DEVELOPMENT OF MICRO 3D STRUCTURED POLYVINYLIDENE FLUORIDE (PVDF) THIN FILM

A Thesis
Presented to the
Faculty of
San Diego State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in
Mechanical Engineering

by
Abtin Sepehri
Fall 2012
SAN DIEGO STATE UNIVERSITY

The Undersigned Faculty Committee Approves the

Thesis of Abtin Sepehri:

Development of Micro 3D Structured Polyvinylidene Fluoride (PVDF) Thin Film

Kee Moon, Chair
Department of Mechanical Engineering

Samuel Kassegne
Department of Mechanical Engineering

Mahasweta Sarkar
Department of Electrical and Computer Engineering

11/2/2012
Approval Date
DEDICATION

To my family, my friends, all my teachers and mentors from childhood until now and the ones who are trying to spread knowledge, peace and happiness for all human beings regardless of their nationality, background, gender, race or color.
If you can’t explain it simply, you don’t understand it well enough.

-Albert Einstein
ABSTRACT OF THE THESIS

Development of Micro 3D Structured Polyvinylidene Fluoride (PVDF) Thin Film

by

Abtin Sepehri

Master of Science in Mechanical Engineering
San Diego State University, 2012

In this study, polymers, their definition and history, and some examples of the most important ones have been explained. The major manufacturing processes for polymer product making and especially thin film polymers also have been described. Polyvinylidene Fluoride (PVDF), which is the focus of this thesis discussed in details and chemical physics and the molecular structures and different configurations of its crystalline assembly and their properties discussed in details. Several PVDF powders and different solvents acquired, the major affective parameters and conditions investigated, and the best ratios and processes in order to achieve the desired solution proper to use for electro-spinning procedure reported. Micro 3D structured features fabricated from SU-8-100 photoresist on the Silicon wafer substrate and all the steps, conditions, chemicals and instruments have been fully described. Electro-spinning machine, its functions and fundamentals explained and one designed, built and used to investigate the properness of this method for depositing PVDF polymer on micro 3D structures. The surface quality and the evaluating measurement tools and techniques have been described. Scanning electron microscope (SEM) as the major evaluating tool used and many experiments with different conditions and parameters set-up conducted to investigate the uniformity and surface quality of the electro-spun chips. Image analysis software was used to quantify the surface quality of the chips in different areas and under different conditions. In addition, EDX spectroscopy was performed to identify the elements of deposited polymer on the microchips.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xvii</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Polymers, Definition and History</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Polymers, Examples and Importance</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Polyvinylidene Fluoride (PVDF)</td>
<td>5</td>
</tr>
<tr>
<td>1.4 Polymer Thin Films and Their Applications</td>
<td>6</td>
</tr>
<tr>
<td>1.5 The Scope of Thesis</td>
<td>6</td>
</tr>
<tr>
<td>2 CHEMICAL PHYSICS OF PVDF</td>
<td>8</td>
</tr>
<tr>
<td>2.1 Molecular Structure</td>
<td>8</td>
</tr>
<tr>
<td>2.2 Phase Transferring Techniques</td>
<td>10</td>
</tr>
<tr>
<td>3 MANUFACTURING AND PRODUCT MAKING METHODS</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Large Part Manufacturing Methods</td>
<td>13</td>
</tr>
<tr>
<td>3.1.1 Casting</td>
<td>13</td>
</tr>
<tr>
<td>3.1.2 Extrusion</td>
<td>14</td>
</tr>
<tr>
<td>3.1.3 Machining</td>
<td>15</td>
</tr>
<tr>
<td>3.2 Thin Film Manufacturing</td>
<td>17</td>
</tr>
<tr>
<td>3.2.1 Solvent Painting</td>
<td>17</td>
</tr>
<tr>
<td>3.2.2 Film Extrusion</td>
<td>18</td>
</tr>
<tr>
<td>3.2.2.1 Basic Film Extrusion</td>
<td>18</td>
</tr>
<tr>
<td>3.2.2.2 Blown Film Extrusion</td>
<td>18</td>
</tr>
<tr>
<td>3.2.3 Spin Coating</td>
<td>19</td>
</tr>
<tr>
<td>3.2.4 Physical Vapor Deposition (PVD)</td>
<td>20</td>
</tr>
<tr>
<td>3.2.4.1 Pulsed Laser Deposition</td>
<td>23</td>
</tr>
</tbody>
</table>
8.4 Microscopy Images of the Results ................................................................. 62
8.5 Energy-Dispersive X-Ray Spectroscopy (EDX) ........................................... 68

9 SURFACE QUALITY ANALYSIS ..................................................................... 73
  9.1 Image Analysis Software ......................................................................... 73
  9.2 Areas of Investigation ............................................................................ 74
    9.2.1 Bottom Flat Area ............................................................................ 74
    9.2.2 Top of the Pillars ............................................................................ 74
    9.2.3 Sidewalls ...................................................................................... 80

10 RESULTS AND CONCLUSION ...................................................................... 84

11 FUTURE WORK ......................................................................................... 86

REFERENCES .................................................................................................... 87
LIST OF TABLES

Table 6.1. General Properties of Kynar PVDF .................................................................47
Table 6.2. Solvent Uptake Percentage .........................................................................47
Table 6.3. Most Commonly Used Solvents and their Boiling and Flash Point
Temperatures ................................................................................................................48
Table 8.1. Percentage of each Element in the Selected Area. (Processing Option: All
Elements Analyzed (Normalized)) .............................................................................72
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>(a) Chemical structure of Polystyrene known also as Thermocole and (b) Polyvinyl Chloride or PVC.</td>
</tr>
<tr>
<td>1.2</td>
<td>Structures of the two principal nucleic acids RNA and DNA. The helices and nucleobases of each protein are also shown.</td>
</tr>
<tr>
<td>1.3</td>
<td>Polymer schematic of epicuticle of keratin fibers of wool, which is responsible for the hydrophobic characteristics of the wool.</td>
</tr>
<tr>
<td>1.4</td>
<td>3D demonstration of Nylon 6,6 polymer chain.</td>
</tr>
<tr>
<td>1.5</td>
<td>3D demonstration of Polyethylene polymer chain (black components are representing Carbon and white components are representing Hydrogen atoms).</td>
</tr>
<tr>
<td>1.6</td>
<td>(a) Monomer and (b) Polymer structure of Poly (Vinylidene Fluoride).</td>
</tr>
<tr>
<td>1.7</td>
<td>Examples of important polymers and their thin film applications.</td>
</tr>
<tr>
<td>2.1</td>
<td>Random orientation of PVDF polymer chain.</td>
</tr>
<tr>
<td>2.2</td>
<td>Molecular conformations and unit cells of the three common polymorphs of PVDF.</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemical structure of α-phase PVDF structure.</td>
</tr>
<tr>
<td>2.4</td>
<td>Chemical structure of β-phase PVDF structure.</td>
</tr>
<tr>
<td>2.5</td>
<td>3D model of a segment of (a) α-phase PVDF molecule with trans gauche conformation, and (b) β-phase with all-trans conformation.</td>
</tr>
<tr>
<td>2.6</td>
<td>The Heckmann diagram relating electric field, mechanical stress, and temperature.</td>
</tr>
<tr>
<td>2.7</td>
<td>Histories of hysteresis loops on a 25µm thick bi-axially stretched PVDF.</td>
</tr>
<tr>
<td>3.1</td>
<td>Comparison of different methods for fabrication of thin film polymers.</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic of a casting machine.</td>
</tr>
<tr>
<td>3.3</td>
<td>Example of industrial machinery of Nylon pipe extrusion production line by Qingdao Deyili Plastic Machinery Company.</td>
</tr>
<tr>
<td>3.4</td>
<td>Extruded nylon pipes, rods and sheets.</td>
</tr>
<tr>
<td>3.5</td>
<td>Machined plastic parts.</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematics of polymer film casting machine.</td>
</tr>
<tr>
<td>3.7</td>
<td>Schematic of tubular blown film extrusion processes.</td>
</tr>
<tr>
<td>3.8</td>
<td>Schematic of spin coating process.</td>
</tr>
</tbody>
</table>
Figure 3.9. Example of surface morphology of PVDF film without (a) and with (b) salicylic acid and (c) cross-sectional image of spin-coated PVDF film. ..........................21

Figure 3.10. Schematic of pulsed laser deposition method. ..........................................................23

Figure 3.11. Schematic of an example of an RF sputtering chamber. PT: polymer target, M: magnetron, Sh: shutter, W: window, Ar: gas inlet, P: to pump to provide flow of inert gas in the chamber. ......................................................................24

Figure 3.12. Schematic of an electron emission chemical vapor deposition set-up. ......................26

Figure 4.1. Some schematics of different lay patterns on surfaces.............................................28

Figure 4.2. Commercial atomic force microscope (AFM) by Agilent Technologies. ..................30

Figure 4.3. Schematic of AFM mechanism. .................................................................................31

Figure 4.4. Schematic of confocal microscope mechanism..........................................................32

Figure 4.5. Schematic of scanning electron microscope (SEM) mechanism. ...............................32

Figure 5.1. Schematic comparison of (a) 2D substrate (flat surface) and (b) 3D substrate (surface with pillars). ................................................................................33

Figure 5.2. SDSU MEMS lab class 100 clean-room and me in full gown making chips! ................34

Figure 5.3. Negative photolithography procedure. ......................................................................35

Figure 5.4. Micro-fabrication of 3D structure using negative photolithography procedures. .......36

Figure 5.5. Film thickness versus spin speed for photoresist SU8-50 and SU8-100......................37

Figure 5.6. Exposure energy versus film thickness (red: SU8-50, blue: SU8-100). .....................37

Figure 5.7. Recommended soft bake time and temperature for SU8-50 and SU8-100. .............38

Figure 5.8. From left to right: isopropyl alcohol, acetone and deionized water used for cleaning and rinsing. .........................................................................................38

Figure 5.9. Ultrasonic bath used for cleaning the substrate. ..........................................................38

Figure 5.10. Air gun connected to filtered and compressed N2 gas.............................................39

Figure 5.11 Spin coating machine; time and speed can be set on its digital panel. .......................39

Figure 5.12. (a) Negative photoresist SU-8 100 and (b) SU-8 developer from MicroChem Inc. .......................................................................................................................39

Figure 5.13. Hot plate. ..................................................................................................................40

Figure 5.14. UV exposure machine. ............................................................................................40

Figure 5.15. UV power meter used to measure the actual output of UV light from the exposure machine. .........................................................................................40

Figure 5.16. Mask designed with software Coventorware with different designs and dimensions. ...............................................................................................................41
Figure 5.17. Microscopy image of the mask ...........................................................................41
Figure 5.18. Micro-fabricated whole Silicon wafers with different microstructures on them ..................................................................................................................................42
Figure 5.19. Micro square SU-8 pillars on Silicon substrate ..................................................42
Figure 5.20. 3D Microscopy image of micro square SU-8 pillars on Silicon substrate ............43
Figure 5.21. Micro structured SU-8 pillars with the shapes of squares with rounded corners ........................................................................................................................................43
Figure 5.22. 3D microscopy image of 70 to 80µm tall square pillars ........................................44
Figure 5.23. 3D image of square pillars with 300µm gap ......................................................44
Figure 6.1. (left) DH-F22Z-2, (middle) 301F, and (right) 2821 PVDF powder .....................45
Figure 6.2. SEM image of Kynar 301F PVDF powder ..........................................................46
Figure 6.3. SEM image of Kynar 2821 PVDF powder ...........................................................46
Figure 6.4. N, N Dimethylformamide (D4551) from Sigma-Aldrich .....................................48
Figure 6.5. Experimental data of making PVDF solutions .....................................................49
Figure 6.6. Some of the soultions made ..................................................................................49
Figure 6.7. Some of the mixed solution samples; PVDF type, percentages, ratios and temperatures are all very important factors to have homogenous mixtures. ...............50
Figure 6.8. Hot plate magnetic stirrer .....................................................................................50
Figure 6.9. Centrifuge machine ..............................................................................................51
Figure 7.1. Schematic of electro-spinning machine ..............................................................53
Figure 7.2. Number of electro-spinning related publications .................................................54
Figure 7.3. Front and backside of Acopian DC high voltage power supply, capable of generating the output voltage of up to 20,000V. .........................................................55
Figure 7.4. Syringe pump from Harvard Co ...........................................................................55
Figure 7.5. Adjustable lab jack(stage) with the adjustable range of 250 mm from Fisher Scientific ..........................................................................................................................56
Figure 7.6. Frame made of plexiglass .....................................................................................56
Figure 7.7. Syringe and butterfly 27 gauge (0.21mm inner diameter) needle with 12” tube .........................................................................................................................................57
Figure 7.8. Electro-spinning machine set-up ..........................................................................58
Figure 8.1. 2D electro-spun PVDF film with 20 nm Aluminum layers on top and bottom .........................................................................................................................................59
Figure 8.2. Electro-spun PVDF film on 3D micro-pillar chip with 20 nm Aluminum layers on top and bottom ..................................................................................................................59
Figure 8.3. Hirox optical microscope. .................................................................60
Figure 8.4. FEI electron scanning microscope (SEM) and me working!! .................61
Figure 8.5. Hitachi TM-3000, tabletop SEM ..........................................................61
Figure 8.6. (a) Non-coated glass surfaces and (b) 3D SU-8 structured pillars. .................62
Figure 8.7. (a) Electro-spun 2D glass surfaces and (b) Electro-spun 3D SU-8 structured pillars .........................................................................................................................62
Figure 8.8. (a) PVDF spin-coated surfaces (rpm: 3000) (a) 2D flat glass substrate and (b) 3D SU-8 structured pillars ...........................................................................................................63
Figure 8.9. (a) PVDF spin-coated surfaces (rpm: 6000) (a) 2D flat glass substrate and (b) 3D SU-8 structured pillars ...........................................................................................................63
Figure 8.10. (a) Non-coated pillar and (b) spin-coated surfaces around the 3D SU-8 structured pillars. (rpm: 6000). .................................................................................64
Figure 8.11. (a) Electro-spun 3D pillars with the flow rate of 80 μl/min and (b) 40 μl/min .................................................................................................................................64
Figure 8.12. SEM image of topography of the surface of electro-spun PVDF layer; flow rate of 40 μl/min. ........................................................................................................65
Figure 8.13. SEM image of topography of surface of electro-spun PVDF layer; flow rate of 80 μl/min ...........................................................................................................65
Figure 8.14. SEM image of topography of surface electro-spun PVDF layer on 3D substrate. Flow rate of 80 μl/min .....................................................................................66
Figure 8.15. SEM image of surface topography of electro-spun PVDF layer on 3D substrate. Flow rate of 80 μl/min .....................................................................................66
Figure 8.16. Zoomed in SEM image of a single pillar of electro-spun PVDF 3D chip. Flow rate of 80 μl/min ........................................................................................................67
Figure 8.17. PVDF electro-spun covered 3D micro pillars from angle. Flow rate of 100 μl/min ................................................................................................................67
Figure 8.18. SEM image of surface finish of electro-spun PVDF layer on 3D substrate. Flow rate of 60 μl/min. X150 magnification .................................................................68
Figure 8.19. SEM image of surface finish of electro-spun PVDF layer on 3D substrate. Flow rate of 60 μl/min. X800 magnification .................................................................69
Figure 8.20. The texture of surface area around a pillar is shown. Flow rate of 40 μl/min. X600 magnification .........................................................................................69
Figure 8.21. SEM image of the surface finish area around pillars. Flow rate of 40 μl/min. X600 magnification .........................................................................................70
Figure 8.22. Spectrum selected from electro-spun PVDF sample for EDX analysis ..........71
Figure 8.23. EDX analysis graph, which shows the intensity of each element existing in the sample chip .........................................................................................71
Figure 8.24. EDX analysis result of the percentage of each element. .....................................72

Figure 9.1. Screen shot of image analysis software UTHSCSA Image Tool. .........................73

Figure 9.2. Surface porosity versus flow rate for bottom flat surface. Gap was set at 120mm and voltage at 10KV. ..................................................................................................74

Figure 9.3. SEM images of the surface porosity in Figure 9.2. Distance: 120mm. Voltage: 10KV. Flow rate: varies. ............................................................75

Figure 9.4. Surface porosity versus distance for bottom flat surface. Flow rate of 80 µl/min and voltage of 10KV was set.................................................................75

Figure 9.5. SEM images of the surface porosity in Figure 9.4. Flow rate: 80 µl/min. Voltage: 10KV. Distance: varies. ........................................................................76

Figure 9.6. Surface porosity versus voltage difference for bottom flat surface. The setting of flow rate of 80 µl/min and distance of 120mm used. .........................76

Figure 9.7. SEM images of the surface porosity in Figure 9.6. Flow rate: 80 µl/min. Distance: 120mm. Voltage: varies. .................................................................77

Figure 9.8. Surface porosity versus flow rate for top flat surface of the micro pillars. Gap was 120mm and voltage 10KV. .................................................................77

Figure 9.9. SEM images of the surface porosity in Figure 9.8. Distance: 120mm. Voltage: 10KV. Flow rate: varies. .................................................................78

Figure 9.10. Surface porosity versus distance for top flat surface of the micro pillars. Flow rate of 80 µl/min and voltage of 10KV was set. .................................................78

Figure 9.11. SEM images of the surface porosity in Figure 9.10. Flow rate: 80 µl/min. Voltage: 10KV. Distance: varies. .................................................................79

Figure 9.12. Surface porosity versus voltage difference for top flat surface of the micro pillars. The setting of flow rate at 80 µl/min and distance at 120mm was used. ..................................................................................................79

Figure 9.13. SEM images of the surface porosity in Figure 9.12. Flow rate: 80 µl/min. Distance: 120mm. Voltage: varies. .................................................................80

Figure 9.14. Surface porosity versus flow rate for the side walls of micro pillars. Gap was 120mm and voltage 10KV. .................................................................80

Figure 9.15. SEM images of the surface porosity in Figure 9.14. Distance: 120mm. Voltage: 10KV. Flow rate: varies. .................................................................81

Figure 9.16. Surface porosity versus distance for the side walls of micro pillars. Flow rate of 80 µl/min and voltage of 10KV was set. .................................................................82

Figure 9.17. SEM images of the surface porosity in Figure 9.16. Flow rate: 80 µl/min. Voltage: 10KV. Distance: varies. .................................................................82

Figure 9.18. Surface porosity versus voltage difference for the side walls of micro pillars. The setting of flow rate at 80 µl/min and distance at 120mm was used. .......83
Figure 9.19. SEM images of the surface porosity in Figure 9.18. Flow rate: 80 μl/min. Distance: 120mm. Voltage: varies.
ACKNOWLEDGEMENTS

I am so honored to have Dr. Moon as my thesis advisor and very thankful to him for his endless support and guidance throughout my research. I also would like to thank Dr. Kassegne; I learned so much from him, not just in engineering and research, but also many life lessons. I would like to thank Dr. Morsi who has always been helpful if there was ever any request from him. Also my special thanks go to Dr. Mehrabadi for his great advices and support throughout my education at San Diego State University. It has always been and will be an honor for me to have real helps and supports from my two great friends Mr. Beejal Mehta and Mr. John Waynelovich. I would like to thank Dr. Barlow and Ms. Adriana Trujillo for helping me with SEM work. I also thank Thomas Murray for his help in conducting some of the experiments. My deep appreciation goes to all SDSU Kassegne MEMS lab’s members, Dr. Morsi’s students, and my great friends at SDSU for their help, friendships and support which made my research and study at SDSU one of the best experiences of my life.
CHAPTER 1

INTRODUCTION

Since decades ago, when for the first time, scientists and engineers became familiar with the polymer structures and then developed the very first synthesized assemblies which one the first record goes back to 1833 [65], researchers always put endless amount of energy in developing new polymers. With now development for the new polymer structures, for sure many new manufacturing processes came along also in order to make new polymer-based products and applications.

1.1 POLYMERS, DEFINITION AND HISTORY

As it has been defined in the science of chemistry and molecular physics, polymers referred to the chain of molecules with some sort of repeating structural patterns. The individual building blocks of these large and complex chains called monomer, which is repeating along the whole polymer network. Monomers mostly connected to each other by covalent chemical bonds [19]. See Figure 1.1 for examples of polymer building blocks [72, 73].

![Chemical structure of Polystyrene](image1.png)  
![Chemical structure of Polyvinyl Chloride](image2.png)

Polymer materials by their definitions are covering a very large portion of materials that we know from the natural ones such as silk, amber and wool to the synthetic ones such as Nylon, PVC, Polystyrene and Polyethylene [59].

One of the first records of making useful polymer is going back to 1833 [59] and Goodyear company has one of the oldest patents related to polymer which is for vulcanization of rubber in 1844 [28].

Celluloid was widely used by the end of the nineteenth century and it is considered as one of the first synthetic plastic polymers. From those years until now, polymers either natural or synthetic ones have extensively been used in many different areas and have so many application in many industries such as automotive, cosmetics, electronics, construction, biomedical devices and pharmaceutical [19].

Polymer chemistry, polymer physics and polymer science are the major academic branches and fields, which are involved in researching and developing of the theories, new polymers, manufacturing processes and new applications.

It is also important to mention here that one of the down sides to the synthetic polymers is that these materials usually are not biodegradable. In the other word, it means that they remain in the environment for a very long time. They are not as the other natural materials, which can get recycled by nature, therefore these synthetic polymers, are causing environmental problems and would be even a bigger issue in the near future for environment and human being. At the other hand, the synthetic polymers are mostly made from petroleum. Because of the limited sources of the oil and gas and also not always having easy access to these sources because of variety of reasons from political reasons to bad weather and engineering hardships, the manufacturing of these now days essential polymers can be challenging.

1.2 POLYMERS, EXAMPLES AND IMPORTANCE

Polymers can be categorized in different ways such as natural and synthesized or human-made ones. Biopolymers such as nucleic acids (Figure 1.2 [37]) which are the foundational structure of DNA and RNA are considered as natural polymers. Wood, wool (Figure 1.3 [47]), silk and potato can be another example of natural polymers also [41, 49]. Our body’s enzymes and proteins are considered as natural polymer material also.
Synesthetic rubber, Nylon, PVC, Polystyrene, Polyethylene and PVDF are just few examples of the long list of synthetic polymers that scientist and engineers could develop so far [19, 41].

In the synthetic polymers category, we can also define four different sub-categories based on the utility of these polymer materials that are thermoplastics, thermosets, elastomers and synthetic fibers.

One example of synthetic polymers is Nylon (Figure 1.4 [68]) or generically known as Polyamides which is one the most known and very widely used in so many different industries. For the first time developed by Wallace Carothers at DuPont’s research facility at the DuPont Experimental Station on February 28, 1935. It is a semi-crystalline thermoplastic
polymer which is demonstrating desirable thermal, mechanical and chemical properties that is making it so proper for many different industries and verities of applications such as automotive, textile and also medical industries [22, 59]

Nylon used as the replacement of the silk in textile industry, also the solid Nylon used for making gears and bearings and general hardware for automotive and aerospace industries.
It has also used for making many biomedical devices shells and their functional components as well. Also very widely has been used for making composite materials.

Polyethylene (Figure 1.5 [69]) is another example of the important polymers developed so far which is the most common plastic. About 80 million metric tons of this plastic is manufactured every year. It is widely used in the packaging industry and products such as plastic bags, plastic films, geo-membranes and all kind of different bottles and containers [50].

![Polyethylene polymer chain](http://en.wikipedia.org/wiki/Polyethylene)


### 1.3 Polyvinylidene Fluoride (PVDF)

Polyvinylidene Fluoride (PVDF) (Figure 1.6 [76]) is a semi-crystalline polymer, which has some very attractive mechanical, chemical and electrical properties. It is a good chemical resistant and has reasonable high mechanical strength and flexibility. It has been used for the parts and applications that require high purity, great mechanical strength, and/or good chemical properties such as resistance to solvents, bases and acids and/or good resistivity to the heat [76].

PVDF is relatively inexpensive in comparison to other polymers and by having the lower melting point around 170 °C and reasonable melting viscosity, it provides an easier and less costly injection molding process.

Beside the powder PVDF, this polymer is mostly available in the forms of piping products, sheets, tubing, films and plates. Injection molding is the most common process of making parts from PVDF.
PVDF has been widely examined for its application as membrane materials [21]. PVDF membranes have been used for proton conduction [24, 32, 48], gas removal and separation, and lastly for biological applications [20, 58, 60, 75].

Hylar (Solvay), Kynar (Arkema) and Solef (Solvay) are the major suppliers and manufacturers of the PVDF powder, products and parts made of PVDF worldwide.

One of the most important discoveries about the characteristics of Polyvinylidene Fluoride (PVDF) is its piezoelectric and pyro-electric behavior.

In 1961, for the first time the piezoelectric Polyvinylidene Fluoride was invented. The piezoelectric plastic that is inexpensive and is highly sensitive that can be used as a good pressure sensor, which is also mechanically and chemically robust.

1.4 POLYMER THIN FILMS AND THEIR APPLICATIONS

The applications of thin film polymers can be countless and are expanding very fast. Figure 1.7 shows some of the most important polymers and their application as thin films [17].

1.5 THE SCOPE OF THESIS

In this study, the main goal is to produce a thin layer of Polyvinylidene Fluoride (PVDF) polymer on a micro 3D structure by performing electro-spinning processes.

The first portion of this work is focused on making the proper solution of PVDF by trying different PVDF powders, solvents and percentages until the good mixture of solution for being used in electro-spinning machine is achieved.

Another focus of this study is about making the desired micro 3D structures by performing the micro-fabrication techniques and photolithography processes.

Building an electro-spinning machine and using it for depositing a thin layer of PVDF polymer on the 3D microstructure is another important part of this study.

In addition, at the end, evaluating the surface quality of the deposited thin film of PVDF and analyzing the different effective parameters is another goal of this study. Scanning electron microscope (SEM) was used as the evaluating tool, and image analysis software for quantifying the surface quality of the deposited polymer on micro 3D structured chips.
CHAPTER 2

CHEMICAL PHYSICS OF PVDF

2.1 MOLECULAR STRUCTURE

As it mentioned in the introduction part, the Polyvinylidene Fluoride (PVDF) (Figure 2.1 [31]) is one of the most attractive polymers. Beside the low price for its powder, it has very good chemical and mechanical robust properties. With some techniques, it can become piezoelectric which is making it a very great candidate for so many different applications. The reason for this interesting property of PVDF lays in the molecular arrangement of its structure.

Four major crystalline structures for PVDF have been discovered so far: α, β, γ and δ. The differences between these configurations is based on the conformation of the C-C bonding with the chain as whole [15,46] (see Figure 2.2).

α-phase PVDF is the most stable formation energy wise, and it is getting shaped in the easiest and most straightforward processes. Most of the crystalline structure of the commercial PVDF powder and films are in this form. Chemical structure of α-phase PVDF is shown in Figure 2.3 [15].
Figure 2.2. Molecular conformations and unit cells of the three common polymorphs of PVDF. Source: Neese, Bret P. “Investigations of Structure-Property Relationships to Enhance the Multifunctional Properties of PVDF-based Polymers.” PhD diss., Pennsylvania State University, 2009.

Figure 2.3. Chemical structure of \( \alpha \)-phase PVDF structure. Source: Chang, Chieh. “Direct-Write Piezoelectric Nanogenerator by Near-Field Electrospinning.” PhD diss., University of California, Berkeley, 2009.
As it can be seen in Figure 2.3, the PVDF chains shaped with the respective polarizations in alternating directions (trans gauche+ trans gauche- conformation, tg+tg-), this is demonstrating the reasons for being a more energy-stabled PVDF structure. [15, 46, 76] α-phase PVDF does not exhibit any piezoelectricity.

As it is shown in Figure 2.4, in β-phase, the components ordered in such a way that the conformation is all-trans (tttt) [15]; dipoles arranged to the one direction therefore they are not canceling each other out as far as their electrical charge orientations (See Figure 2.5 [34]).

β-phase structured PVDF, because of its piezoelectricity behavior and great capability of converting the mechanical and electrical energy to each other. It is very valuable polymer for many different companies and industries such as measurement instrumentation companies, precision positioning manufacturers or energy harvesting related companies.

### 2.2 Phase Transferring Techniques

In general, phases of crystalline structures of PVDF and their properties are related and transferable to each other. By performing specific mechanical and/or electrical procedures on the polymer, specific molecular structure can be achieved and therefore the desired properties [36]. These relations and required procedures have described by Heckmann [12] and are shown in Figure 2.6.
Figure 2.5. 3D model of a segment of (a) $\alpha$-phase PVDF molecule with trans gauche conformation, and (b) $\beta$-phase with all-trans conformation. Source: Jee, T. K. “Nanoscale Characterization of Solution-Cast Poly(vinylidene fluoride) Thinfilms Using Atomic Force Microscopy.” Master’s Thesis, Texas A&M University, 2005.

Figure 2.6. The Heckmann diagram relating electric field, mechanical stress, and temperature. Source: Buchanan, Relva C., ed. Ceramic Materials for Electronics. 3rd ed. New York: Marcel Dekker, 2004.
One of the most common procedures performed on PVDF polymer for transferring α crystalline configuration to β-phase shape is polling [62]. These procedures have also been used for polymer characterization and property constant measurement processes also [16, 42].

In polling procedure, a very high voltage power (mostly 5KV to 20KV) will be applied to the two sides of the film along with heat and some mechanical stretching [56, 57]. These treatments will periodically be repeated many times and constantly the piezoelectricity of the material is measured and the procedure will end when the desired piezoelectricity property occurs [74] (See Figure 2.7 [62]).

CHAPTER 3
MANUFACTURING AND PRODUCT MAKING
METHODS

Polymers are usually coming in the forms of different size of powders and granules after they have been synthesized mostly from petroleum. Many techniques and procedures have so far been developed to make the desired parts and products from the polymer powders such as sheets, pipes, rods, films and many custom shaped parts.

The focus of this work is on producing thin film PVDF polymer. Thin films have been defined as a very thin layer of material (here PVDF polymer) which can be from couple of nanometer up to tens of micrometer in thickness. Thin film polymers have so many applications and are used in many areas such as packaging, coating and making high-tech product such as monitor screens, electronics and sensors.

Some examples of the techniques from the most common and basic methods to the high-tech procedures for making the polymer products specially polymer films which are more relevant to this study are briefly described in bellow. Figure 3.1 shows the comparison and availability of the techniques for manufacturing thin film polymers based on Chrisey et al. work.

In the next couple of sub-chapters, some of the major bulk and large part manufacturing and then some important thin film manufacturing processes have explained.

3.1 LARGE PART MANUFACTURING METHODS

In this section, some of the very common bulk-part making methods are described.

3.1.1 Casting

Generally, casting (Figure 3.2 [14]) in manufacturing subject is referred to the manufacturing process that the material (here polymer) is heated until it gets molten and then the liquid or semi-liquid molten material be poured into a mold. Mold is a hollow cavity, which is designed, based on the final desired product shape. Material in the mold will be
solidified and cooled either naturally or by force by providing the low temperature atmosphere [54]. Casting has history of more than 6000 years. Usually the casted parts need some finishing procedures to be performed on them in order to have good quality finishing surfaces. It is not very useful process for fabricating polymer products especially thin layer of polymers.

### 3.1.2 Extrusion

Extrusion is referred to the manufacturing process that the material, which is already liquid or semi-liquid, is pushed or drawn through a die of the desired cross-section. Two benefits of this procedure are that first, it is possible to produce very complex cross-sectioned parts and products. Second, because in the extrusion process, materials are just subject to compressive and shear stresses, therefore this technique is very suitable for brittle materials
that cannot tolerate the hammering and hard impact machining processes. Most of the time the product of extrusion machine have good quality surfaces and no more finishing processes are needed (Figure 3.3 [22] and 3.4 [53]).

In extrusion procedure in general, the temperature of the material, speed of the rollers, pullers and extruder, the speed of cooling the product and sometimes some additives are the major parameters involved in producing high quality extruded products.

### 3.1.3 Machining

Machining is called to the procedure that the final product formed by removing some material from a raw piece of solid cut of a material. Turning, drilling, milling, shaping, broaching, sawing, planning, boring, reaming, and tapping are some of the most common technique which fall into the machining category of manufacturing procedures. Most of these mentioned sub-category procedures nowadays are performed by CNC (computer numerical control) machines, which are much faster and making more accurate final products.

Machining is very common procedure in making polymer-based products for industrial use and usually performed in combination with other manufacturing procedures as

one the final production stages (Figure 3.5 [64]). This technique is not a good choice for making relatively thin layer of polymers.

![Machined plastic parts](http://www.vaneflon.be/en/products/machined-parts.aspx#.UE_sobL8s_o)

**Figure 3.5. Machined plastic parts.**

### 3.2 THIN FILM MANUFACTURING

The following methods are few examples of many methods developed to manufacture thin film products.

#### 3.2.1 Solvent Painting

Solvent painting is usually referred to the process of making the solution of the desired material (polymer) and then like very regular painting work just deposit the solution onto the surfaces by brush. The result of this method is relatively thick film, inhomogeneous and very sensitive to the viscosity of the fluid, and evaporation rate of the solvent. After the solvent has applied to the surface, mostly it would be air dried and therefore solidified. It is not a very reliable technique and the result is not constantly the same, mostly uneven coating and not easily repeatable. It is used typically in the processes that the even coating and thickness is not a very sensitive and important factor, but at the same time, it should be mentioned that this method is very easy and not expensive.
3.2.2 Film Extrusion

Two different film extrusion methods are explained as the following.

3.2.2.1 Basic Film Extrusion

Film extrusion (also known as film casting) is customized extrusion procedure that the final product would be films or thin sheets. It is one of the best quality and least expensive methods of producing polymers films. As it shown in schematic Figure 3.6 [4], the polymer powder will poured into the hopper then the extruder is compressing and melting them and pushing the semi-liquid polymer forward to the melt pump. Polymer powder would be completely melted and pushed through the slit die. A thick film is coming out of the slit compare to the final product. Polymer film because of being pulled between the chilling and the other rollers will get thinner and thinner and uniform. The final output of the machine will be a thin and uniform high quality polymer film [4].

![Figure 3.6. Schematics of polymer film casting machine. Source: Aniuoh, Kenneth Kanayo. “An Experimental and Numerical Study of the Film Casting Process.” PhD diss., Clemson University, 2007.](image)

3.2.2.2 Blown Film Extrusion

This method is the same as the other extrusion procedures until the die, which is an upright cylinder, and with the help of compressed air, the thin film polymer will blow to the
shell of the cylinder and will be formed to that shape. This method is the major process of making plastic bags and thin shell parts [13, 23] (See Figure 3.7 [13]).

Figure 3.7. Schematic of tubular blown film extrusion processes. Source: Cantor, Kirk. *Blown Film Extrusion: An Introduction*. Cincinnati, OH: Hanser Gardner.

### 3.2.3 Spin Coating

Spin coating process is relatively a straightforward process compared to other thin film making methods.

In this method the material (here polymer) will be deposited in the form of liquid (Polymer solutions) on the surface of the substrate which is kept in place by the vacuum force applied to its bottom. Then the stage of machine will spin at the desired speed and the proper acceleration rate, which can be set.

Centrifugal force will cause the liquid spread over the substrate and excess amount of material will fly off the substrate. Faster the spin and/or less viscosity for the deposited material will result with the thinner and uniform thin film. After this step, the material on the substrate will be dried and solidified naturally or by being exposed to the heat sources. If the material is sensitive and reactive to air, this process can be performed under the vacuum or in exposure to desired gases (See Figure 3.8 [11]).
Sometimes additives are used to adjust the substrate surface stickiness and/or change
the deposition material characteristics.

Figure 3.9 [26] is showing the surface of spin coated PVDF.

### 3.2.4 Physical Vapor Deposition (PVD)

Physical vapor deposition term was first used in the 1966 in the book named “Vapor
Deposition” by C. F. Powell, J. H. Oxley and J. M. Blocher Jr. PVD describes the methods
that removing material particles from the target is performed by purely applying physical
techniques rather than chemical methods to fabricate thin film layers. There are number of
different methods which can fall in this category such as “Cathodic Arc Deposition” or
“Electron Beam Physical Vapor Deposition” which are not useful methods for depositing
polymers. As far as the most of the polymers are not conductive and the mentioned methods
are typically functional for conductive metals and metal-based material, therefore they cannot
be good options for fabricating thin film polymers. However, there are some examples of
Figure 3.9. Example of surface morphology of PVDF film without (a) and with (b) salicylic acid and (c) cross-sectional image of spin-coated PVDF film. Source: Gaihre, Babita, Gursel Alici; Geoffrey M. Spinks, Julie M. Cairney. “Synthesis and Performance Evaluation of Thin Film PPy-PVDF Multilayer Electroactive Polymer Actuators.” Sensors and Actuators A: Physical 165, no. 2 (2011): 321-328.
other PVD techniques and methods, which have been used for depositing polymers; two of them are briefly described in the following sections:

3.2.4.1 PULSED LASER DEPOSITION

Based on demonstrating of D. B. Chrisey et al. [17] work and others, depositing a high quality and smooth surfaced thin layer of polymer can be performed by following the process of pulsed laser deposition.

In this method, as it is shown in the schematic Figure 3.10, the laser beam passes through the optical components and then goes into the vacuum chamber. It will hit the target, which is usually rotating; the energy of laser will result with some sort of ejected forward-directed plume of material that will land on the surface of the substrate and forming a thin film of material [17, 18].


Wavelength of the laser, the pulsing frequency and power of laser are some of the most important factors for successful and high quality deposition in this method.

3.2.4.2 RF SPUTTERING

This process is referred to plasma polymerization technique, which the result of it is the deposited thin films of plasma polymers (See Figure 3.11 [9]). The ejected atoms from
the surface of the solid target, which get loose because of bombardment of the target by energetic particles, will fly off from the target, guided onto the new surface, and will be deposited there. When the inert gas flows into the chamber, then the RF power source turns on and starts generating the energetic wave through the plasma to ionize the gas atoms. The ionized gas atoms start hitting the target and etching it and then those small broken pieces of material (here polymer) will fly off and be deposited on the substrate and forming the thin film coating [9].

This method widely has been used for fabricating the Polytetraflouroethylene (PTFE) thin film [8, 10, 29, 30, 44, 51, 61] which is used as good dielectric films [44] and low friction coverings [10, 29]. It has some optical applications as well [10].
3.2.5 Chemical Vapor Deposition (CVD)

This technique is considered as the other alternative method to “Physical Vapor Deposition”. CVD is a chemically activated process and some actual chemical reactions are taking place near or on the surface of the substrate, opposite to PVD methods, which target particles eject because of physical treatments to the surface of the target.

The first attempt of using CVD technique goes back to 1893 [35] and has been matured over the time with so many different configurations and set-ups for depositing many different materials. CVD is a very common technique for micro-fabrication processes and in MEMS field.

As an example of CVD method, “Electron Emission Chemical Vapor Deposition” is briefly explained in bellow. This set-up was used by Jianjun Wang et al. for producing thin film polymers.

As it is shown in the schematic Figure 3.12 [65], Tungsten wire was used as the filament and the substrate is hold in place by the Aluminum substrate holder. Ceramic insulating block is at the bottom. The AC voltage would apply to the filament and DC voltage to the substrate holder. The gap between the filament and substrate is adjustable. The whole set-up is in a vacuum chamber connected to a vacuum pump, then Acetylene and N2 gases introduced to the chamber [65].

The AC and DC voltages and currents, gap between the filament and substrate and flow rate of gases are important factors in this method.
Figure 3.12. Schematic of an electron emission chemical vapor deposition set-up.  
CHAPTER 4

SURFACE FINISH QUALITY

4.1 DESCRIPTION AND IMPORTANCE

Nowadays, many devices and applications especially in optical, electronics and biomedical devices industries require very precise and controlled surface finish quality in all the areas of the surfaces especially for the parts with more complicated topography and shapes. The surface finish in new high-tech devices plays a very essential and important role and sometimes devices would not work at all just because of not having proper and desired coating finish layers. These days, companies and R&D labs are even having their new branches called surface engineering department working and focusing just on the surface finish quality. Modifying the surfaces and achieving superior performance or new functionalities for the surfaces and layers are their ultimate goals [38, 52].

Surface finish, which also called as surface texture, is referred to the topography and characteristics of a surface. In the other word, the surface finish can be referred to those mountains and valleys of the deposited layers or generally, any surfaces, which depending on the expected quality of the surface it can be limited to just few nanometers [52, 71].

4.2 ELEMENTS AND FACTORS

Three major classic components defined for surface finish quality that are surface roughness, lay and waviness [71].

4.2.1 Surface Roughness

The surface roughness is referred to the height or depth of those mountains and valleys on the surface compare to the flat level of the surface. It can be defined also as vertical difference between the desired level of the surface and the bumps or holes on the surface. This factor is what it commonly referred as smoothness of a surface.
4.2.2 Lay

Lay is mostly referred to the patterns and those continuously imperfections on the surfaces remained on the surface after the manufacturing process of the component, mostly caused by machining process (See Figure 4.1 [71]).

![Schematics of different lay patterns](http://en.wikipedia.org/wiki/Surface_finish)

4.2.3 Waviness

Waviness like lay is an imperfection on the surface finish, which mostly caused by the deficiency in manufacturing processes. They are more widely spaced and are have more gradual defects compared to lay and roughness, which makes it harder to recognize and measure.

Beside the categories described above, the functionality and characterization of the surfaces can be reported in so many more ways. Chemical composition of the surfaces, which can contribute to how degradable the surfaces are, can be another factor of investigating the surface quality. Mechanical properties like hardness, fracture toughness or coefficient of friction, which can lead to the durability of the surfaces in contact with other material also, can be investigated for different surfaces [52].

4.3 Methods and Tools of Evaluation

There are two main categories for all the methods used for surface finish quality evaluation and measurements, which are contact and non-contact techniques.

4.3.1 Contact Methods

In the contact methods category, some actual physical probes or profilometer will travel on the surfaces of the component and then data from the tip of the probe, like the coordination and angle of the tip, will be read and recorded. Atomic force microscope (AFM) is capable of scanning and investigating the surface topography and surface finish of layers and components down to the atom level (See Figure 4.2 [1] and 4.3 [66]).

4.3.2 Non-contact Methods

In the non-contact category there are many different methods such as photogrammetry, interferometry, field emission microscopy (FEM) which is capable of investigating the surface structures down to molecular level. All kinds of different microcopy techniques like optical microscopy, confocal microscopy, X-Ray microscopy and scanning electron microscopy (SEM) are falling in the this non-contact category of surface finish evaluating techniques. SEM imaging method was used in this study for evaluating the surface finish of the deposited PVDF layers (See Figures 4.4 [67] and 4.5 [70]).

CHAPTER 5

MICRO-FABRICATION OF 3D STRUCTURE

5.1 FROM 2D TO 3D

The process of making the micro 3D structured platform to serve as the substrate for electro-spinning the PVDF polymer on is a good portion of this work. As it is shown in Figure 5.1, the effort here is to go from a flat substrate to a substrate with many micro pillars on it. Obviously the 3D chip will have much higher surface area compare to the flat chip which can be beneficial for future applications.

![Figure 5.1. Schematic comparison of (a) 2D substrate (flat surface) and (b) 3D substrate (surface with pillars).](image)

5.2 MICRO-FABRICATION OF 3D STRUCTURE

The micro-fabrication process is referred to the series of steps and procedures in order to build and create miniature structures, mostly in the range of microns. The process is followed in the clean-room facilities, which the existence of any dust or generally any particles is very limited in order to provide an almost dust-free atmosphere. [25, 39]

All the micro-fabrication processes of this research have been done at the facilities of San Diego State University MEMS lab and class 100 clean-room. (Figure 5.2)
5.2.1 Micro-fabrication Procedure

The summary of required steps for negative photolithography procedure [33, 40] shown in Figure 5.3 and all the descriptions and details of each step of the process along with all the critical parameters for every stage are explained in Figure 5.4.

Figures 5.5, 5.6, and 5.7 [63] are the data and recommendations for using the SU-8 photoresist from the manufacturer of the resist material, Microchem Company.

5.2.2 Chemicals and Equipment

Figures 5.8 to 5.15 are the chemicals and equipment used based on the procedure explained in Figure 5.4.

5.2.3 Mask design

By using the Coventorware software, several masks were designed with different shapes and dimensions for negative and positive lithography procedure; then the designs were sent to specialized mask printing company for print (Figures 5.16 and 5.17).
Figure 5.3. Negative photolithography procedure.
5.3 MICRO-FABRICATED 3D STRUCTURES

The micro-fabricated whole Silicon wafer is shown in Figure 5.18. Figure 5.19 to 5.23 are microscopy images of micro-fabricated SU-8 pillars on Silicon substrate.
Figure 5.5. Film thickness versus spin speed for photoresist SU8-50 and SU8-100. Source: Vahidi, Nasim Winchester. “Electrical Characterization of Three Dimensional DNA-Based Bionanoelectronics Platforms.” Master’s Thesis, San Diego State University, 2011.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Thickness (µm)</th>
<th>Pre-bake @ 65°C</th>
<th>Softbake @ 95°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8 50</td>
<td>40</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>SU-8 100</td>
<td>100</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>30</td>
<td>90</td>
</tr>
</tbody>
</table>

Figure 5.7. Recommended soft bake time and temperature for SU8-50 and SU8-100. Source: Vahidi, Nasim Winchester. “Electrical Characterization of Three Dimensional DNA-Based Bionanoelectronics Platforms.” Master’s Thesis, San Diego State University, 2011.

Figure 5.8. From left to right: isopropyl alcohol, acetone and deionized water used for cleaning and rinsing.

Figure 5.9. Ultrasonic bath used for cleaning the substrate.
Figure 5.10. Air gun connected to filtered and compressed N2 gas.

Figure 5.11 Spin coating machine; time and speed can be set on its digital panel.

Figure 5.12. (a) Negative photoresist SU-8 100 and (b) SU-8 developer from MicroChem Inc.
Figure 5.13. Hot plate.

Figure 5.14. UV exposure machine.

Figure 5.15. UV power meter used to measure the actual output of UV light from the exposure machine.
Figure 5.16. Mask designed with software Coventorware with different designs and dimensions.

Figure 5.17. Microscopy image of the mask.
Figure 5.18. Micro-fabricated whole Silicon wafers with different microstructures on them.

Figure 5.19. Micro square SU-8 pillars on Silicon substrate.
Figure 5.20. 3D Microscopy image of micro square SU-8 pillars on Silicon substrate.

Figure 5.21. Micro structured SU-8 pillars with the shapes of squares with rounded corners.
Figure 5.22. 3D microscopy image of 70 to 80µm tall square pillars.

Figure 5.23. 3D image of square pillars with 300µm gap.
CHAPTER 6

PVDF SOLUTIONS

6.1 PVDF POWDER

For conducting this research three different Polyvinylidene Fluoride powders have been acquired from three different companies with the following commercial names (See also Figure 6.1):

- PVDF with grade name “301F” with the brand name of Kynar 500 from Arkema Inc. (Figure 6.2)
- Kynar with the grade name “2821” from Arkema Inc. (Figure 6.3)
- PVDF with the grade name “DH-F22Z-2” from a Chinese manufacturer Dowfluo Company.

Figure 6.1. (left) DH-F22Z-2, (middle) 301F, and (right) 2821 PVDF powder.

In the very first attempts, solving the different powders in different solvents (which will be discussed with more details in the next pages) has been tried. The initial results for the powder from Dowfluo Company were not promising. The mentioned powder was not providing good solution maybe because of its bigger powder size; therefore, the rest of the work continued with the first two types of PVDF.

One of the most studied PVDF powder in the market for conducting electro-spinning research, in order to achieve piezoelectric PVDF, has been shown to be Kynar 301F which
Figure 6.2. SEM image of Kynar 301F PVDF powder.

Figure 6.3. SEM image of Kynar 2821 PVDF powder.
also in this study was chosen as the main PVDF powder to conduct the rest of research based on (See Tables 6.1 and 6.2 [5-7]).

Table 6.1. General Properties of Kynar PVDF

<table>
<thead>
<tr>
<th>PVDF Type</th>
<th>Melt Viscosity (kilopoise)</th>
<th>Melting Point (°C)</th>
<th>Density (at 23°C) (ASTM-D792)</th>
<th>Homopolymer or Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>KYNAR 301F</td>
<td>29-33</td>
<td>155-165</td>
<td>1.75-1.77</td>
<td>H</td>
</tr>
<tr>
<td>KYNAR 2821</td>
<td>12-20</td>
<td>140-145</td>
<td>1.76-1.80</td>
<td>C</td>
</tr>
</tbody>
</table>

Table 6.2. Solvent Uptake Percentage

<table>
<thead>
<tr>
<th>Grade</th>
<th>Dimethylcarbonate (DMC)</th>
<th>Diethylcarbonate (DEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 30°C</td>
<td></td>
</tr>
<tr>
<td>KYNAR 301F</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>KYNAR 2821</td>
<td>60</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>at 60°C</td>
<td></td>
</tr>
<tr>
<td>KYNAR 301F</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>KYNAR 2821</td>
<td>Dissolved</td>
<td>45</td>
</tr>
</tbody>
</table>

6.2 PVDF SOLVENTS

List of the most common solvents of PVDF powder and their critical temperatures provided in Table 6.3 [5].

In this study, N,N- Dimethylformamide (D4551) has been chosen as the main solvent and has been acquired from Sigma-Aldrich Company. (Figure 6.4)

Some percentage of Acetone has also been added to the solution for the purposes of electro-spinning process.

6.3 MAKING THE PVDF SOLUTIONS

Figure 6.5 is containing all the data and parameters used for making several solution samples. Figures 6.6 and 6.7 are showing some of the actual solutions that were made.
Table 6.3. Most Commonly Used Solvents and their Boiling and Flash Point Temperatures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point (°C)</th>
<th>Flash Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Formamide (DMF)</td>
<td>153</td>
<td>67</td>
</tr>
<tr>
<td>Dimethyl Acetamide (DMAC)</td>
<td>166</td>
<td>70</td>
</tr>
<tr>
<td>Tetramethyl Urea</td>
<td>177</td>
<td>65</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide (DMSO)</td>
<td>189</td>
<td>35</td>
</tr>
<tr>
<td>Triethyl Phosphate</td>
<td>215</td>
<td>116</td>
</tr>
<tr>
<td>N-Methyl-2-Pyrrolidone (NMP)</td>
<td>202</td>
<td>95</td>
</tr>
</tbody>
</table>


Figure 6.4. N, N Dimethylformamide (D4551) from Sigma-Aldrich.

For all the solution samples, the mentioned amount of PVDF powder pre-dried at 50°C for 24 hr. in the oven to make sure no water and humidity remain in the powder.

The solutions have mixed on the hot plate magnetic stirrer at mentioned temperature in Figure 6.5 and 250 rpm (Figure 6.8).

Due to introducing some air bubble to the solution during the mixing process, the solutions have spun in the centrifuge machine for 30sec and at 3000rpm to achieve the most homogenized and air-free state of the solution (Figure 6.9).
<table>
<thead>
<tr>
<th>Solution No.</th>
<th>Solvent (DMF / Acetone) Ratio</th>
<th>Solution weight ratio (PVDF/solvent)</th>
<th>Mixing time (hr)</th>
<th>Mixing temp. (°C)</th>
<th>PVDF type</th>
<th>PVDF amount (gr)</th>
<th>Total amount (gr)</th>
<th>Result/Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8/2</td>
<td>25 % wt</td>
<td>0.5</td>
<td>25</td>
<td>DH-F22Z-2</td>
<td>2.5</td>
<td>12.5</td>
<td>Not dissolved</td>
</tr>
<tr>
<td>2</td>
<td>8/2</td>
<td>15 % wt</td>
<td>2</td>
<td>50</td>
<td>DH-F22Z-2</td>
<td>1.5</td>
<td>11.5</td>
<td>Not dissolved</td>
</tr>
<tr>
<td>3</td>
<td>N/A</td>
<td>10 % wt</td>
<td>24</td>
<td>80</td>
<td>DH-F22Z-2</td>
<td>1</td>
<td>11</td>
<td>Not dissolved</td>
</tr>
<tr>
<td>4</td>
<td>N/A</td>
<td>10 % wt</td>
<td>24</td>
<td>80</td>
<td>DH-F22Z-2</td>
<td>1</td>
<td>11</td>
<td>Not dissolved</td>
</tr>
<tr>
<td>5</td>
<td>8/2</td>
<td>50 % wt</td>
<td>4</td>
<td>25</td>
<td>301F</td>
<td>5</td>
<td>15</td>
<td>Very limited dissolved</td>
</tr>
<tr>
<td>6</td>
<td>7/3</td>
<td>50 % wt</td>
<td>24</td>
<td>75</td>
<td>301F</td>
<td>5</td>
<td>15</td>
<td>Partially dissolved - Not clear</td>
</tr>
<tr>
<td>7</td>
<td>8/2</td>
<td>25 % wt</td>
<td>4</td>
<td>75</td>
<td>301F</td>
<td>2.5</td>
<td>12.5</td>
<td>Dissolved - Higher viscosity</td>
</tr>
<tr>
<td>8</td>
<td>8/2</td>
<td>15 % wt</td>
<td>4</td>
<td>75</td>
<td>301F</td>
<td>1.5</td>
<td>11.5</td>
<td>Clear solution - Completely dissolved</td>
</tr>
<tr>
<td>9</td>
<td>7/3</td>
<td>15 % wt</td>
<td>4</td>
<td>75</td>
<td>301F</td>
<td>1.5</td>
<td>11.5</td>
<td>Dissolved - Higher viscosity</td>
</tr>
<tr>
<td>10</td>
<td>8/2</td>
<td>20 % wt</td>
<td>4</td>
<td>75</td>
<td>301F</td>
<td>2</td>
<td>12</td>
<td>Dissolved - Higher viscosity</td>
</tr>
<tr>
<td>11</td>
<td>7/3</td>
<td>50 % wt</td>
<td>24</td>
<td>75</td>
<td>2821</td>
<td>5</td>
<td>15</td>
<td>Partially dissolved - Not clear</td>
</tr>
<tr>
<td>12</td>
<td>8/2</td>
<td>25 % wt</td>
<td>4</td>
<td>75</td>
<td>2821</td>
<td>2.5</td>
<td>12.5</td>
<td>Dissolved - Higher viscosity</td>
</tr>
<tr>
<td>13</td>
<td>8/2</td>
<td>15 % wt</td>
<td>4</td>
<td>75</td>
<td>2821</td>
<td>1.5</td>
<td>11.5</td>
<td>Clear solution - Completely dissolved</td>
</tr>
<tr>
<td>14</td>
<td>8/2</td>
<td>20 % wt</td>
<td>4</td>
<td>75</td>
<td>2821</td>
<td>2</td>
<td>12</td>
<td>Dissolved - Higher viscosity</td>
</tr>
</tbody>
</table>

**Figure 6.5.** Experimental data of making PVDF solutions.

**Figure 6.6.** Some of the solutions made.
Figure 6.7. Some of the mixed solution samples; PVDF type, percentages, ratios and temperatures are all very important factors to have homogenous mixtures.

Figure 6.8. Hot plate magnetic stirrer.
As other researchers experienced also, if solutions are kept for a while, they become cloudy, this event appears due to the crystallization of the polymer [43].

Solution samples number 8 and 13 in Figure 6.5 were the best solutions chosen to use for the next steps and at the end, to limit the number of affecting factors in the results, the experiments continued just based on the solution number 8.
CHAPTER 7

ELECTRO-SPINNING

7.1 BASICS OF ELECTRO-SPINNING MACHINE

In this method, as it is shown in Figure 7.1 [15], the material dispenses from the tip of a needle, flies through air or vacuum, and lands on the surface of the substrate. The force causing the material’s particles to travel through the air is provided by the existence of a very high power electric field. The voltage difference between the needle and stage is generated by a high voltage power supply. (See Figure 7.1 [15] and Figure 7.8, p. 58)

The important parameters and settings of the machine, which each has great impact on the result of the process, are [2, 3, 45]:

- Dispense ratio;
- Distance between the tip and stage;
- Voltage difference applied between the needle tip and stage.

7.2 HISTORY

Electro-spinning technique for making thin films has been widely developed and tried by many researchers in the past decades and has been accelerated (See Figure 7.2 [55]).

Capability of this method in providing a good coverage for surfaces and being a good method for depositing conductive and non-conductive particles are examples of the benefit of this technique.

One other benefit of this procedure is that because of using the high voltage difference between the needle and substrate, the orientation of the deposited particles on the substrate will somehow be aligned with each other. This can be a very beneficial event for making the devices that the orientation of their particles matter for their functionality. For example, PVDF films show good piezoelectricity if the polymer blocks are oriented in the same direction, which this method can contribute to that matter.
7.3 BUILDING THE ELECTRO-SPINNING MACHINE

In the following, the important components and the final set-up of the electro-spinning machine is explained.

7.3.1 Components

The electro-spinning machine has several important essential components, which are:

- High DC voltage supply (Figure 7.3)
- Syringe pump (Figure 7.4)
- Adjustable stage (Figure 7.5)
- Holders and frames (Figures 7.6)
- Syringe, tubes and Connectors (Figure 7.7)
Figure 7.3. Front and backside of Acopian DC high voltage power supply, capable of generating the output voltage of up to 20,000V.

Figure 7.4. Syringe pump from Harvard Co.
Figure 7.5. Adjustable lab jack(stage) with the adjustable range of 250 mm from Fisher Scientific.

Figure 7.6. Frame made of plexiglass.
7.3.2 Final Electro-Spining Machine Set-up

Figure 7.8 exhibits the final set-up of the electro-spinning machine. Voltmeter has been used for reading the output voltage of the power supply and Aluminum sheet has been installed on top of the stage to provide the conductive surface for connecting the connector. Because the generated current from the power supply is in micro amps range, therefore the regular alligator connectors have been used for completing the electric circuit.
Figure 7.8. Electro-spinning machine set-up.
CHAPTER 8

MICROCOPY IMAGING AND EDX SPECTROSCOPY

8.1 Final Samples

Figures 8.1 and 8.2 are two samples of PVDF covered chips. Both have been electro-spun using the mixed solution of Kynar 301F PVDF powder and Dimethylformamide (DMF) solvent with 15% weight ratio.

Figure 8.1. 2D electro-spun PVDF film with 20 nm Aluminum layers on top and bottom.

Figure 8.2. Electro-spun PVDF film on 3D micro-pillar chip with 20 nm Aluminum layers on top and bottom.
8.2 CONDITIONS

Because of the existence of so many different factors affecting the results of the process, it has been decided to limit the number of settings and conditions of the experiments in order to have a better understanding of the effects of each factor.

All tests have conducted in the room temperature and in air atmosphere. Time of electro-spinning has also been limited to 60 seconds.

The PVDF solution sample number 8 in Figure 6.5 have been chosen to be the polymer solution to deposit on the chips. As it is seen in the mentioned table, the solution contains 15% PVDF 301F.

In addition, all the chips have been made in the condition of the flow rate of 80 μl/min, 100 mm gap between the needle tip and the sample, and 10 KV for the voltage difference, unless otherwise mentioned.

8.3 MICROSCOPY AND IMAGING

The microscopy images of this study have been generated by using the Hirox optical microscope with the capability of 3D imaging (Figure 8.3) and FEI scanning electron microscope (SEM) model QUANTA FEG-450 (Figure 8.4) and tabletop SEM model Hitachi TM-3000 (Figure 8.5).
Figure 8.4. FEI electron scanning microscope (SEM) and me working!!

Figure 8.5. Hitachi TM-3000, tabletop SEM.
8.4 Microscopy Images of the Results

In the following, the optical microscopy and scanning electron microscopy (SEM) images of the topography of the surfaces of the flat areas (2D) and 3D structures covered by PVDF film are shown.

Figure 8.6 shows the plain and non-coated 2D and 3D area of the substrates; Figure 8.7 is electro-spun PVDF on 2D glass substrates and 3D SU-8 pillars structured.

(a)                                                                       (b)

Figure 8.6. (a) Non-coated glass surfaces and (b) 3D SU-8 structured pillars.

(a)                                                                          (b)

Figure 8.7. (a) Electro-spun 2D glass surfaces and (b) Electro-spun 3D SU-8 structured pillars.
Figure 8.8 and 8.9 show the surfaces of spin-coated PVDF 2D flat glass and 3D structured substrates at 3000 rpm (Figure 8.8) and 6000 rpm (Figure 8.9) for one minute for the reason of comparison with electro-spun chips. The speed was gradually ramped up to give enough time to the material to cover the whole chip and then was steady at the desired speed; the polymer was spread evenly forming a thin layer about 40 to 60µm.

As it is shown in Figures 8.10 and 8.11, the differences between spin-coated substrates and electro-spun chips, in zoomed-in images are clear around the 3D pillars.
Figure 8.10. (a) Non-coated pillar and (b) spin-coated surfaces around the 3D SU-8 structured pillars. (rpm: 6000).

Figure 8.11. (a) Electro-spun 3D pillars with the flow rate of 80 μl/min and (b) 40 μl/min.

In Figures 8.12 and 8.13, the scanning electron microscopy (SEM) images of the topography of surface of electro-spun PVDF layer on flat areas are shown.

In Figures 8.14 to 8.17, topography of the surface of the electro-spun PVDF on the 3D substrates with SU-8 pillar features at different magnifications are shown.
Figure 8.12. SEM image of topography of the surface of electro-spun PVDF layer; flow rate of 40 μl/min.

Figure 8.13. SEM image of topography of surface of electro-spun PVDF layer; flow rate of 80 μl/min.
Figure 8.14. SEM image of topography of surface electro-spun PVDF layer on 3D substrate. Flow rate of 80 μl/min.

Figure 8.15. SEM image of surface topography of electro-spun PVDF layer on 3D substrate. Flow rate of 80 μl/min.
Figure 8.16. Zoomed in SEM image of a single pillar of electro-spun PVDF 3D chip. Flow rate of 80 μl/min.

Figure 8.17. PVDF electro-spun covered 3D micro pillars from angle. Flow rate of 100 μl/min.
8.5 Energy-Dispersive X-Ray Spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDS or EDX) referred to an analytical technique that provides very extensive chemical analysis and characterization of materials [27].

Figures 8.18 to 8.21 are also demonstrating the texture of the deposited PVDF layer on the 3D substrate. The contrast of the images are set in a way to show the surface texture better.

![Figure 8.18. SEM image of surface finish of electro-spin PVDF layer on 3D substrate. Flow rate of 60 μl/min. X150 magnification.]

The core fundamental physics behind the functionality of these machines are because different materials and elements have different reactions to X-ray excitation based on their different unique atomic structures. First, the equipment detects these unlike to each other responses from different elements in the sample. Then it will compare those readings to its database of all different materials, which is done by the computer software that comes with the device. At the end, the equipment can report existence and also the percentages of all elements presenting in each point or an area of the sample that has been examined.
Figure 8.19. SEM image of surface finish of electro-spun PVDF layer on 3D substrate. Flow rate of 60 μl/min. X800 magnification.

Figure 8.20. The texture of surface area around a pillar is shown. Flow rate of 40 μl/min. X600 magnification.
Figure 8.21. SEM image of the surface finish area around pillars. Flow rate of 40 μl/min. X600 magnification.

Figure 8.22 shows the area and spectrum selected from electro-spun PVDF sample for EDX analysis. Figure 8.23 is the graph generated by the software showing the intensity of each element in the selected area.

Figure 8.24 shows the quantitative result of EDX analysis with the percentage of existence of each element.

Table 8.1 is another generated data by EDX software, which contains the percentages of each element in the spectrum.

As it is expected, the only elements of Carbon (C) and Fluorine (F), which are the main elements of PVDF, presented in the EDX analysis results. A very limited amount of Aluminum (Al) has also been reported which was because of the 6nm Aluminum layer deposited on top of the chip.
Figure 8.22. Spectrum selected from electro-spun PVDF sample for EDX analysis.

Figure 8.23. EDX analysis graph, which shows the intensity of each element existing in the sample chip.
Figure 8.24. EDX analysis result of the percentage of each element.

Table 8.1. Percentage of each Element in the Selected Area. (Processing Option: All Elements Analyzed (Normalized))

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>In stats.</th>
<th>C</th>
<th>F</th>
<th>Al</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>Yes</td>
<td>57.80</td>
<td>42.12</td>
<td>0.08</td>
<td>100.00</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>57.80</td>
<td>42.12</td>
<td>0.08</td>
<td>100.00</td>
</tr>
<tr>
<td>Std. deviation</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Max.</td>
<td></td>
<td>57.80</td>
<td>42.12</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Min.</td>
<td></td>
<td>57.80</td>
<td>42.12</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 9

SURFACE QUALITY ANALYSIS

9.1 IMAGE ANALYSIS SOFTWARE

By using the image analysis software “UTHSCSA Image Tool” version 3.0, the investigation for the surface finish quality of the electro-spun chips has been performed (See Figure 9.1). The readings from the software for analyzing the SEM images of the chips are presenting the surface porosity. In the other word, the readings from the software are representing the amount of pores versus pores plus the flat and even areas, which is the total amount of the surface area of the chip. Therefore, these surface porosity percentage numbers are good indicators of the uniformity and surface quality of the deposited material. Lower the reading of porosity means better quality and more uniform coverage on the surface.

Figure 9.1. Screen shot of image analysis software UTHSCSA Image Tool.
9.2 AREAS OF INVESTIGATION

This analysis has been performed on three different areas of the 3D structured chips: flat bottom areas of the chips, horizontal top part of the pillars and on the sidewalls of the microstructures. For each area three different parameters has been analyzed in order to understand the effectiveness of that particular factor in the surface quality.

9.2.1 Bottom Flat Area

Figures 9.2 and 9.3 are demonstrating the data points and SEM images for surface porosity percentages when only parameter of flow rate was changing.

![Figure 9.2. Surface porosity versus flow rate for bottom flat surface. Gap was set at 120mm and voltage at 10KV.](image)

Figures 9.4 and 9.5 are showing the surface porosity when the gap between the needle tip and stage was changed. Figures 9.6 and 9.7 are demonstration of the changes in the surface uniformity and porosity when the voltage difference between the needle tip and stage was changed.

9.2.2 Top of the Pillars

Figures 9.8 to 9.13 are demonstrating the surface quality and surface porosity data points and their SEM images of the top part of the micro pillars when just the mentioned parameters have been changed, other parameters were the same as initial setting.
Figure 9.3. SEM images of the surface porosity in Figure 9.2. Distance: 120mm. Voltage: 10KV. Flow rate: varies.

Figure 9.4. Surface porosity versus distance for bottom flat surface. Flow rate of 80 µl/min and voltage of 10KV was set.
Figure 9.5. SEM images of the surface porosity in Figure 9.4. Flow rate: 80 μl/min. Voltage: 10KV. Distance: varies.

Figure 9.6. Surface porosity versus voltage difference for bottom flat surface. The setting of flow rate of 80 μl/min and distance of 120mm used.
Figure 9.7. SEM images of the surface porosity in Figure 9.6. Flow rate: 80 μl/min. Distance: 120mm. Voltage: varies.

Figure 9.8. Surface porosity versus flow rate for top flat surface of the micro pillars. Gap was 120mm and voltage 10KV.
Figure 9.9. SEM images of the surface porosity in Figure 9.8. Distance: 120mm. Voltage: 10KV. Flow rate: varies.

Figure 9.10. Surface porosity versus distance for top flat surface of the micro pillars. Flow rate of 80 µl/min and voltage of 10KV was set.
Figure 9.11. SEM images of the surface porosity in Figure 9.10. Flow rate: 80 μl/min. Voltage: 10KV. Distance: varies.

Figure 9.12. Surface porosity versus voltage difference for top flat surface of the micro pillars. The setting of flow rate at 80 μl/min and distance at 120mm was used.
9.2.3 Sidewalls

Figures 9.14 to 9.19 are showing the changes in the surface quality of sidewalls of the micro pillars when the electro-spinning parameters changed as mentioned.

Figure 9.14. Surface porosity versus flow rate for the side walls of micro pillars. Gap was 120mm and voltage 10KV.
<table>
<thead>
<tr>
<th>Flow Rate: 40 µl/min</th>
<th>Flow Rate: 60 µl/min</th>
<th>Flow Rate: 80 µl/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate: 100 µl/min</td>
<td>Flow Rate: 120 µl/min</td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.15. SEM images of the surface porosity in Figure 9.14. Distance: 120mm. Voltage: 10KV. Flow rate: varies.
Figure 9.16. Surface porosity versus distance for the side walls of micro pillars. Flow rate of 80 μl/min and voltage of 10KV was set.

Figure 9.17. SEM images of the surface porosity in Figure 9.16. Flow rate: 80 μl/min. Voltage: 10KV. Distance: varies.
Figure 9.18. Surface porosity versus voltage difference for the side walls of micro pillars. The setting of flow rate at 80 μl/min and distance at 120mm was used.

Figure 9.19. SEM images of the surface porosity in Figure 9.18. Flow rate: 80 μl/min. Distance: 120mm. Voltage: varies.
CHAPTER 10

RESULTS AND CONCLUSION

In this study, different types of polymers, manufacturing processes especially thin-film manufacturing methods were explained. Definitely electro-spinning is one of the good options for fabrication of the thin film polymers such as PVDF. This method would be even more beneficial when orientation of the particles matter and/or the substrate is not just a 2D flat surface. In addition, it has also been shown the spin-coating technique would not be a good method for coating micro 3D structure and will not provide very uniform and smooth coverage everywhere on the chip surface especially around the 3D structures.

Even though the electro-spinning is, a promising method for fabricating thin film polymer, but it should also be remembered that the porous texture of the surfaces of the chips could be beneficial or a very challenging factor depending on the desired application.

In this work, it is also shown that scanning electron microscopy (SEM) is one of the proper investigation methods for examining the surface quality of the deposited polymer on the chips. The surface quality of chips, observed in the SEM images can be translated to meaningful numbers with the help of image analysis computer software.

Varieties of different crystalline structures and phases of PVDF were explained and analyzed. The previous studies showed that β phase PVDF is demonstrating good piezoelectric property which can be widely used in different applications.

In this work, it was demonstrated that negative photolithography procedure with using the SU-8-100 is a proper method for making micro 3D structured platforms. The Silicon wafer can perform as a good substrate.

Many different factors in the micro-fabrication processes are involved and affective. It was observed that the higher spin coating speed will result with shorter 3D structures and more viscous SU-8 photoresist can provide thicker layer and therefore taller features. Soft and hard baking temperatures and their times are important factors for fabricating good quality micro features as well.

The following conclusions also can be drawn:
1. Temperature is playing a very important role in achieving the desired PVDF solution. 75°C showed to be the right temperature for mixing and making the desired solutions used in this study.

2. Several PVDF powders and solvents with different ratio and at different conditions have been tried and several mixtures have been made. The best solution chosen for electro-spinning in this study was 4/1 DMF to Acetone with 15% solution weight ratio of Kynar 301F PVDF powder.

3. It has shown the best powders among the ones tried in this work for making proper solutions were Kynar 301F and Kynar 2821 PVDF powder.

4. The average time for mixing to achieve a homogenies solution would be 4 hours.

5. Energy-dispersive X-ray spectroscopy (EDX) analysis was completed and the existence of the elements of Carbon (C) and Fluorine (F) were confirmed. Percentages of each element have also been reported.

6. The best results in this work for uniform coating and lower surface porosity were for the distance of 120 to 140mm between the needle tip and stage.

7. The proper voltage difference for performing the electro-spinning in this work tends to be around 10KV, but not dramatic changes in the surface porosity for changing the voltage have been observed.

8. The flow rate of 80 to 100 µl/min tends to provide the good uniform surfaces of PVDF polymer in this work.

9. By comparing the graphs for the surface quality of the top, bottom and sidewalls of pillars for the 3D microchips, we can conclude that surface quality on the top and bottom parts are slightly better than the sidewalls; but the surface porosity on the side walls are in a good acceptable range also. Over all we can expect to achieve a relatively good uniform coating quality on the micro 3D structures everywhere by using the electro-spinning method.
CHAPTER 11

FUTURE WORK

Obviously, the possibilities for the future research and work are unlimited, but as some suggestions, the following works can be considered:

1. The electro-spinning of other polymers on 3D microstructures can be tried. Also creating a mixed polymers layer by using multi-nozzles electro-spinning machine can be interesting. It would possibly be a beneficial try in order to achieve new combinations of polymers for new applications.

2. Other designs and settings for electro-spinning machine such as adding vibrating stage or rotational nozzle or multiple nozzles can be tried.

3. The polling process with different parameters such as time and voltages applied to the film can be tried and importance and effectiveness of each parameter be observed. The polling process improvement can be continued until a reliable, robust and sensitive enough PVDF piezoelectric film is achieved.

4. Other shapes and forms of 3D structured can be investigated. Combination of different geometrical shapes and forms can also be tried and optimization of the pattern can be performed.

5. Adding surfactants such as Zonyl®UR or carbon nanotube (CNT) to the PVDF solution can be examined and investigate their effects on the piezoelectricity and sensitivity of the PVDF film.

6. In addition, more in depth investigation can be completed on the effects of each parameter of the electro-spinning machine and also adding and controlling other factors such as temperature or humidity. These tests can also be tried in vacuum atmosphere or in existence of different gasses and then compare the results.

7. Fabricating new devices and finding novel applications based on 2D and 3D micro structured PVDF films, such as implantable pressure sensors can be very beneficial and challenging goals for the future.
REFERENCES


[45] Nasir, Muhamad, Hidetoshi Matsumoto, Tetsuya Danno, Mie Minagawa, Toshihira Irisawa, Masatoshi Shioya, and Akihiko Tanioka. “Control of Diameter, Morphology,


