, while wall thickness and deposition rate are functions of the CVD process. Carbon nanotubes that are produced using this method are amorphous and due to the solid template, the need for nano-assembly is eliminated. In general, chemical vapor deposition kinetics is very sensitive to changes of the temperature and reaction rates of the precursor gases and time of deposition plays a very important role in determining the thickness of the walls.

2.3.3 Mechanical Polishing

Polishing is considered as one of the oldest fabrication processes [29]. There are four main components that influence the polishing mechanism:

1. Workpiece: the aim of polishing is to transform the workpiece into the desired structure. The work piece properties can differ throughout its dimensions. These variations can be either discrete or continuous. Lateral variations may be caused by different materials, phases or grain orientations and range from scale of nanometers to millimeters.

Depth variations is either caused by various bonds from surface to the bulk which is inherent for each material or is caused during manufacturing processes like CVD and PVD which may cause density variation of material deposited on the surface [29].

One of the variables is chemical composition of the workpiece that can vary due to different chemical bonds [29]. Purity of the workpiece is another factor to be considered because different materials can be subject to different polishing regimes.

2. Fluid: properties of fluid part of slurry can influence material transport and fluid dynamics [29]. Density, viscosity and thermal conductivity are some of these properties which are functions of temperature, pressure and sometimes chemical composition.

The fluid can contain acids, bases or buffer systems in order to control the pH (since surface properties can alter for some materials in different pH values) [29]. Also, in CMP (chemical mechanical polishing) fluid may contain active ingredients in addition to secondary ingredients such as inhibitors, or physically active additions like surfactants.

3. Solid Granules: solid particles in slurry take part in mechanically polishing the material from the surface [29]. These particles can be characterized by their concentration, chemical composition and geometry (size and shape). In terms of chemical composition, the granules can be multi-phase, single or polycrystalline, and may vary in purity. Regarding geometry of the particles, average size and size distribution are two parameters to be considered. Size of slurry particles vary between tens of nanometers and microns. For a given concentration, a slurry of small particles contains more particles than a slurry with larger particles. Moreover, agglomeration can occur with small particles which changes both average size and size distribution. Fracture of particles during polishing can also occur which affects the size and shape of particles. Particles can be spherical, elliptical, cubic or sharply fractured.

4. Concentration can play an important role in case of CMP or have an insignificant effect in some other cases and can be defined by weight percentage of particles per volume [29]. However, weight percentage can be confusing since it is unable to define active particles participating in polishing process.

One type of polishing is the free abrasive polishing which is a finishing process that uses hard particles between flexible polishing pads on a rigid plate or a soft metal wheel [30]. In this type of polishing, abrasive particles which are harder than at least one of the surfaces roll and slide between the surfaces and wear at least one of them away via abrasion. The initial theory about abrasive polishing was surface abrading with fine abrasive particles which wear away the surface roughness and replacing it with a smoother surface. Beilby put some doubts on this theory and proposed another mechanism in polishing. He believed that in polishing the depressions of the rougher surface are covered with a layer of smoother surface and this layer under surface tension passes through the liquid state and solidifies amorphously but to date no

evidence could prove this hypothesis. Current evidence proves that the dominant mechanisms in free abrasive polishing is plowing and cutting.

One way to measure the depth of wear for depths more than 0.5 micron is to measure the weight of workpiece before and after polishing [30]. For depths that are less than 0.5 micron, a micro indentation technique can be used to measure the depth of indentations before and after polishing. The roughness of surface can be measured by a non-contact optical profiler and examined by optical microscope.

Particle size, polishing pad and contact pressure are the important factors in determining the polishing rate [30]. The wear rate is proportional to contact pressure but the wear increasing rate decreases as the pressure goes higher. Contact pressure can have different effects on roughness of the surface depending on the workpiece material.

Surface roughness is mostly a function of particle size and polishing pad hardness and it is almost independent of contact pressure [30]. Particle type can have a significant or negligible effect on the surface roughness and wear rate depending on the structure and composition of the workpiece. Generally, larger particles and harder pads produce more abrasion. Larger particles also result in a rougher surface, however smaller particles may agglomerate and leave some blemishes on soft surfaces which reduces the surface smoothness. In case of hard work piece, diamond slurry due to higher deformation resistance, compared to Al2O3 slurry, is able to yield a higher wear rate together with a smoother surface.

In polishing the material is pressed down to a polishing pad and rotate around its own axis, due to this relative rotational motion, force and hard slurry particles, the material removing from the surface occurs [30]. The greater rotational speed causes an increase in centrifugal force

which causes escaping of slurry from the polishing pad. This removing process becomes challenging when the uniformity finds importance. We can mention, type and size of the slurry, polishing pad, and rotational velocity as factors that have an impact on this homogeneity [30–32]. In general, to get the desired surface out of mechanical polishing, there are some determining parameters such as slurry flow rate, friction force, force applied (pressure), time, rpm (velocity), lubrication, consumables such as size and type of the slurry and polishing pad which play an important role in material removing process and should be optimized.

Mechanical Planarization

Planarization means minimizing the thickness variations of each layer in order to achieve minimal topography [33]. Topography is defined based on the non-planarity of the surface which can be intensified by adding layers to the surface. One method to planarize a surface is filling the low spots and other is removing the high spots. CMP stands for chemical mechanical polishing which initially was applied to optical glass and wafer polishing. It is a global planarization technique which is referred to a technique that achieves surface uniformity by decreasing the step height across the surface. The usual CMP tool is a polishing machine which develops a certain pressure and a relative motion between the wafer carrier and polishing pad while using an abrasive slurry to remove materials from the surface. The polisher movement is defined by the manufacturer and it can either rotate the wafer carrier or the platen or both. CMP can achieve uniformity very fast by removing the high parts to get to a specified flatness and it can be used for a wide range of materials.

The efficiency of the CMP process is defined by two terminologies [33]. On one hand, “Planarity” determines the surface topography differences that range from microns to

millimeters. On the other hand, “Uniformity” measures the thickness differences that vary between millimeters to centimeters. According to these two definitions a wafer can be only planar, uniform or both. The uniformity can differ between various planarized areas. To describe wafer nonuniformity we need to consider within wafer nonuniformity and wafer to wafer nonuniformity. The former describes the thickness variations across a single wafer while the latter indicates the thickness variations in multiple wafers.

Consumables in a CMP process are slurry and polishing pad. Slurry is a mixture that contains abrasive particles that are used to remove materials [31]. It is critical to control the mixing of slurry to have consistency from wafer to wafer and from batch to batch. Uniform distribution of slurry on the wafer also needs to take into consideration. The quality of slurry has a direct effect on getting a surface with minimized surface scratch.

Polishing pads are usually made of polyurethane and have a porous and sponge-like structure which helps to keep slurry inside them [34–36]. While we expect a uniform polishing rate, random irregularities on the pad surface cause unequal force distribution on the wafer and poor polishing quality. Commercially available polishing pads cannot be used directly with the wafer due to the fact that the smooth surface of the new pad results in a significant difference between the first polished wafer and the other wafers with the same polishing parameters. Break-in is a process of conditioning the new pad and polishing several dummy wafers to get to the steady-state polishing condition. Break-in process provides us with a consistent roughness while exposing the internal pores of the pad. After a pad is consumed in several polishing processes, it starts to flatten, this incident which is called “glazing” results in losing pad ability to hold the slurry which reduces the polishing rate significantly. To delay the glazing polishing pads are regularly conditioned to recreates roughness on the pad surface and provide a uniform polishing

rate during the pad life. Pad conditioning is defined as increasing the roughness of the pad surface and can be done using mechanical abrasion or water jet. Pad conditioning is an effective factor to increase the pad life [33–35].

In some processes multiple polishing pads are stacked to obtain a desirable hardness and softness [33]. In general, maintaining polishing pad properties is a challenging process and of high importance since it directly influences the repeatability of the results. Hard pads provide local polishing by skipping he lower spots and removing materials from higher spots which creates more polishing at high points compared to lower areas. Soft pads are useful for minimizing the scratches.

Polishing rate is the pace at which the material is removed in the polishing process [33]. Increasing force and rotation speed will result in higher removal rate in a trade off with surface smoothness and uniformity. On one hand, increased force may cause surface damage and contamination with hard pads and on the other hand, it helps increasing wafer to wafer uniformity. In general, it is suggested that hard pads work the best with lower forces. Higher features are under higher pressures and are polished faster while the lower parts face smaller pressures which results in less polishing rate. These differences in polishing pace can affect the CMP results adversely.

The rotational forces along the surface of the wafer drives more slurry to the edges and higher polishing rates are observed at these areas (referred to as center slow tool) [33]. To make up for this effect, some manufacturers apply back pressure using N_2 or give the carrier a slight convex shape to get the center higher and achieve more pressure at the center.

Polish time has a direct dependency on the thickness to be polished [34]. In order to reduce polishing time, we need to minimize the thickness of the material that was deposited prior to polishing step referred to as “overburden”, while keeping enough thickness to achieve planarity. Polishing time should be defined based on the thickness and the planarity level. The force and plate speed are chosen depending on the desired removal rate and nonuniformities. The carrier speed influences the nonuniformity directly.

Challenges

The challenge in an efficient polishing process is to control the interaction of many influential parameters on planarity and uniformity. Parameter optimization should be done differently for each application.

Two types of nonuniformity can be seen on the surface of the wafer [33]. first type is when the center is being polished faster than the area around it and the second type is when center is polished slower than the area around it. Inappropriate pad contour, as a result of overly worn pads, plays an important role in this issue. Unsuitable choice of force, speed, slurry flow rate and viscosity are the other reasons for the nonuniformity. Moreover, deformation of backing film on the sample holder prevents providing a flat surface to begin the process with.

Glazing of the polishing pad might happen when the pad is being excessively worn out. pad conditioning and break-in is necessary to get a consistent polishing process. pads need to be conditioned under proper parameters regularly and need to be replaced on a regular basis [33,35].

Large slurry particles may be created when dried slurry particles agglomerate and mix with slurry or agglomeration may happen in the slurry itself or the slurry quality might be poor to

begin with [33]. This issue can be addressed by real-time filtration or using stabilizers or higher quality slurries.

2.3.4 Wet Etching

Etching is a process in which undesirable areas of the materials get removed [36]. Etching can be done in mainly two forms of wet etching and dry etching. Dry etching is basically forming unstable products is reaction with plasma gases. Wet etching is dissolving undesirable materials using a chemical solution. In wet etching an etchant is used to remove materials by consuming the initial reactants and producing new reactants. Wet etching has 3 main steps:

First, the etchant liquid diffuses into the material that is going to be etched away. Secondly, the etchant goes into a reduction-oxidation reaction with the material, oxidizes and dissolves the oxidized material. Lastly, the byproducts of the reaction diffuse from the surface.

Etching rate can be defined as the removed thickness per time unit and it is a function of etching time, etchant solution and its concentration, temperature and agitation, composition and structure of the material (porosity, purity, etc.) [32]. Among the mentioned parameters agitation and concentration are hardest to control due to constant changes during the wet etching process.

Etching either removes the material uniformly in all directions that is isotropic etching, or it happens only in vertical direction which is anisotropic etching [33]. While wet etching involves merely isotropic etching, dry etching offers a great control on the thickness of sidewalls in anisotropic etching, good uniformity within a wafer and from wafer to wafer and results in reducing cost of chemical usage and disposal. A method to determine the etch uniformity is

selecting certain number of the samples, measuring etch rate in specific spots and compare the uniformity for each specimen and for all samples.

3.0 Research Objectives

To have a good estimation of the polishing procedure and obtain a better understanding of the origins of variability, it is necessary to repeat the suggested procedure and compare the results. Answering questions about repeatability of results and how different factors such as operator's skill and other variables influence the product is the main focus of this research.

Repeating the process provides us with a good understanding of the factors that need to be studied to improve the manufacturing process. After identifying the source of variability in results, testing several alternatives for materials and methods is necessary to determine an optimized process with maximized consistency and efficiency.

A major part of this research has been dedicated to exploring faster and more cost-efficient testing techniques and instruments to get more consistent and effective results. Finding efficient quality testing techniques that can provide us with an early detection of possible defects is a critical step in time and cost saving.

The other issue that has been addressed is minimizing the influence of variable factors such as operator's expertise. To this end, every step was closely observed and studied, alternative methods were proposed, tested and proved to be useful to the process improvement.

4.0 Experimental Methods

Several materials and methods were tried in this project to optimize the results. This section introduces each of them for the reference of next chapter on experiments. Materials and methods used are ordered and explained by the stage they are used at.

4.1 Annealing: Materials, Tooling and Process Description

The first step is annealing AAO membranes to increase their resistance to deformity due to high temperature process of CVD. Whatman Anodisc inorganic filter membranes are made of high purity aluminum oxide and are produced electrochemically. They have a highly ordered and packed porous structure. The nominal pore diameter is 0.02 µm. Membranes are nominally 60µm in thickness and 13mm in diameter. They are autoclavable, hydrophilic and compatible with most contains no additives which may cause sample contamination and they are optically transparent. Their porous structure and regularity of the pores make them a proper template to grow nanostructures inside them.

Each time, 14 membranes are sandwiched between two quartz plates and put in a closed-tube furnace. These plates are made of quartz and are suitable for high temperature applications. The weight of this plates works to prevent deformation of the membranes at high temperatures during the annealing process. During annealing, the membrane becomes resistant to possible curling and quartz plates will not be required in the next steps.

The reactor that is used to provide the temperature is a three-stage tube furnace (Carbolite, TZF17/600) with inner tube diameter of 7 cm and tube length of 152 cm. The furnace in this process is not capped and the process is done in the atmospheric pressure. is heated up to 730℃

and the annealing process runs at this temperature for 4 hours and then the furnace is cooled down to 100℃. Considering the heating and cooling time the whole process takes about 10 hours to be done.

4.2 Chemical Vapor Deposition: Materials, Tooling and Process Description

CVD process has been done with 7 annealed membranes placed in the center of a custom quartz boat that is used to hold the membranes upright and perpendicular to the gas flow in the middle of a closed-tube furnace. CVD process consists of 3 sub steps and takes approximately 11 hours for 7 membranes. The reactor used in this stage is the same as the one used for annealing process (Carbolite, TZF17/600, three-stage furnace). However, in the CVD process, furnace is capped with the quartz boat in the middle of the furnace.

The first step is heating up the furnace to 705 ℃ under high purity argon gas to purge the furnace and remove the oxygen. Second step is carbon deposition for 5 hours under the flow of a 30/70 (vol %) Ethylene/Helium gas to proceed with the reactions required for the carbon deposition. The third and last step is cooling down the furnace under high purity argon gas.

4.3 Mechanical Polishing: Materials, Tooling and Process Description

In our manufacturing method, mechanical polishing is a surface finishing process that is considered crucial for next stage, wet etching. After annealing the membranes and depositing carbon on them, they are polished during a mechanical material removal process. Mechanical polishing by removing the undesirable lattice layer helps to reduce the required time for wet etching. In absence of mechanical polishing, wet etching needs to be done much longer that causes the template to corrode unevenly and finally results in the collapsing of the tubes. Using

mechanical polishing provides us with a surface free of lattice layer and makes us able to shorten the time of wet etching and expose a certain height of the tubes without having them collapsed as a result of over etching. The polishing process contains of three sub steps of mounting membranes, polishing the mounted membranes with polishing machine and detaching them from the stubs.

A steel bar with the diameter of 30.2 mm was cut in pieces with 7.6 mm height and polished to be used as a holder for membranes in the polishing process. To attach the membranes to the steel mounting stubs, stubs are heated up to 170℃ using an electronic hotplate. The hot surface of the stub is then used to soften the 7071 Blanchard holding wax bar (J.H Young Co.). Wax bar is rubbed on the hot surface of the stub and melts. Then, the membranes are put on the wax and tapped by the tweezers to get the membrane flat on the stub, stubs are then cooled down quickly in water and the melted wax solidifies. The extra wax around the membrane and on the stub is then cleaned by rubbing the stub on a Kim wipe that has acetone on it. The time consumed in this part is variable depending on operator's skill to get the membrane even and flat on the stub. A variety of other adhesive materials including double-sided conductive carbon tabs (usually used as adhesive for SEM samples), ParaFilm, double-sided pressure-sensitive silicon-based tape and double-sided flexible foam tape (Martin Senour) were also tried to provide a sufficiently strong and uniform attachment between the membranes.

Two polishing machines were used during this process both manufactured by Struers: Tegrapol-15 and Laboforce-100. Tegratol-15 is able to fit 3 and Laboforce-100 6 stubs at a time. The polishing process was done with different parameters including speed, force and time with water-based diamond suspensions with different particle sizes manufactured by Struers (DiaPro). The suspension contains cooling lubricant which provides proper amount of lubrication during

the process. Circular polishing cloths with 300mm diameter (MD-Floc) and (MD-Nap) manufactured by Struers were used in the material removal process via mechanical polishing.

In detaching the membranes, the stubs with membranes on them are reheated with the hot plate to 170℃. Then, high purity acetone (>%99.9) is used to dissolve the adhesive and detach the membranes from the stub and also for removing any residues from mounting and polishing process from the membranes.

4.4 Wet Etching: Materials, Tooling and Process Description

The last step is wet etching the polished membranes. A 1 Molar solution of sodium hydroxide is made using reagent grade sodium hydroxide pellets and DI water. The solution is then poured in 3 different dishes, and membranes are put in the solution for 5 minutes and a gentle motion is also applied. After 5 minutes the membranes are placed in distilled water for another 5 minutes to stop the etching process and get rid of possible etchant in pores. The etching process takes 10 minutes for 3 membranes.

4.5 Characterization

To improve the consistency in polishing it is important to understand what happens during every step in this process. Optical microscopy and 3D profilometry were used to characterize the membranes and test their flatness and roughness changes after each step. Moreover, membranes were imaged using SEM to check the quality of the tubes after polishing and confirm the results that were obtained from optical profilometry.

4.5.1 Optical Microscope

Carl Zeiss optical microscope was used to measure the thickness of the membranes at the cross section.

4.5.2 3D Optical Profilometer

NANOVEA ST400 profilometer uses axial chromatism to provide us with data on the surface characteristics like roughness. These data are used to study the effect of different parameters on the product of polishing.

4.5.3 Scanning Electron Microscopy

Tescan Mira3 scanning electron microscope is used to provide us with a high resolution and magnification of nanotubes, their uniformity in size and shape and also tube blockage. The results from different characterization methods are expected to support each other.

5.0 Results and Discussion

5.1 Determining the Consistency of the Current Manufacturing Method of CNT Arrays

To determine the consistency of the initially recommended procedure, the exact proposed steps by the last operator were taken to verify that the results can be reproduced. Moreover, the time consumed in each step was carefully measured for further studies on scaling-up possibilities. Annealing and CVD steps are consistent steps and they take 16 hours for 7 membranes. However, polishing step is where the variability starts to appear. The number of membranes that are perfect and polished after polishing differs depending on the mounting quality and tegrapol-15 stability and polishing process takes 5 minutes to be done. The last step is wet etching the polished membranes which takes 10 minutes and shows a good consistency. In total, for getting possibly three membranes and due to uncertain efficiency of polishing process, we need in average 17 hours. However, the process seems too inefficient considering the time consumed and inconsistency. The variability is observed after the polishing step which makes this step responsible for the inconsistency. The next steps are experiments which are designed and conducted to revise the materials, tooling and method used during the polishing process.

5.2 Determining Responsible Factors for Inconsistency

Repeating the same procedure revealed that main problem appears after polishing step. In many cases crushed or totally detached membranes were observed after 5 minutes of polishing. The faulty samples after polishing are showed in Figure 7.

Figure 7: Failed polishing when mounted by tweezers.

There are three possible reasons for this observation:

1. The membranes are not uniform
2. Mounting quality is low
3. Polishing machine is unstable and has uncontrolled variables.

5.2.1 Characterization of Anodized Aluminum Oxide Membranes

Uniformity and flatness of the aluminum oxide membranes are the key characteristics that influence the final product significantly. Achieving a uniformly polished surface consistently with a certain set of process parameters needs initial uniformity and consistency. To test the

flatness of the membrane, optical profilometer was used to define the approximate thickness and curvature of the membranes. Seven samples were scanned, and three types of profiles were observed. Figure 8 illustrates the schematic of the different profiles that were observed in the samples. These shapes are resulted from scanning both sides of the membranes and combining them to identify the general curvature of the membrane.

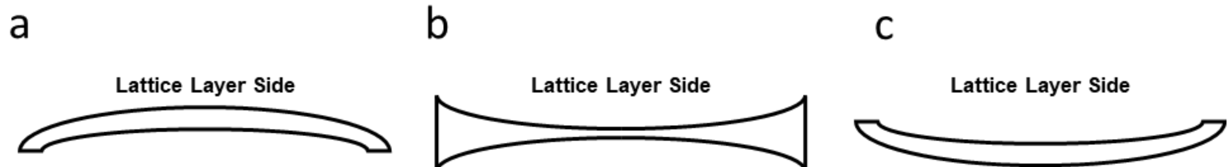

Figure 8: Schematic of three profile types observed in AAO membranes: a) convex b) hour-glass c) concave.

To measure the thickness, the membranes were broken in half and the cross section was observed by optical microscope and SEM and measured using ImageJ. Further studies suggested that membranes from the same box mostly show a similar trend in terms of thickness and curvature. The three different trends were from three different boxes of membranes and membranes that are from the same box are almost similar. Although the membranes are not uniformly flat, mounting method and polishing parameters may still be able to compensate for this uniformity.

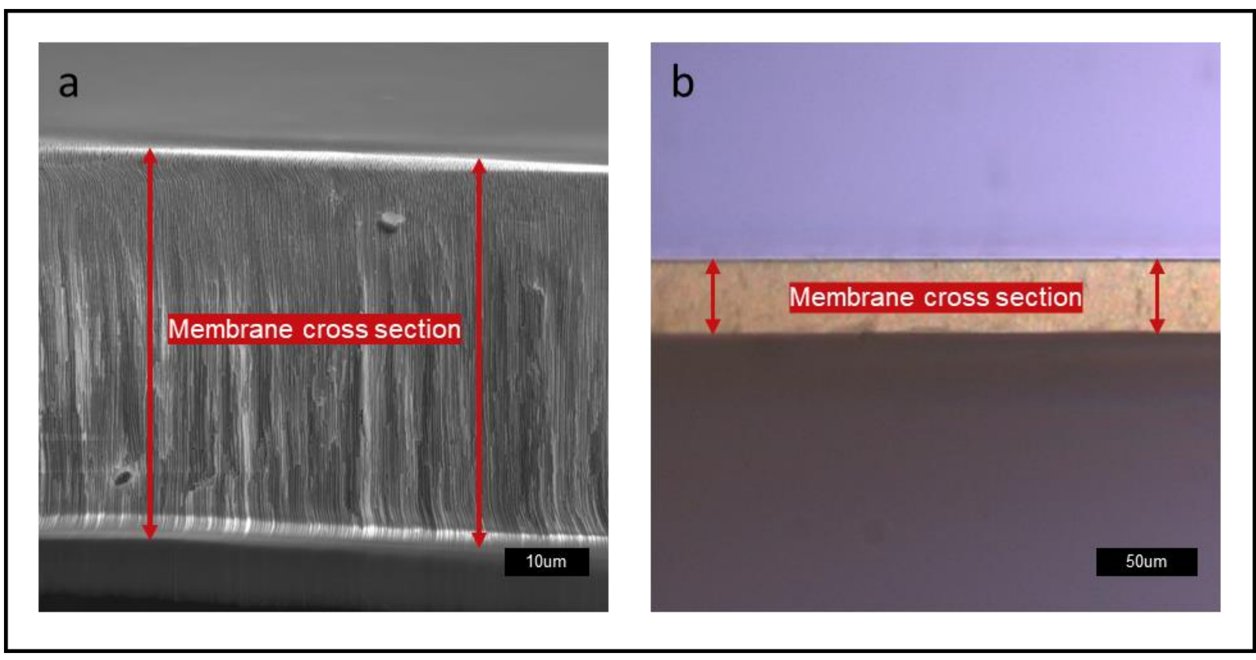

Figure 9: Cross section of an AAO membrane in a) SEM and b) OM.

5.2.2 Effect of Mounting Method on Flatness of Membranes and Polishing Quality

Several mounting methods were tested to identify their effect on the uniform polishing. Blanchard wax, ParaFilm, double-sided pressure-sensitive tape, double-sided carbon tape and double-sided foam tape were used as the attaching method and the effect on flatness and polishing uniformity were studied using optical profilometer and SEM.

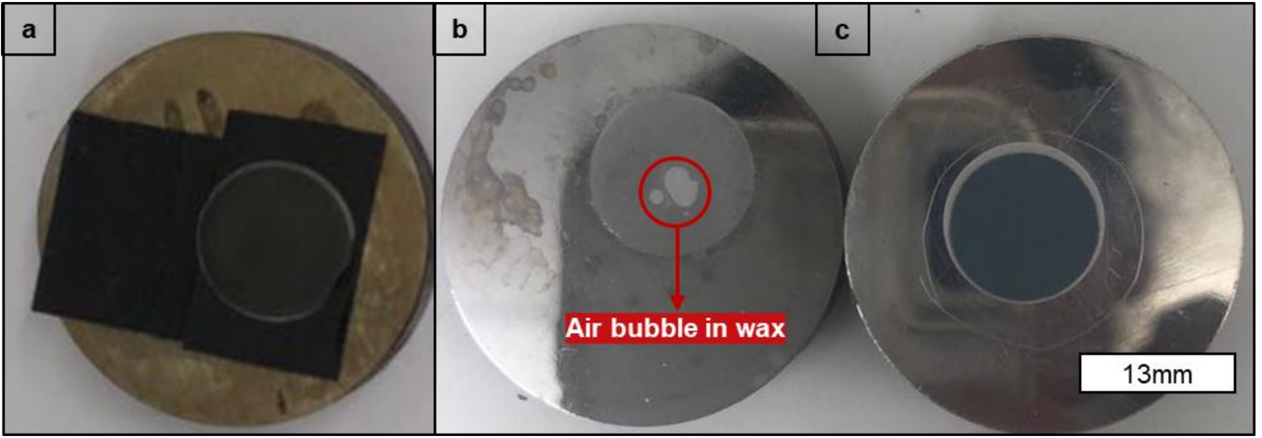

Figure 10: Attaching methods: a) flexible tape, b) wax and c) carbon tape.

5.2.2.1 Blanchard Wax

Blanchard wax is the primary adhesion method that was proposed for attaching membranes to the polishing stubs. The proposed method included 3 steps:

1. Rubbing the solid wax bar to the heated polishing stub and melting it on the stub surface at 175°C

2. Placing the membrane on the wax and flatten it using tweezers

3. Cooling down the stub in cold water for wax solidification

If these steps are consistent, it is expected to see all membranes that are being polished simultaneously, either undamaged or flawed. However, our observation does not match with the expectation which lead us to the probability of faulty mounting process.

The proposed method suggests extra careful measures for mounting the membranes which can be obtained by practice. Mentioning the accuracy and experience, it becomes clear that the

operator's expertise is the key factor in obtaining desired quality. The dependence of quality on operator's expertise brings the human error as an undeniable variable in the process. However, even with the highest level of experience one cannot be sure that the membrane is completely flat by tapping tweezers on a surface. Moreover, the need for skillful staff means a significant increase in expenses that affects the efficiency of project directly.

As mentioned before, most membranes are crushed or completely detached from the stub using the initially proposed method. For crushed membranes the first assumption was unevenness of the surface which causes focused stress on higher zones during the polishing process. The higher spots become the crack nucleation sites which at the end results in a crushed membrane. The unevenness of the wax needs to be solved. A few alternative methods were proposed and tested.

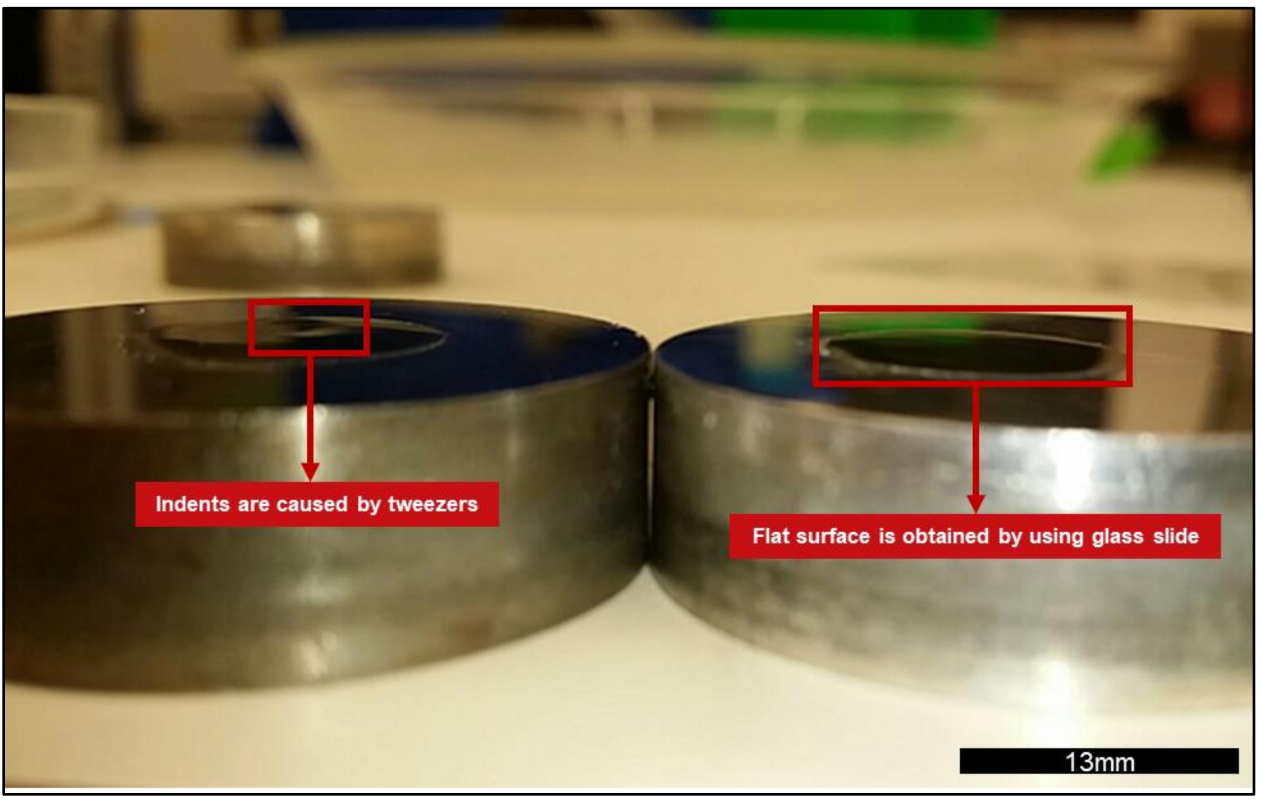

Figure 11: Mounting with tweezers (left) and with glass slide (right).

Tweezers are only able to push down some random spots and as a result focused stress sites are created. A flat surface in needed to uniformly apply pressure on membrane. Therefore, as an alternative technique, a glass slide which covered whole membrane's surface and stub weight was used to press down the membrane. As shown in Figure 11, the method can ensure flatness. However, extra wax was pushed out and as a result glass slide adhered to the stub and around the membrane and the attempts to remove it broke the membrane, Figure 12.

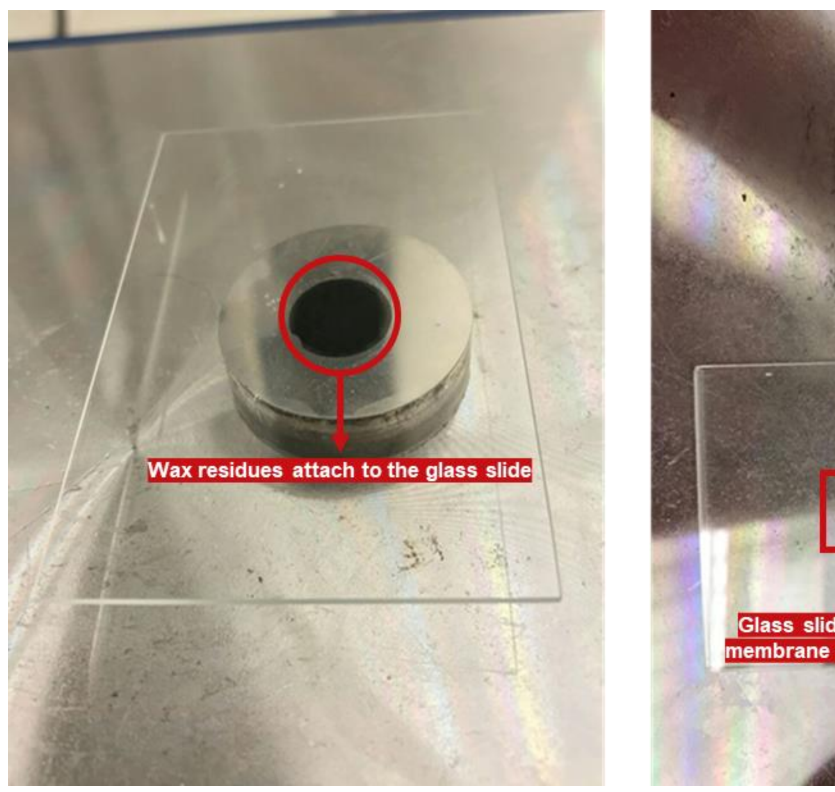

Figure 12: Glass slide experiment: applying the glass slide (left) and failure in removing it without damaging the membrane.

From the experiment of glass slide it was concluded that an equal or smaller surface is needed to push the membrane down on stub. Therefore, a cylindrical stamp with a smaller diameter than the membrane's diameter was designed and produced, Figure 13. In this

experiment the waviness of the membranes was apparently solved. Membranes that were mounted by this method were polished, but the outer part of the membranes were crushed or worn away. It was assumed that the smaller diameter causes the wax to flow out of membrane and weakens the attachment in outer parts of membranes.

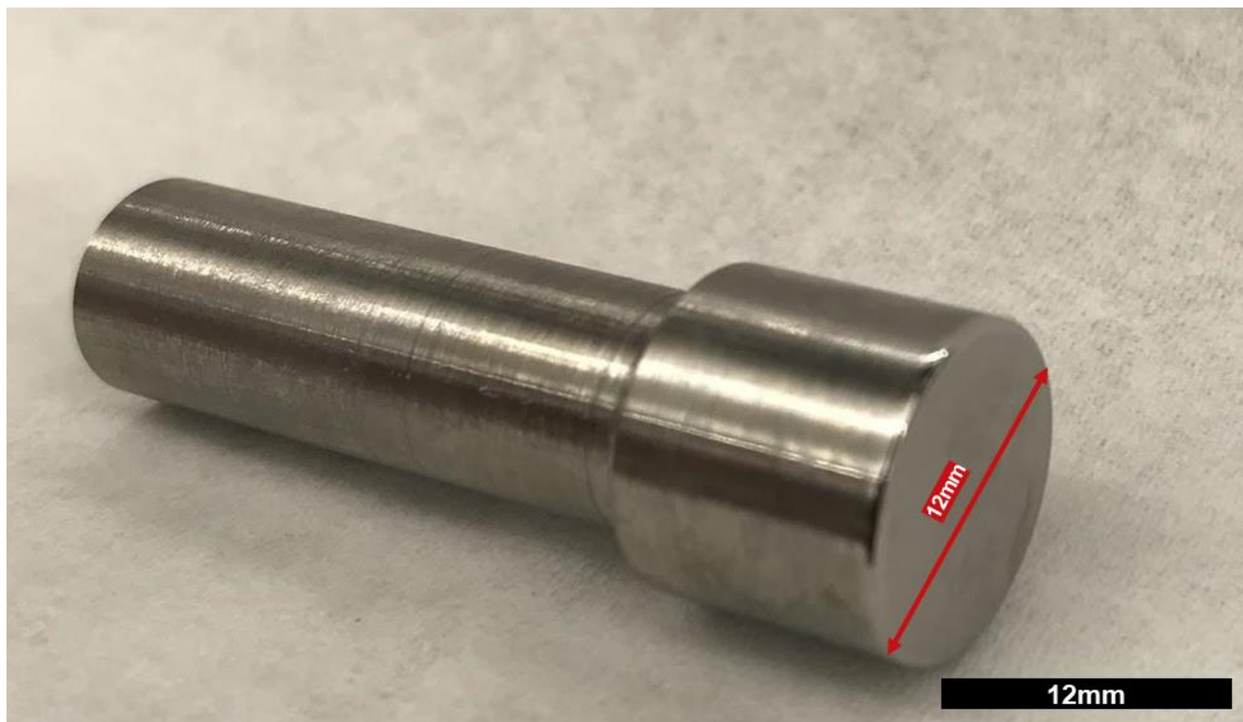

Figure 13: Stamp with 12mm diameter and smaller than membrane for mounting.

To minimize the amount of wax that is being pushed out of the membrane, the wax was melted before and a small drop of it was applied right on the center of stub and the membrane was put on that center. The result was more acceptable using this technique, but still the efficiency was affected by the need for operator's accuracy on putting the stamp exactly concentric with the membrane and by partially detached membranes after polishing.

Considering the detached membranes, insufficient adhesion between the stub and membrane is the most probable cause. Inadequacy in bonding may be due to unsuitable material used as an adhesive or insufficient mass of wax is used. The material must have been good enough, because detaching does not happen for all membranes and we sometimes are able to get perfect membranes using it. Therefore, there is a need to examine the adequacy of wax used for mounting.

Pressing the membrane to the hot stub or applying a drop of liquid wax to the stub are not good ways to quantify the mass of consumed wax. To measure the weight of wax, wax stick was broken into some small particles and weight of each of these particles were measured. The particles ranged from 7 mgs to 32 mgs. solid particles were put on 175℃ stubs, the membranes were placed above them, then the stamp was carefully placed concentric on the membranes for a few seconds and stubs were cooled down to solidify the wax. After polishing membranes, it was observed that 14 to 22 mgs of wax are the proper amount of wax that can decrease the risk of detachment during the polishing process to zero.

With solving the inefficiency of mounting process, we were able to investigate other probable parameters and techniques which are causing inconsistency in the manufacturing process. Going forward with the newest technique for mounting, results were more consistent, and the membranes were not damaged after polishing step.

Although the efficiency was improved by quantifying and determining the adequate amount of wax, the effect of operator's skill was still affecting the results. The experiments have demonstrated that the consistency of this mounting process is still dependent on several variables. Moreover, the second main goal of this research was looking into potential options for

getting higher quantities. Using the stamp method for mounting is a time-consuming and risky method itself. If the stamp is not concentric with membrane it may break part of membrane when removing it; therefore, it is extremely important to perform this method accurately and as a result, the mounting process can take much longer time than required. At 170℃, the wax is not completely in liquid state, so pressure is needed to make it flow uniformly beneath the membrane. If the wax becomes less viscous it can flow more easily with no need for extra pressure.

An experiment was designed to test the effect of temperature on wax viscosity and distribution under the membranes. Stubs were heated up to 230 ℃ the measured particles of wax were put on them, as expected the wax viscosity was much less and flowed faster due to the increase in temperature. The membranes were put on the flowing wax. As a result of the easier wax flow, flat membranes were observed without any extra wax outside them. The polishing process was successful and 100% efficient. Moreover, the need for operator's accuracy was decreased significantly. Also, the time consumed was decreased since post cleaning process was not required anymore.

Although using the recent mounting technique has solved the detachment during the polishing process and flatness problems, further studies have shown that there is another inconsistent factor in the mounting process. AAO membranes are optically transparent and if mounted before carbon deposition the wax distribution beneath them can be observed. Experiments revealed that due to the process of heating the wax, several small air bubbles (bubble diameter < 1mm) or a single large air (bubble diameter ≥ 1mm) bubble can be formed mainly in the center of the membrane; however, the bubbles have been observed at other areas under the membrane, too. After the wax is cooled down and solidified, touching the areas where

larger bubbles are observable shows that there is a flexibility in these zones. If polishing force can depress these areas, the polishing pad will not be as effective at them and results in unpolished areas. This phenomenon can explain how the halo devices, that have an unpolished area on the center, are produced. It also identifies the cause of random holes on the membrane after polishing since the area with an air bubble does not receive as much support as an area with solidified wax. Several AAO membranes were mounted, polished and characterized using SEM images which showed that lattice layer is observed wherever the bubble is observable. However, the position and size of the bubble are random and uncontrollable.

Figure 14: Air bubbles in different sizes and at different locations in the wax beneath the membrane.

Effect of temperature on formation of bubbles was tested by trying several temperatures and there was not a significant change in the results. However, further experiments on the rate of cooling down the polishing stubs suggest that slower rates can transform a single large bubble into multiple finer bubbles. This transformation often causes the depressing polishing force to be distributed on a larger area and not have the same effect on getting a large zone inaccessible for the polishing pad. Therefore, it is strongly recommended that stubs are cooled down in room temperature with slower rates rather than being quenched in cold water. Figure 15 shows how a large air bubble can create weak points in membranes and result in cracks or even removal of the spot with an air bubble beneath it.

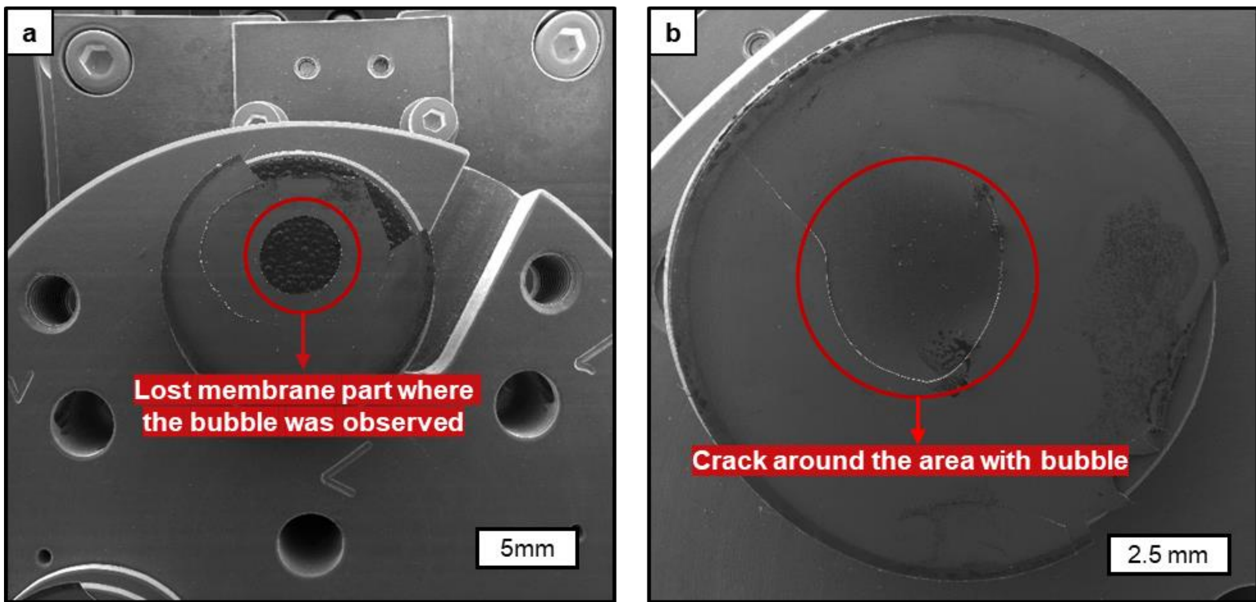

Figure 15: Air bubbles in hot wax create weak spots in membranes and result in a) partial removal or b) cracks in membranes.

The other challenge in the proposed method is that breaking the wax bar into particles that are exactly in the desired range, sometimes can take a very long time. An easier and faster way can help us getting closer to the other goal of this project which is a faster more efficient process that eventually contributes to scaling up the process. Melting wax and take quantified drops that are equivalent to a mass that is in the proper weight range (14-22 mgs) has shown to be a desirable technique for us. The measured drop can be put on a surface like an aluminum foil or a glass slide. Using the aluminum foil has showed to be more effective since it makes removing the solidified wax tablets easier.

Membranes should be detached from the polishing stub after polishing for further processes. After polishing the membranes, the polishing stubs are heated up again and the softened wax is dissolved using acetone. Then, the detached membranes are soaked in acetone for 10 minutes to make sure there is no wax on them since any kind of contamination can interfere with cell culture process.

5.2.2.2 Double sided Carbon Tapes and Double-sided Pressure-sensitive Tapes

Although wax can provide a reasonably flat surface, there is a possibility of forming a bubble under heat. However, the bubble formation probability, size and position are nor controllable and neither consistent which will create challenges in obtaining a uniformly polished surface. These inconsistencies have led us to investigate alternative adhesives for the purpose of attaching membranes to the stub. Double-sided carbon tapes, 12mm in diameter, were our first choice due to their availability. Several experiments proved that these tapes can provide us with a very strong adhesion. Flatness achieved by this method is highly dependent on the applied force during attaching process. To guarantee a flat surface, one side of the tape was carefully attached

to the stub. Then, the membrane is attached to the other side of the tape by using a glass slide and applying a uniform force on the whole surface of the membrane. The surface looked significantly flatter compared to wax and polishing results were promisingly uniform. However, detaching membranes turned out to be our only and major challenge in this process. Acetone which is effective in dissolving the bond between wax and membrane cannot break the bond of carbon tape and membrane. According to the tape manufacturer, alcohols and toluene are effective solvents for this purpose. Isopropyl alcohol, ethanol, methanol, 2-propanol and toluene were tested to break the bond and all of them were ineffective. In the next steps, soaking the stub with the mounted membrane in these solvents for 3 days was tested. As a result, the tape was detached from the steel stub but could not be detached from the membrane. Due to the brittle nature of the membranes applying even small physical forces will result in breakage of them and residues of the carbon tape were still observable on the broken parts, Figure 16.

Although the mentioned challenge makes the usage of carbon-tape as the adhesion method impractical for the ultimate goal of this project, it was used as consistent mounting method to eliminate the variation in mounting process and study other factors such as polishing parameters on the final product.

Figure 16: Membranes stick to carbon tape and break during detaching process.

5.2.2.3 Double-Sided Foam Tape

Foam tapes are double-sided flexible tapes which are ticker than carbon tape. Initially, we used these tapes for testing another adhesive that is removable. A piece of tape was attached to the stub and membrane was attached to it and after putting a glass slide on the membrane and applying force it was attached. Fragility of the membranes prevented the proper detachment of them again. However, the post-polishing characterization has shown that having a flexible bed under the membranes can make up for intrinsic unevenness defects of the membrane and provide

us with higher chances of uniform polishing independent of the existing defects. First, the high points touch the pad, but then, they are pushed down and get to the same level as lower points because they have soft material beneath them. However, this method is very sensitive since the brittle membranes may easily break during the mounting process. Moreover, the same challenges for detaching still exist and this method cannot be used before finding the proper solvent to remove the membrane from the tape.

5.2.2.4 ParaFilm and Pressure-sensitive Tapes

ParaFilm and pressure-sensitive tape could not provide strong enough attachments and moreover, detachment could not be done without damaging the membranes. Therefore, they were not chosen for further studies of flatness and polishing quality.

Comparing roughness data obtained from optical profilometer has shown that as the bed under the membrane becomes more flexible there is a better chance to get a smoother and more uniform polished surface. Figure 17 shows the graph comparing the effect of flexibility of the attachment method on surface smoothness. solidified wax as our hardest material and foam tape with highest flexibility are compared. It was observed that soft foam tape compensates for the inherent nonuniformity of the membranes and provides us with a smoother surface than wax. However, since the AAO membranes are very brittle this softness can become disadvantageous and result in membrane breakage.

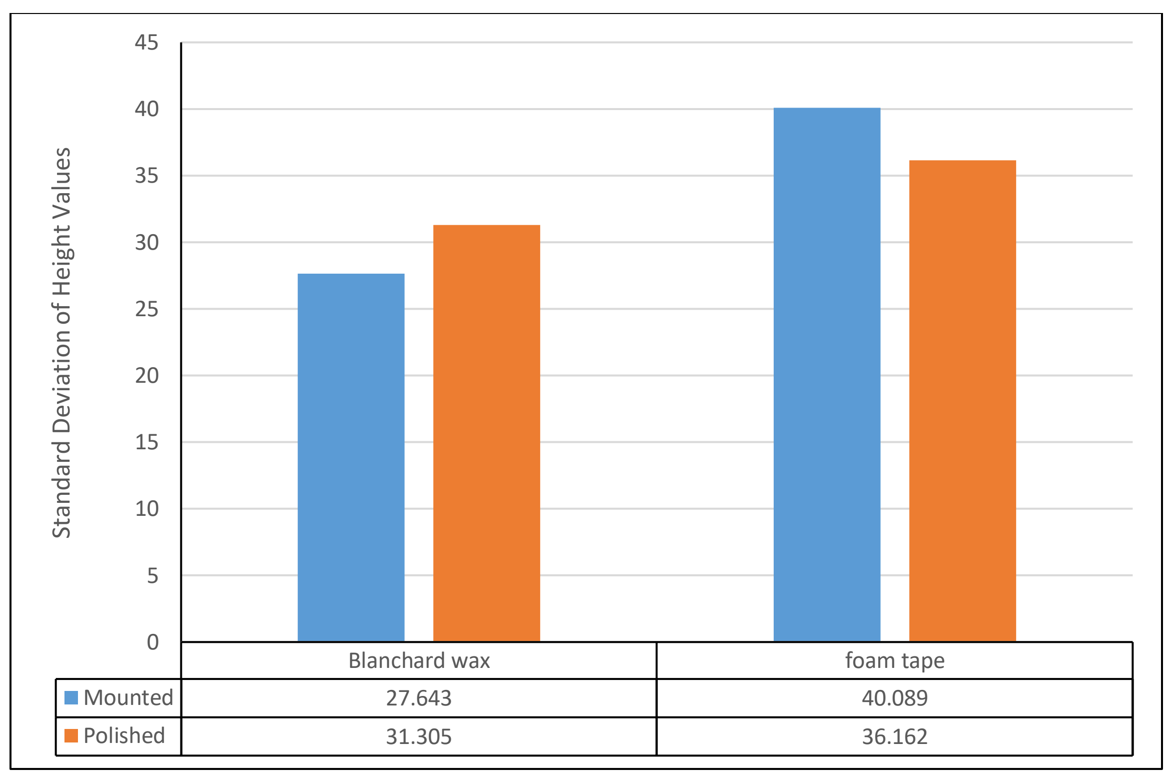

Figure 17: Effect of attaching agent flexibility on surface smoothness and polishing quality: Right: Roughness of an AAO membrane attached with wax (hard) before and after polishing; Left: Roughness of an AAO membrane attached with foam tape (soft) before and after polishing.

Carbon tape seems to be the most efficient attaching method to minimize the height variations throughout the surface. Foam tape is really sensitive to the applied pressure and that results in indents and damage to membrane where the pressure is higher. However, efforts to dissolve the adhesive agent and detaching the membranes were only successful for the wax which does not have a satisfactory consistency and unpredictable bubble formation in various locations under the membrane leaves us with too many variables in the process.

5.2.3 Surface Planarization

In this project two different polishers were used: Tegrapol-15 and Laboforce-100 manufactured by Struers. We had different challenges with each polisher but the two main challenges in both are:

1. Uneven material removal rate on the membrane surface

2. Tube damage and clogging

In this chapter challenges using each of the polishers are studied and potential solutions for them have been explored.

5.2.3.1 Polishing by Tegrapol-15

Going forward with the latest technique proposed for mounting, polishing step was done much easier and membranes appeared to be perfect after polishing. However, we observed that all membranes obtained from the same CVD batch have two distinct part a central part which seemed matt and a halo around it which was shiny and reflective, membranes were imaged with SEM, shown in Figure 18, and it was observed that there is a repeating trend among all 7 membranes in a batch. On one hand, the central part which appeared to be matt had still lattice layer on it which indicates that the central part was not polished properly. On the other hand, the halo section around the center of membrane which was shiny had all open tubes all around it. These observations answered one of very first questions of this research that if obtaining open CNT arrays is dependent on the location of membranes on the CVD boat. The answer obviously in negative, because in one batch under the same condition we observed the exact similar trend in all our samples independent of their location.

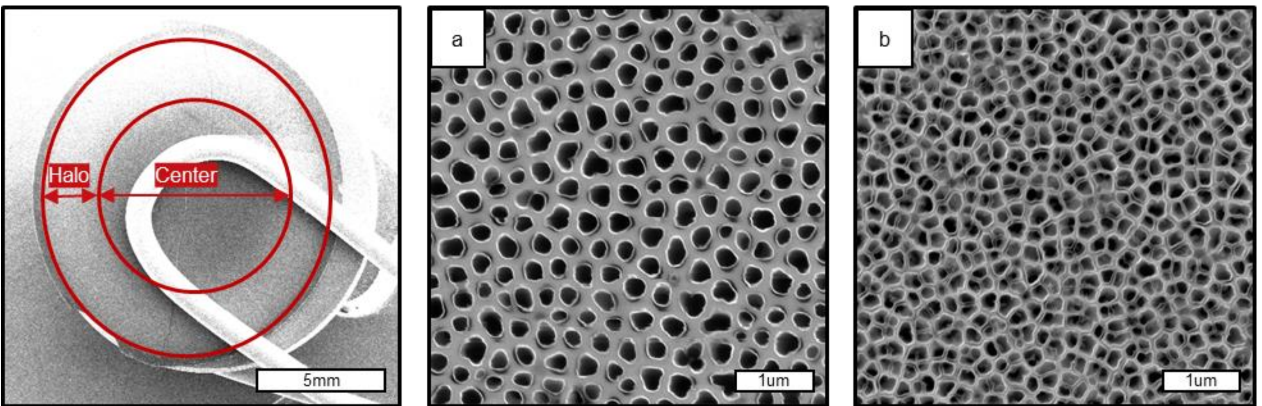

Figure 18: Wide field image of nonuniformly polished membrane, (a) high quality polishing on the halo, (b) poor quality polishing and lattice layer persistence on the center.

Other experiments with similar parameters were done to test the consistency of this trend. The results were not similar, and it turned out that the trend is still existing but the tubes on the halo section are not open anymore. The major difference that could explain the difference was the instability of the polishing machine which started a random vertical motion that incurred sudden and uncontrollable impacts on the samples during the polishing process. The assumption was that this motion caused stress on the tubes and eventually crushed them. Figure 19 shows the SEM image of clogged and open tubes.

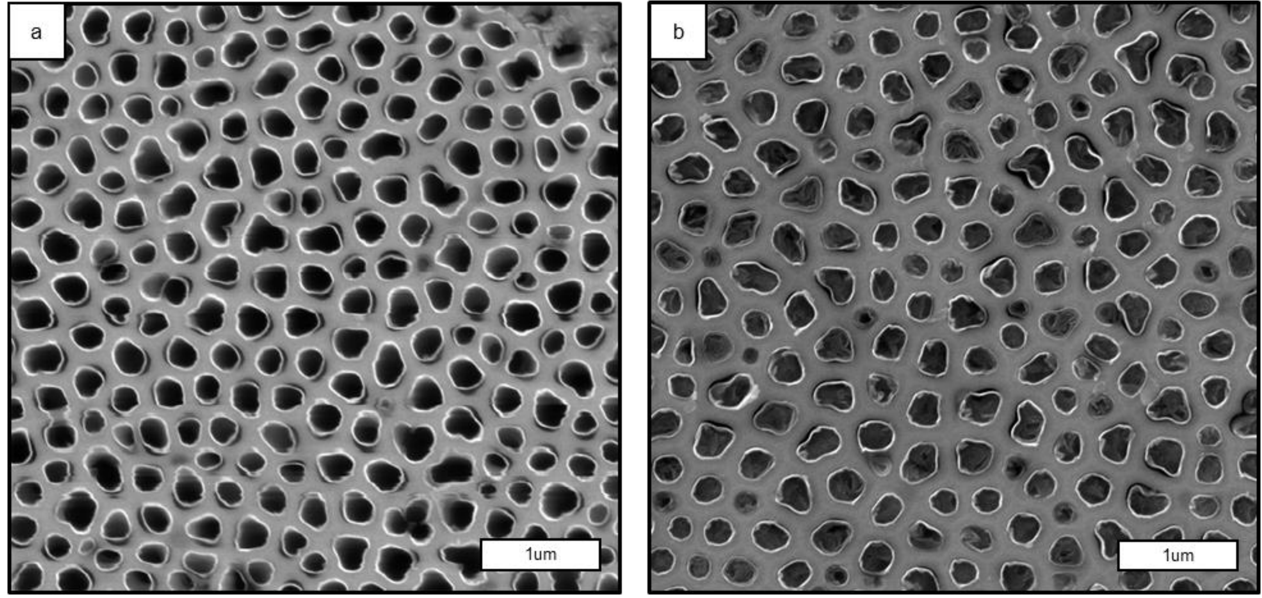

Figure 19: a) Open tubes look black and empty, b) Clogged tubes look gray and stuffed.

The polishing machine was calibrated, relatively reducing the random vertical polishing head movement, and the same experiment was repeated. Less clogging was seen compared to the previous experiment. It can be concluded that polishing machine can affect the results and reproducibility of them. To get the highest proficiency out of our samples, the lattice layer in the center needs to be removed. Therefore, we may need probably a rougher polishing process to reach the center of the membrane and get it polished. Rougher polishing was done by having polishing done by a slurry with rougher particles in one experiment and using the same slurry for a longer time in another one.

In one experiment we aimed to see whether longer time with 250 nm diamond slurry is enough to remove the central lattice layer or not. The polishing time was increased by 5 minutes and polishing pad was also replaced. After doing the experiment the matt central part was gone, SEM imaging verified the removal of the lattice layer, but clogging was observed all around the surface of membranes. This clogging can be attributed to two possible reasons:

1. Fine particles might break into smaller pieces in longer periods and block tubes

2. Longer periods produce excessive tension on the tubes and partially crush them and residual fragments of carbon block the tubes

Another experiment studies the effect of rougher particles on polishing process, 1µm diamond slurry was used for 5 minutes. The matt central part, which is an indicator for lattice layer, was not present anymore, moreover SEM images showed reasonably open tubes all over the membranes.

By repeating experiments, it was observed that eliminating the lattice layer is not consistent and it can still be seen within some samples. This can be attributed to inconsistent membranes, mounting process or abrasion process itself. Our method in determining the origin of this variability was characterizing the membrane before and after each step by measuring roughness using optical profilometer. It was mentioned that in the same polishing batch of 3 membranes which were mounted on the polishing stub using wax some variability in the results were observed. Those variations were related to inconsistencies in mounting process. However, it was also observed that the polisher Tegrapol-15 had a random vertical motion that caused sudden impacts on the samples. This problem in the polisher created uncontrollable variation from batch to batch. Therefore, even with solving the mounting issues in a batch, differences would still exist between batches. The assumption was that this motion causes stress on the tubes and ultimately crushes them. The problem with using an unstable polisher like Tegrapol-15 is that any variation in results can be attributed to the random motions of the polishing machine. Especially, because of the changes of this motion from batch to batch, testing the repeatability with such equipment becomes impossible. This uncontrollable random motion and its

unpredictability prevent us from identifying the main root of inconsistencies. Moreover, this polisher is only able to polish only three membranes at a time. After consulting with the polisher manufacturer to investigate possible solutions, it got cleared that our current machine is not being produced anymore and calibrating it cannot be a long-term solution. Therefore, it was decided to replace the old polishing machine with the latest version of it, Laboforce-100.

The new polisher, Laboforce-100, was used for the rest of experiments to provide us with a uniform force throughout the process. Laboforce-100 is a reliable polisher since it is a semi-automatic system with automatic sample mover and slurry doser. It also uses a bigger plate (300 mm in diameter) and can polish 6 membranes at a time which serves the goal of scaling up the project. It has separate settings for plate and carrier speed and rotational direction which give us more freedom in testing different cases.

5.2.3.1 Polishing by Laboforce-100

Laboforce-100 is a semi-automatic machine with an automatic specimen mover and dosing unit. Constant speed independent of the load can provide us with ensured reproducibility. It is equipped with cooling system and pneumatic head which decrease the need for recalibration. Moreover, it can polish 6 samples at a time.

Laboforce-100 with a new suggested polishing pad (MD-Nap) were tried. SEM imaging has showed that parameters which were used on the old machine are not enough to polish the lattice layer, and new tests are required to determine the new effective parameters.

Polishing Parameters

Laboforce-100 is the new generation of tegrapol-15. Therefore, the same parameters that proved to be the most effective with tegrapol-15 were applied with Laboforce-100. The results indicate that the current parameters were not effective in removing enough thickness of the surface and as a result, the lattice layer was almost intact throughout the surface. The initial possible reason for this observation was that the random vertical motion that was produced by Tegrapol-15 was actually helping the process by applying more force and make the insufficient parameters seem to be effective. Therefore, new experiments were designed to determine the new set of effective parameters with the new polisher, Laboforce-100.

In this set of experiments, effect of polishing parameters including speed, force and time were explored to determine the parameters that are able to provide us with a uniform polishing independent of the inherent non-uniformities within the membranes. Table 1 shows a summary of the experiments on the effect of polishing parameters. Optical profilometry and scanning electron microscopy were used as our characterization method.

Table 1: Summary of experiments to determine best set of polishing parameters.

Parameter	Range
Time	5-30 min
Relative Angular Speed	0 and 150 rpm
Force	30 – 50 N

Optical profilometry provides us with several height parameters and statistical data. Standard deviation of the height values measured on the surface reported as S_q in the software is a good indication of surface roughness since as the deviations become smaller, the surface becomes smoother. An effective polishing process is supposed to provide us with a smoother surface. Therefore, characterizing the surface and analyzing the height variations is a valuable technique in testing polishing quality.

SEM provides us with magnified images of the nanostructures after polishing. The quality of the membranes is determined based on their characteristics like geometry and uniformity. If the lattice layer is removed properly, we are supposed to see distinct circular and uniformly sized nanotubes in a SEM image.

Our characterization techniques have shown that an effective polishing process smoothens the surface and creates specific visual features. Several observations and data analysis demonstrated an agreement between the change in roughness and visual properties of the nanotubes; this means for a properly polished membrane for which the roughness decreases after polishing the nanotubes show desired features in a SEM image as well.

Five areas, as showed in Figure 20, were selected and studied in each membrane in both methods and results from optical profilometer and SEM to compare and check if they confirm each other.

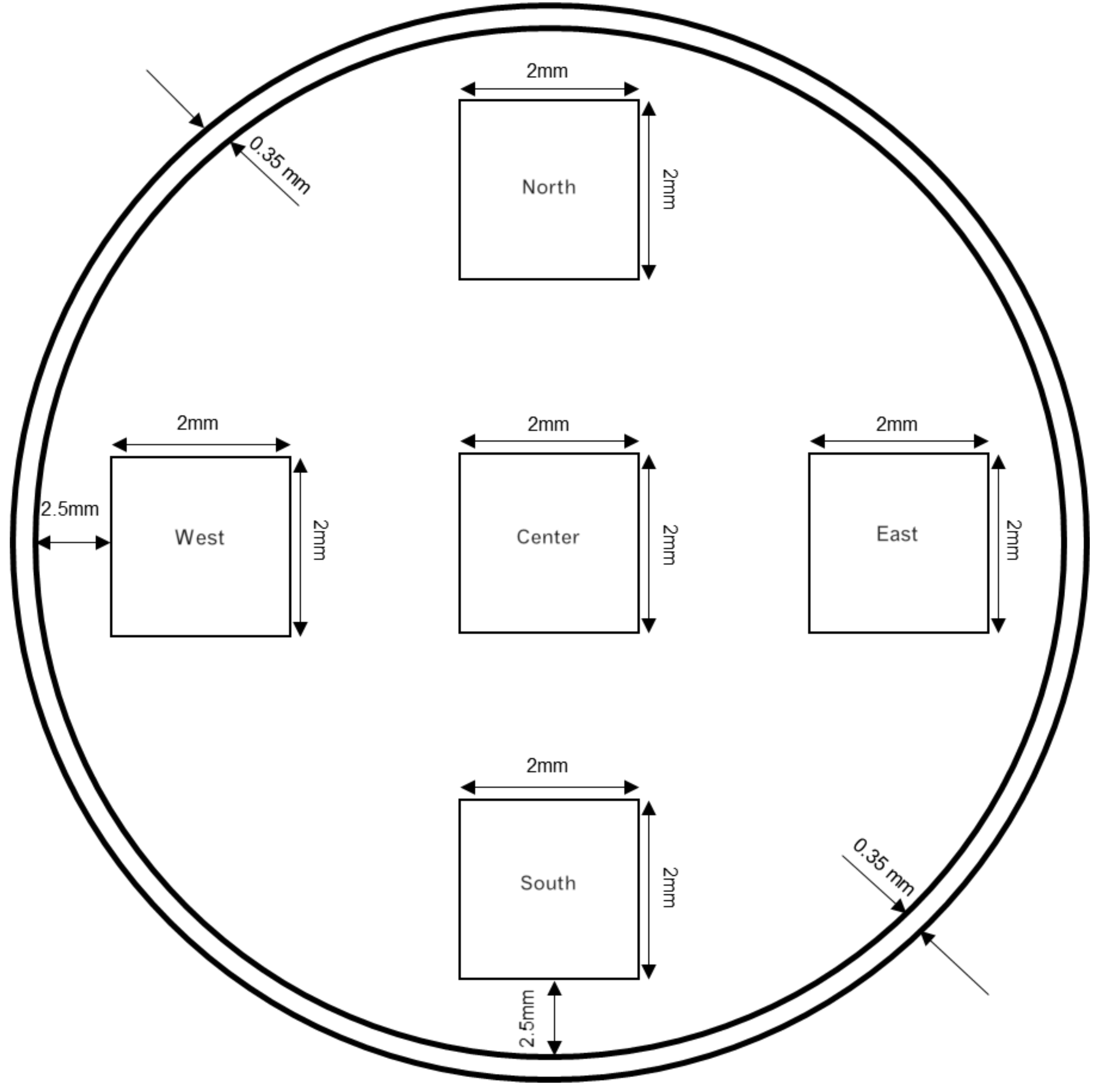

Figure 20: Five areas were studied in each membrane before and after polishing in every experiment.

The first parameter to be studied is the effect of time. following table shows the effect of time while keeping other parameters the same.

Table 2: Summary of experiments to determine effect of time and force on the polishing process.

Experiment	Force (N)	Time (min)	Carrier Speed (rpm)	Plate Speed (rpm)	Slurry Size (µm)	Pad
1	30	5	150	150	1	MD-Floc
2	30	10	150	150	1	MD-Floc
3	30	15	150	150	1	MD-Floc
4	30	20	150	150	1	MD-Floc
5	30	25	150	150	1	MD-Floc
6	30	30	150	150	1	MD-Floc

SEM images in Figure 21 show that with increasing time no significant change happens which would lead to believe that time is not an influential parameter in polishing. However, further studies and experiments showed that time is an effective parameter if other parameters meet their minimum requirement.

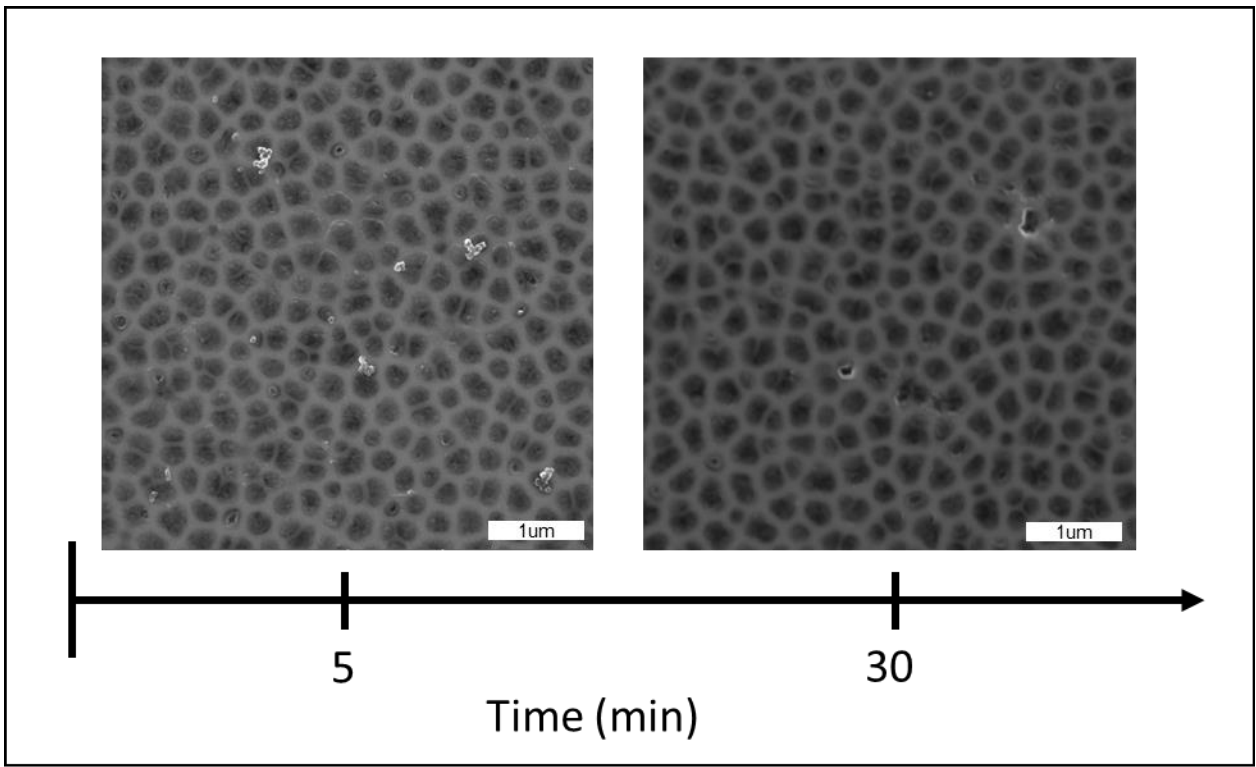

Figure 21: Polishing AAO membranes with 30 N and 150 rpm on carrier and plate with different times does not show a significant change in structure, (image area: center of membranes), scale bar 1μm.

In these set of experiments, the rotation speed of the carrier and plate speed were both 150 rpm which means the angular speed at which the two parts are moving together is zero. However, since the radius of rotation is different the linear speed is different. SEM images indicate that this velocity difference is not enough to remove material even by increasing other parameters like time. Therefore, the angular speed at which the carrier and the plate are moving relative to each other should be more than zero to make the other parameters work. Figure 22 shows a schematic of how polishing plate and carrier move relative to each other.

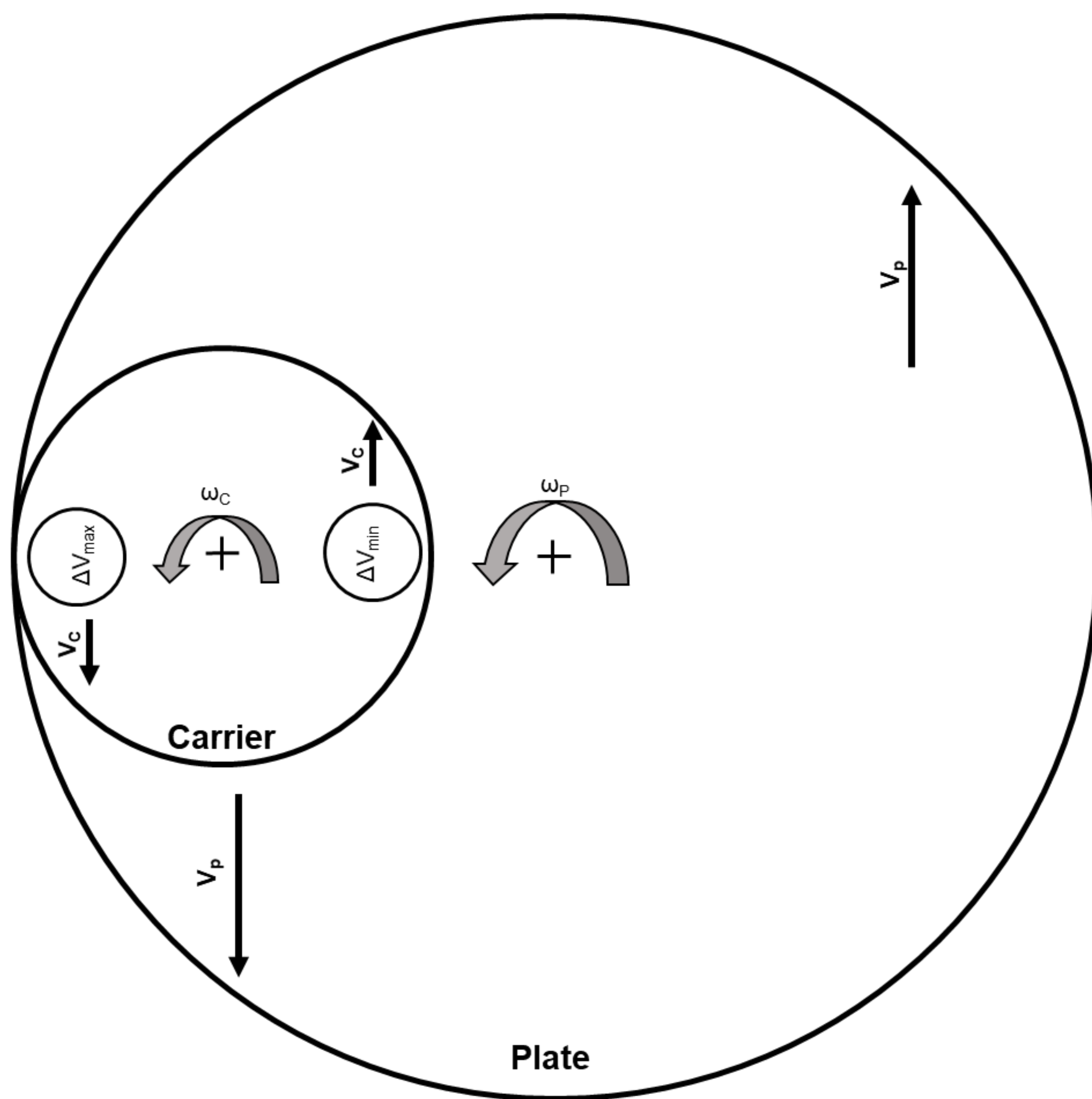

Figure 22: Schematic of angular and linear velocity of the polishing plate and carrier.

The following experiments studied the effect of relative angular and linear velocity on the quality of the polishing process.

Table 3: Summary of experiment to determine best set of polishing parameters

Experiment	Time (min)	Carrier Speed (rpm)	Plate Speed (rpm)
1	5	150	150
2	5	50	200

$$1\text{rpm} \ = \ 6\text{rad/s} \rightarrow \begin{bmatrix} 50\,rpm = 300\dfrac{rad}{s} \\ 150rpm = 900\dfrac{rad}{s} \\ 200rpm = 1200\dfrac{rad}{s} \end{bmatrix}$$

$$V = r\omega \rightarrow$$

$$Case\ 1\ at\ Point\ A: \begin{bmatrix} carrier\ angular\ speed = 900\dfrac{rad}{s} \rightarrow V = 0.044 * 900 = 39.6\dfrac{m}{s} \\ plate\ angular\ speed = 150rpm = 900\dfrac{rad}{s} \rightarrow V = 0.036 * 900 = 32.4\dfrac{m}{s} \end{bmatrix}$$

$$Case\ 1\ at\ Point\ B: \begin{bmatrix} carrier\ angular\ speed = 900\frac{rad}{s} \rightarrow V = 0.044 * 900 = 39.6\frac{m}{s} \\ plate\ angular\ speed = 150rpm = 900\frac{rad}{s} \rightarrow V = 0.124 * 900 = 111.6\frac{m}{s} \end{bmatrix}$$

$$Case\ 1: \begin{bmatrix} angular\ speed\ difference = 900 - 900 = 0\ rpm \\ (Linear\ speed\ difference)_A = 39.6 - (-32.4) = 72\frac{m}{s} \\ (Linear\ speed\ difference)_B = 111.6 + (-34.2) = 72\frac{m}{s} \\ mean\ of\ linear\ speed\ difference = \frac{72 + 72}{2} = 72\frac{m}{s} \end{bmatrix}$$

$$Case\ 2\ at\ Point\ A: \begin{bmatrix} carrier\ angular\ speed = 300\frac{rad}{s} \rightarrow V = 0.044 * 300 = 13.2\frac{m}{s} \\ plate\ angular\ speed = 150rpm = 1200\frac{rad}{s} \rightarrow V = 0.036 * 1200 = 43.2\frac{m}{s} \end{bmatrix}$$

$$Case\ 2\ at\ Point\ B: \begin{bmatrix} carrier\ angular\ speed = 300\frac{rad}{s} \rightarrow V = 0.044 * 300 = 13.2\frac{m}{s} \\ plate\ angular\ speed = 150rpm = 1200\frac{rad}{s} \rightarrow V = 0.124 * 1200 = 148.8\frac{m}{s} \end{bmatrix}$$

$$Case\ 2: \begin{bmatrix} Angular\ speed\ difference = 150\ rpm \\ (Linear\ speed\ difference)_A = 43.2 - (-13.2) = 56.4\frac{m}{s} \\ (Linear\ speed\ difference_{)B} = 148.8 + (-13.2) = 135.6\frac{m}{s} \\ mean\ of\ linear\ speed\ difference = \frac{56.4 + 135.6}{2} = 96\frac{m}{s} \end{bmatrix}$$

The relative speed for case 1 is not enough to remove enough material for our purpose. Therefore, the further experiments are done with case 2 speed parameters. Figure 23 shows that by providing some rotational speed, effect of time becomes obvious.

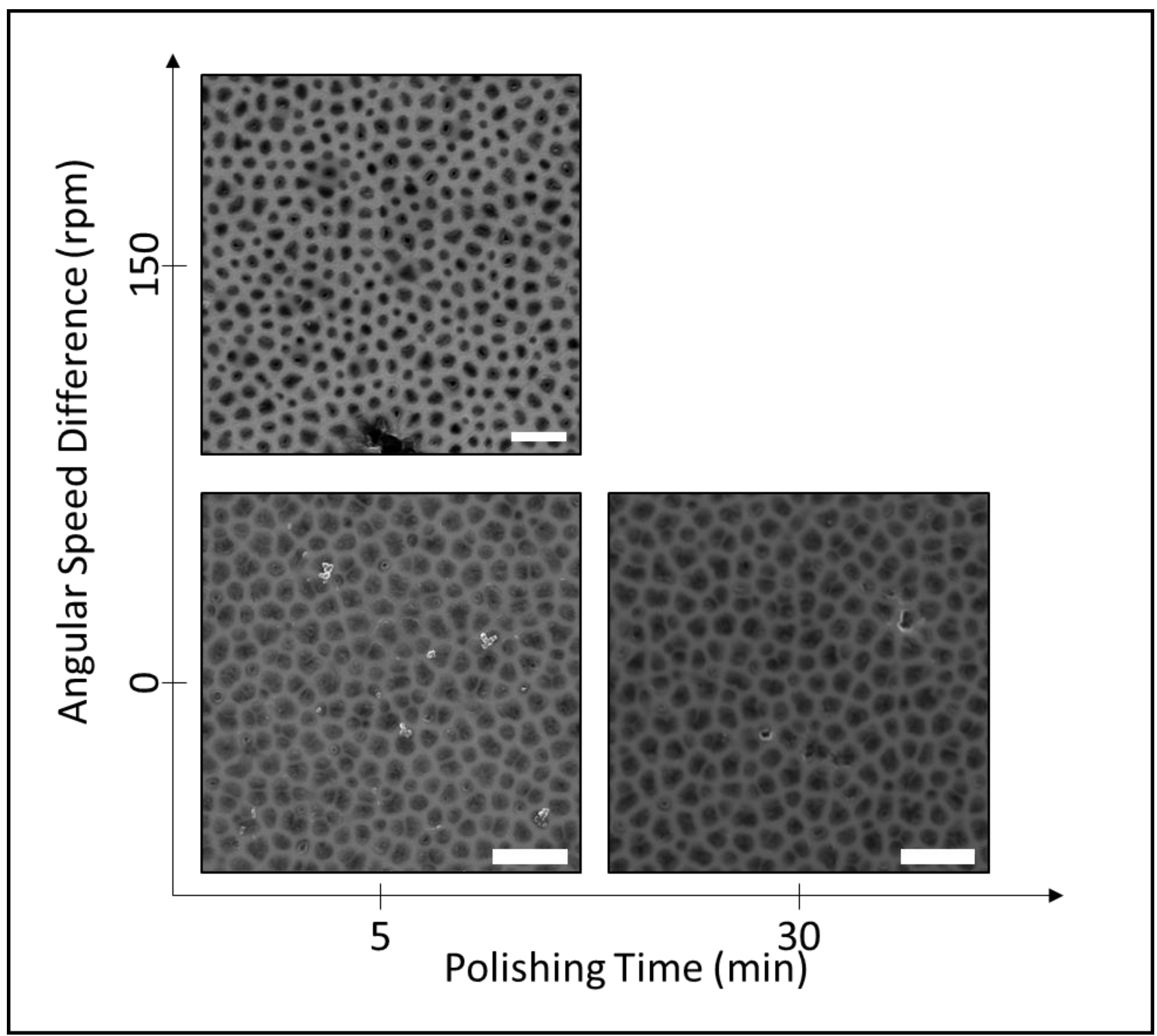

Figure 23: Comparing the of effect of time and angular velocity difference, (image area: center of membranes), scale bar 1μm.

The next set of experiments studies the effect of time with at three different forces. According to the last experiment, it is expected that little changes in time, 5 and 10 minutes, cannot influence the results as considerably as changes in force. Comparing results proved that

force has a more significant influence on making a change on the surface than time and the difference between 5 and 10 minutes of polishing with the same force is negligible.

In the next set of experiments, 5 different forces were tested while keeping the rest of the parameters constant (t=5 min, ω_p = 200 rpm, ω_c = 50 rpm, 1μm diamond slurry). Figure 24 summarizes the results for this experiment. For similar membranes that are obtained from the same box, increasing the force can see provide a better quality in polishing before reaching the critical force after which the force causes serious damage to the structure of the tubes and crushes them.

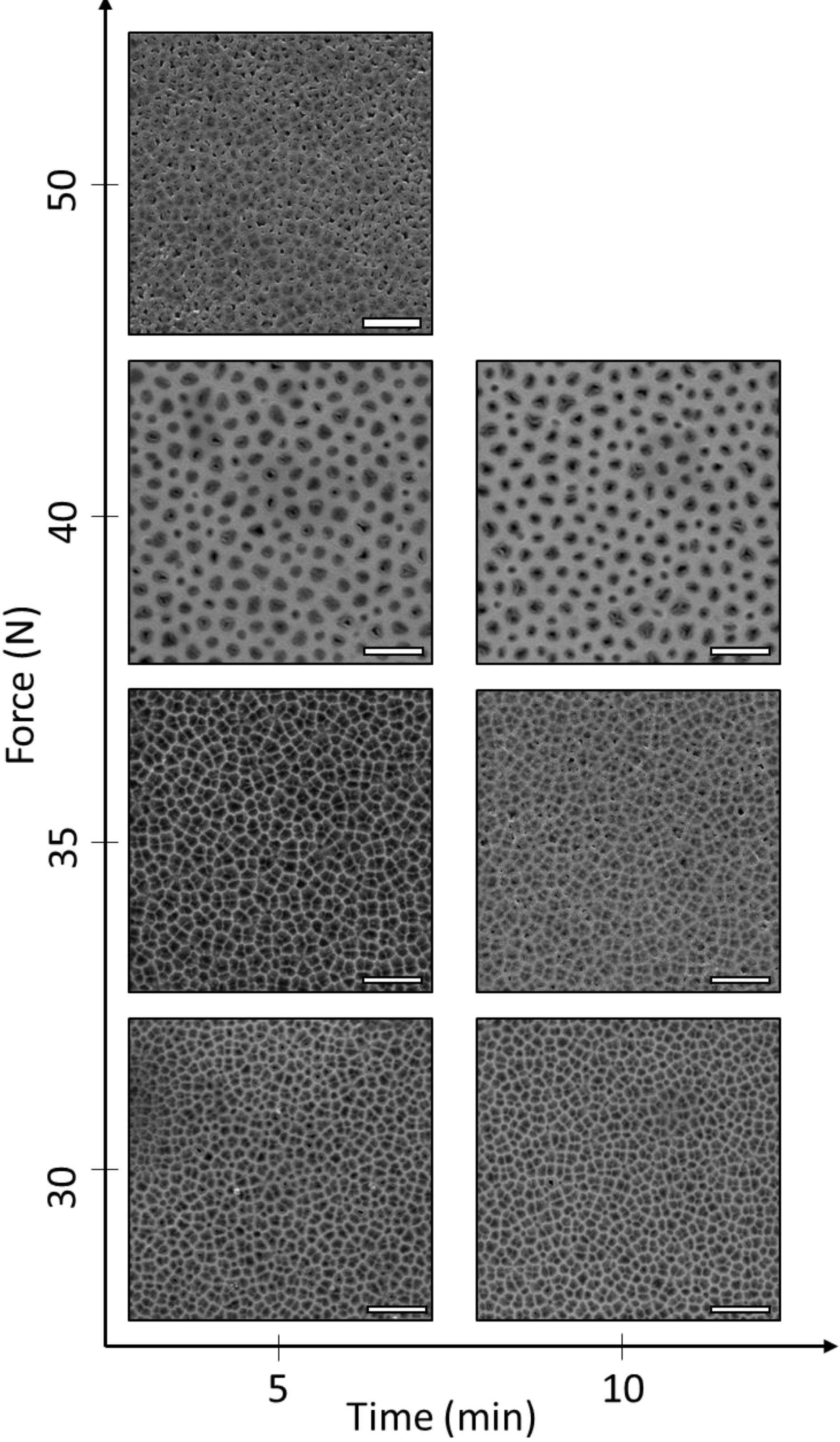

Figure 24: Comparing the of effect of time and force, (image area: center of membranes), scale bar 1µm.

Samples profile were studied before and after polishing and roughness of 5 areas including center, north, east, west and south were measured, Figure 26. The exact same areas were imaged by SEM. A decrease in roughness was expected for a sufficient polishing which will be an equivalent for images that show distinct circular tubes with no lattice structure on top of them. More than 85% of SEM and optical profilometer results confirm each other and results from each can predict what we can expect in the other. Figure 30 show examples of this comparison.

In Figure 31, (a) shows an area of a membrane that is very well polished for our application is shown. The lattice layer is not present, and tubes are separated from each other, circular and uniform in size. We expect that this area of our membrane has been smoothened after polishing. Going to the roughness data, the expected change is present, and our roughness has decreased.

In another example in Figure 25, by looking at the roughness data in (b), we see that our surface has got rougher after polishing. It is expected to see a very poorly polished surface under SEM which is correct by looking at our SEM image for this area we see a lattice layer present which cause a nonuniform set of tubes.

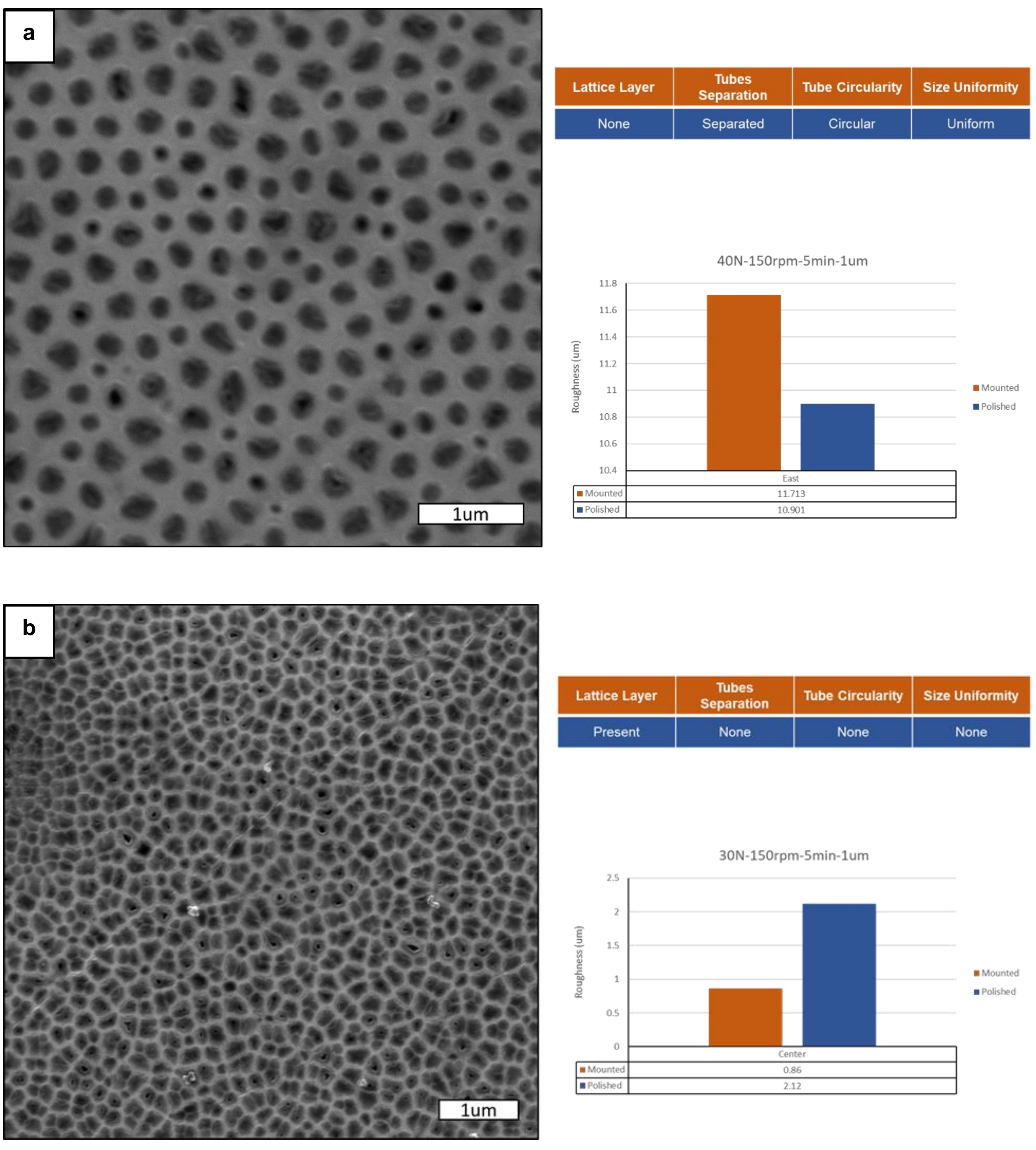

Figure 25: Agreement between roughness data and visual characteristics for: (a) A well-polished surface) (area: east) and (b) A poorly polished surface (area: center).

In every set of conducted experiments, we still see inconsistency in our results mainly due to the variability in the current mounting process using wax and the inherent variability of the membranes. However, the results can be grouped by the polishing evenness. Figure 26 shows the schematic of three groups of polished membranes. The following groups are ordered by their observed frequency:

1. Samples with unpolished center and polished surrounding area
2. Samples with randomly positioned unpolished areas
3. Samples that are evenly and thoroughly polished

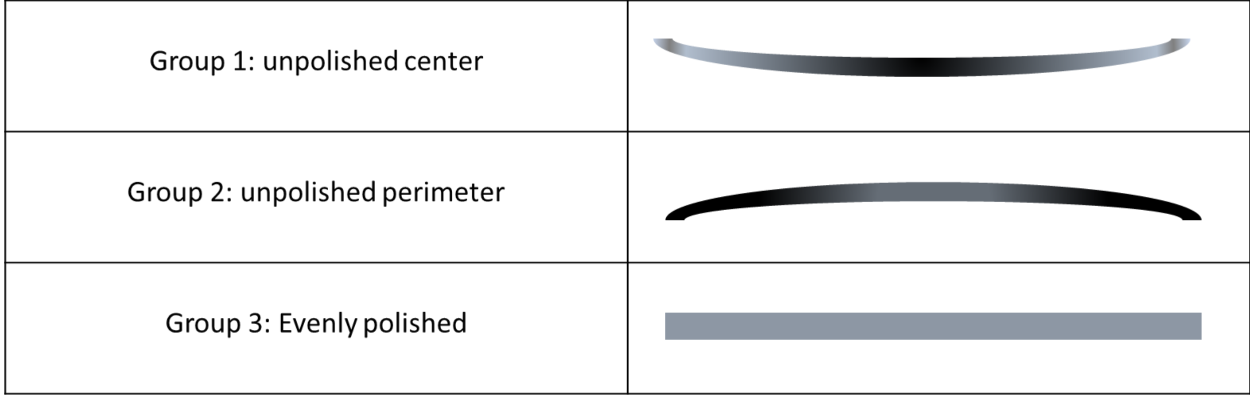

Figure 26: Schematic of three groups of polished membranes.

As it was mentioned earlier, the inconsistency in mounting process and the variability in membranes will cause the polishing process with similar parameters to produce different results. We barely see membranes that are completely polished and the ones with unpolished areas do not show a consistent trend on the location of these areas. Therefore, it cannot be guaranteed that a set of parameters that has worked perfectly with one batch will work the same way with the

next one. To address this issue, apart from proposing more consistent mounting processes, stronger polishing parameters were used to see if they can cover the whole existing variabilities. However, it turned out that these extreme parameters will cost us the membrane and/or CNT arrays damage. The areas where we see intact lattice structure, were not accessible to the polishing pad which suggests height difference in our samples, Figure 27. The insufficiently polished areas were positioned at a lower level compared to polished ones and cannot get polished before getting leveled with the higher areas. In this case, we need parameters that can level the two areas and provide sufficient polishing on the whole surface of the membranes. If the height difference is too significant, an even and sufficiently polished surface without damaging the samples is not achievable.

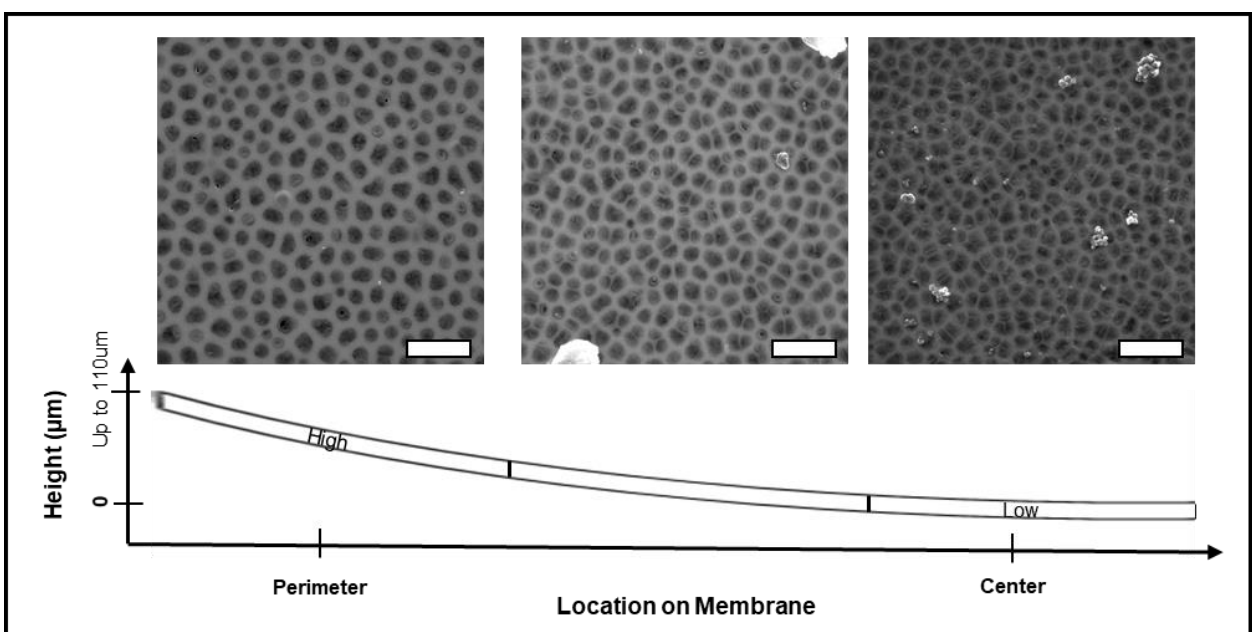

Figure 27: SEM image of the intact lower spots and polished higher spots after polishing, scale bar 1 µm.

5.3 Determining Responsible Factors for Tube Clogging

Even with completely polished membranes, most of them do not have open tubes after polishing. The main components of the polishing process that can cause the clogging are wax, diamond slurry and the deposited carbon on the membrane and inside the tubes. In each chapter, experiments were conducted to determine the source of tubes blockage.

1. Blockage Due to Mounting Wax:

The idea is that melted wax gets into the tubes and when solidified the cleaning method using acetone is not enough to remove wax residues from inside the pores. The first experiment was designed to check how the blockage changes if membranes are soaked in acetone for longer time and sonicating was used to assist the process. Increasing the time from 5 minute to 30 minutes has not indicate a difference in the results. The second experiment was using another mounting method to confirm the initial results. Membranes that were mounted with this method still had clogged tubes. Therefore, the source of clogging cannot be wax residues.

2. Blockage Due to Diamond Slurry:

Diamond particles used in this process are 1μm and pores on the membrane are 200 nm. Considering the hardness of diamond, and the size of particles it is not possible for these particles to fit the pores. So, diamond slurry is not the origin of the tube clogging, either.

3. Blockage Due to Carbon:

The easiest experiment to decide if the carbon is the source of blockage is oxidizing the carbon on the membranes that have clogged tubes by placing them in an open-tubed furnace and check if the tubes are open after this process. A batch of membranes with highly clogged tubes

were tested and after oxidization the tubes were open. Therefore, carbon is the main source of tubes clogging in AAO membranes.

6.0 Conclusions

CNT arrays can have a wide variety of applications in biomedical field if the manufacturing method is efficient and consistent. The focus of this research is addressing the inconsistency issues in the current fabrication method which involves mechanical polishing of the carbon deposited membranes and wet etching them. The inconsistencies originate from the mechanical polishing step and several factors are responsible for the variability of the results. The approach of this research was studying each stage in the mechanical polishing process, finding the related problems and suggesting a general solution for all or most of them. In this process, membranes were characterized using surface profilometry and scanning electron microscopy before and after each step. This chapter summarizes the main conclusions from the data obtained by several experiments:

- The commercially available AAO membranes can vary in thickness and general form from batch to batch. There were three different categories that have been observed in this research:
  - Uniform thickness with concave form
  - Uniform thickness with convex form
  - Thickness growth from center to the edge with flat form

- CVD process is independent of number of membranes and their location in the CVD boat. Therefore, efficiency of CVD process is increased by putting more membranes in each batch by saving time and resources.

- The inherent nonuniformities in the membranes needs to be compensated to obtain an evenly polished surface with consistency.

- The initially proposed mounting process involved melting the Blanchard wax and re-solidifying it to attach the membranes to polishing stubs. After several modifications on the wax application method, temperature and cooling rate, it turned out that this method not only cannot make up for the defects of the membranes, but it even adds up to the variability in results. During the solidifying process, air bubbles are made at random locations beneath the membranes and creates weak spots that may result in defective products.

- Several other adhesion methods, including double-sided carbon tape, flexible foam tape, pressure-sensitive tape and ParaFilm were used in mounting process. The mutual problem in all these methods was that detaching the membranes without damaging it could not be done. However, as the flexibility of the adhesion agent under the membrane increases, the chance of even polishing increases. It turns out that the higher points on the sample get suppressed onto the flexible bed and are leveled with the lower spots.

- In characterizing the samples, SEM images and roughness data obtained from optical profilometer are used. If the polishing is not sufficient, roughness increases and if the process is effective, roughness should increase. The SEM images which show lattice layer, non-uniform tube size, irregular geometry or inadequate separation between tubes are an indicator for inadequate polishing while effective polishing provides an array of uniformly sized and shaped tubes without any lattice layer and good separation. SEM images and roughness data measured through optical profilometry confirm each other in more than 85% of the cases. Therefore, results from each of these techniques can predict the results from the other one.

- All polishing parameters should meet a certain minimum requirement for the general process to be effective, otherwise, increasing other parameters will not be influence the results.
- Increasing polishing parameters provide us with more aggressive process that might be able to compensate for some of the variations.
- Current set of parameters that has proved to be effective in polishing standard samples might not work with samples with different shapes and thicknesses since the polishing process is very sensitive to surface topology and thickness.

This research made the following contributions to active research and the general field of nanomanufacturing by:

1. Identifying the sources of variability by examining every step of the polishing process and defining inconsistent factors by implementing several characterization techniques including scanning electron microscopy, optical microscopy and optical profilometry

2. Developing a more consistent mounting technique using Blanchard wax that minimizes operator error resulting in faster, more effective and reliable polishing of porous membranes.

3. Demonstrating the relation between polishing quality, surface roughness data and visual characteristics of nanotubes and introducing surface profilometry as a quicker and cheaper characterization method compared to SEM imaging for initial testing.

7.0 Future Work

Since it was proved that commercially available AAO membrane can vary in thickness and general form, further studies are required to explore parameters that are able to compensate for the inherent unevenness. Studies can be focused on alternative mounting techniques and/or a more flexible type of attachment which showed to be a better material to suppress the high spots to the level of lower spots. However, non-destructive detachment method requires to be considered as a critical factor. Different polishing pads can be explored as another option since there are so many parameters that can be investigated about them and there is a lot of flexibility in designing experiments.

Uniformity in polishing the surface, with respect to unpredictable variation between them, always remain a challenge in using contact material removing methods like mechanical polishing. Considering material removing methods that are insensitive to surface topography is another subject that can be explored in future work. Optical profilometry can be used as a quick and reliable testing method to test a few samples from every new box of Whatman AAO membranes.

Although many samples have shown to have intact areas after polishing or clogged tubes, cell studies need to be done to evaluate the effectiveness of these samples and provide us with a comparison between what we consider clogged sample and open sample. If there is not a significant change in the efficiency, process will be consistent for its ultimate objective in transfection.

8.0 References

[1] "Http://Patients.Ambrygen.Com/General-Genetics/Know-the-Basics/about-Genetic-Disorders/Statistics."

[2] "Http://Desispeaks.Com/Gene-Therapy/."

[3] "Https://Www.Fda.Gov/ForConsumers/ConsumerUpdates/Ucm589197.Htm."

[4] Niidome, T., and Huang, L., 2002, "Gene Therapy Progress and Prospects: Nonviral Vectors," Gene Ther., **9**(24), pp. 1647–1652.

[5] Golshadi, M., Wright, L. K., Dickerson, I. M., and Schrlau, M. G., 2016, "High-Efficiency Gene Transfection of Cells through Carbon Nanotube Arrays," Small, **12**(22), pp. 3014–3020.

[6] Ahmed, A., "Efficient Template-Based Nanomanufacturing of Carbon Nanotube Arrays for Cell Applications," p. 109.

[7] "Http://Www.Dictionary.Com/Browse/Phenotype?S=t."

[8] Collins, M., and Thrasher, A., 2015, "Gene Therapy: Progress and Predictions," Proc. R. Soc. B Biol. Sci., **282**(1821), p. 20143003.

[9] Jelkmann, W., and Lundby, C., 2011, "Blood Doping and Its Detection," Blood, **118**(9), pp. 2395–2404.

[10] Varmus, H. E., Vogt, P. K., and Bishop, J. M., 1973, "Integration of Deoxyribonucleic Acid Specific for Rous Sarcoma Virus after Infection of Permissive and Nonpermissive Hosts," Proc. Natl. Acad. Sci., **70**(11), pp. 3067–3071.

[11] Li, S., and Ma, Z., 2001, "Nonviral Gene Therapy," Curr. Gene Ther., **1**, pp. 201–226.

[12] Somiari, S., Glasspool-Malone, J., Drabick, J. J., Gilbert, R. A., Heller, R., Jaroszeski, M. J., and Malone, R. W., 2000, "Theory and in Vivo Application of Electroporative Gene Delivery," Mol. Ther., **2**(3), pp. 178–187.

[13] Liu, F., and Huang, L., 2002, "A Syringe Electrode Device for Simultaneous Injection of DNA and Electrotransfer," Mol. Ther., **5**(3), pp. 323–328.

[14] Newman, C. M., Lawrie, A., Brisken, A. F., and Cumberland, D. C., 2001, "Ultrasound Gene Therapy: On the Road from Concept to Reality," Echocardiography, **18**(4), pp. 339–347.

[15] Amabile, P. G., Waugh, J. M., Lewis, T. N., Elkins, C. J., Janas, W., and Dake, M. D., 2001, "High-Efficiency Endovascular Gene Delivery via Therapeutic Ultrasound," J. Am. Coll. Cardiol., **37**(7), pp. 1975–1980.

[16] Song, J., Chappell, J. C., Qi, M., VanGieson, E. J., Kaul, S., and Price, R. J., 2002, "Influence of Injection Site, Microvascular Pressureand Ultrasound Variables on Microbubble-Mediated Delivery of Microspheres to Muscle," J. Am. Coll. Cardiol., **39**(4), pp. 726–731.

[17] Liu, F., and Huang, L., 2002, "Noninvasive Gene Delivery to the Liver by Mechanical Massage," Hepatology, **35**(6), pp. 1314–1319.

[18] He, B., Yang, Y., Yuen, M. F., Chen, X. F., Lee, C. S., and Zhang, W. J., 2013, "Vertical Nanostructure Arrays by Plasma Etching for Applications in Biology, Energy, and Electronics," Nano Today, **8**(3), pp. 265–289.

[19] VanDersarl, J. J., Xu, A. M., and Melosh, N. A., 2012, "Nanostraws for Direct Fluidic Intracellular Access," Nano Lett., **12**(8), pp. 3881–3886.

[20] Xie, X., Xu, A. M., Leal-Ortiz, S., Cao, Y., Garner, C. C., and Melosh, N. A., 2013, "Nanostraw–Electroporation System for Highly Efficient Intracellular Delivery and Transfection," ACS Nano, **7**(5), pp. 4351–4358.

[21] Shingubara, S., 2003, "Fabrication of Nanomaterials Using Porous Alumina Templates," J. Nanoparticle Res., **5**(1/2), pp. 17–30.

[22] Han, C. Y., Willing, G. A., Xiao, Z., and Wang, H. H., 2007, "Control of the Anodic Aluminum Oxide Barrier Layer Opening Process by Wet Chemical Etching," Langmuir, **23**(3), pp. 1564–1568.

[23] Lohrengel, M. M., 1993, "Thin Anodic Oxide Layers on Aluminium and Other Valve Metals: High Field Regime," Mater. Sci. Eng. R Rep., **11**(6), pp. 243–294.

[24] Leach, R., ed., 2011, *Optical Measurement of Surface Topography*, Springer, Berlin.

[25] "Electron Microscopy and Analysis - Goodhew - Taylor 3rd 2001.Pdf."

[26] William D. Callister, Jr., *Materials Science and Engineering An Introduction*, John Wiley & Sons, Inc.

[27] Park, J.-H., and Sudarshan, T. S., *Chemical Vapor Deposition*, Materials Park, Ohio : ASM International, 2001.

[28] Golshadi, M., Maita, J., Lanza, D., Zeiger, M., Presser, V., and Schrlau, M. G., 2014, "Effects of Synthesis Parameters on Carbon Nanotubes Manufactured by Template-Based Chemical Vapor Deposition," Carbon, **80**, pp. 28–39.

[29] Evans, C. J., Paul, E., Dornfeld, D., Lucca, D. A., Byrne, G., Tricard, M., Klocke, F., Dambon, O., and Mullany, B. A., 2003, "Material Removal Mechanisms in Lapping and Polishing," CIRP Ann., **52**(2), pp. 611–633.

[30] Xie, Y., and Bhushan, B., 1996, "Effects of Particle Size, Polishing Pad and Contact Pressure in Free Abrasive Polishing," Wear, **200**(1–2), pp. 281–295.

[31] Runnels, S. R., 1994, "Tribology Analysis of Chemical-Mechanical Polishing," J. Electrochem. Soc., **141**(6), p. 1698.

[32] Jianfeng Luo, and Dornfeld, D. A., 2001, "Material Removal Mechanism in Chemical Mechanical Polishing: Theory and Modeling," IEEE Trans. Semicond. Manuf., **14**(2), pp. 112–133.

[33] Quirk, M., and Serda, J., 2001, *Semiconductor Manufacturing Technology*, Prentice Hall.

[34] Hooper, B. J., Byrne, G., and Galligan, S., 2002, "Pad Conditioning in Chemical Mechanical Polishing," J. Mater. Process. Technol., **123**(1), pp. 107–113.

[35] Wu, K.-C., Jose, S., Gan, W. R., Clara, S., and Wong, K., "(54) Pad Break-In Method For Chemical Mechanical Polishing Tool Whch Polishes With Cera-Based Slurry," p. 13.

[36] Mann, Richard P, Avinash P. Nayak, M. Saif Islam, V. J. Logeeswaran, Edward Bormashenko, Kerry Allan Wilson, and Frank Vollmer, 2012, "Wet and Dry Etching," Encyclopedia of Nanotechnology.