Master’s thesis

Fabrication and characterization of individually addressable Polypyrrole Trilayer Microactuators

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Fabrication and characterization of individually addressable Polypyrrole Trilayer Microactuators
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Abstract:
Conjugated polymers are organic polymers that can conduct electricity. They undergo a volume change upon redox reaction and can be used as an active material in some micro-actuator system. Micro-actuators are useful in biomedical and electronic application. We have fabricated a patterned Polypyrrole (PPy) trilayer microactuator device that has individually addressable microactuators (a micro walker) which can operate in air. Furthermore, the PPy trilayer microactuator device is fabricated using standard microfabrication method called photolithography to pattern PPy on PVDF membrane material. An etching process was used to achieve the patterning process. We presented the result of characterization of speed as a function of voltage and thickness of PPy film. Secondly, distance as a function of applied voltage and thirdly, the work density as a function of applied voltage. The procedures for fabrication of PPy microactuator device, using clean room facility is detailed in this thesis.
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1.0 Introduction:

1.1 Background:
Electroactive polymers (EAP) are active materials that can be employed in micro-actuator systems [1-3]. There are two classes of EAP namely: electronic EAP and ionic EAP [1]. Electronic EAP are dry materials that normally operate at high voltage while ionic EAP operates at low voltage and generally, they are wet materials. Examples of ionic EAP are conducting polymers, carbon nanotubes and electroactive gels [1].

Polymer microactuators have been fabricated using conducting polymer as an active material [3-9]. In this report we have micro-fabricated a trilayer microactuator working in air based on redox reaction of the conjugated polymers, especially polypyrrole, which have been commonly used as an EAP microactuator due to their numerous advantages such as biocompatibility, low power consumption, low operating voltage, easy to manufacture, stability with large volume change and capability to work in liquid and air environment [1, 3, 5].

The working of conducting polymer microactuator is based on the volume change in the conducting polymer. Electrons are removed from the polypyrrole (PPy) chain when a certain voltage is applied to material causing it to change from its neutral state (PPy) to its oxidized state (PPy⁺). The process is reversible when the polarity of the applied voltage is reversed. The change in polarity will cause addition of electrons to the PPy. which reduces PPy from its oxidized state back to its neutral state (PPy⁰) [1-5, 10-14]. In other words the oxidized state is called the doped state which causes volume expansion in a material while the reduced state is called the undoped state which causes volume contraction in the material.

The redox reaction of the conducting polymers when voltage is applied leads to a change in conductivity and color in addition to the volume change [4, 6]. The redox reaction of the conjugated polymer can be illustrated below:

\[ \text{P}^{+} (\text{a}^{-}) + e^{-} \leftrightarrow \text{P}^{0} + \text{a}^{-} (\text{aq}) \ldots (1) \]

Where P is a polymer doped with small, mobile anion (a⁻) in contact with an electrolyte containing both mobile cation and anion [1]. The ions inserted and de-inserted into the polymer are anions. The anions are inserted/expelled into/out of the polymer matrix due to the charge imbalance.

The trilayer actuator consist of three materials: it is made up of two conductive polymers at both ends and a poly(vinylidene fluoride) (PVDF), coated on both side with a gold layer in between them. The PVDF film stores the electrolyte that is used during electrochemical transition.

Polypyrrole microactuators have numerous potential applications in cell biology, biotechnology, nano- or picoliter chemistry, etc. and they have been used in cell sealable micro-vial, which is a micrometer sized cavity in a substrate that can be closed by a lid or to make cell clinics [5]. It is
also used in a tapper in order to reveal cellular responses to mechanical stimuli [5]. In addition, it can be used in making artificial muscles and microrobotics. Jager et al. have fabricated microrobots for micrometer-sized objects in aqueous media: potential tools for single-cell manipulation [5, 7].

One drawback of polypyrrole microactuator at present is that they need a liquid electrolyte (a salt solution) to function. The polypyrrole microactuators have been operated in a number of salt solutions, for instance blood plasma, urine and cell medium but are still limited to work in liquid environment [4].

1.2 Aim
The aim of this report is to microfabricate trilayer microactuators that can work in air and can be individually controlled using a photolithograph and microfabrication techniques, to develop reproducible fabrication protocol, and evaluate and characterize the triple layer microactuator that can individually controlled. The final goal is to fabricate a first, simple device having individually addressable microactuators such as a finger with individually controllable joints or microgripper/hand/microwalker.

1.3 Method
The method used in this work was based on laboratory experiment. Relevant literature, book and journal articles related to this work were studied in order to know what problems encountered by other researchers in polypyrrole microactuator. The device was fabricated in the clean room and the PPy was synthesis using Iviumstat potentiostat with software interface. The results obtained were evaluated and analyzed using Ivium CompactStat Potentiostat with respect to applied voltage.

2.0 Theory

2.1 Polypyrrole volume change
Polypyrrole is a conducting polymer that can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomers [10]. It has a resonance that is similar to the aromatic or quinoid forms. The volume change of polypyrrole is caused by ion insertion and removal during electrochemical redox processes [1-4, 6-7]. In the oxidized state radical cations are formed that are usually delocalized over several pyrrole units [10]. Polymers are not conducting in their neutral state; they only conduct in the oxidized state. Potentiostatic techniques (when a constant potential is applied between a working electrode and a reference electrode) and amperostatic techniques (when a constant current is passed between a working electrode and a reference electrode) can be used to electro polymerize polypyrrole.

There are two types of mechanism for ion flow and redox reaction. First, for polymers doped with small, mobile anions, the anions are expelled when reducing the polymer to the neutral state and anions are inserted when oxidizing the polymer in order to compensate for the charge
imbalance. On the other hand, for polymers doped with large, immobile anions, in contact with an electrolyte containing small mobile cations $M^+$, the cations are inserted when the polymer is reduced and they are expelled when the polymer is oxidized, [1, 12]. In this report we will focus on the former case.

**Figure 1**: Chemical reaction during oxidation and reduction of a conducting polymer. Adapted from reference [11]
When a constant current or potential difference is applied between two PPy coated electrodes, the polypyrrole is oxidized at the positively charged electrode while at the negatively charged electrode the polypyrrole is reduced. Volume expansion occurred when the anion (TFSi) is moved from the electrolyte into the positive charged polymer electrode. To maintain charge neutrality within the polypyrrole layers, anions will leave the negatively charged electrode at the same time which resulted in volume contraction, also causing it to become uncharged [2]. See figure 1 above.

The redox reaction of the polypyrrole P doped with small mobile anion (TFSi) in contact with an electrolyte contains both mobile cation and anion is:

\[
\text{PPy}^+ (\text{TFSi}) + e^- \leftrightarrow \text{PPy}^0 + \text{TFSI}^- (\text{aq})
\]  

The physical form of polypyrrole is usually like insoluble film, resulted from electropolymerization [10]. The volume change is extremely anisotropic and according to Gadegaard and Smela [13], the in situ volume change measurement using atomic force microscopy could be up to 30 to 40% for 0.8-1.5µm film in a perpendicular direction.

**2.2 Polypyrrole actuators**

Polypyrrole actuators are based on the doping induced volume expansion and contraction that is controlled by an applied voltage on a polymer electrode in the electrochemical cell as explained in the previous section [1-3, 14-20]. Polypyrrole is used as an active material in an actuator. The actuation can be formed in different modes shown in figure 3. These are bulk expansion used in a piston-like actuator, the linear strain use for linear actuator like stripes and tubes and bending actuator use in rolling sheet or living in bi or multilayer devices [12].
Figure 3: shows different forms of actuators, two sides of it are attached to a point. Copied from reference [12] with permission.

Actuators operating in liquid electrolyte may use three electrode configurations. The working electrode is connected to the sample and immersed in a liquid electrolyte with which it can exchange ions. The reference and counter electrodes are also immersed in electrolyte and the counter electrode is in parallel with the working electrode [11].

According to Maw et al [18] the strain transverse to the plane of the film varied inversely with the deposition current density under voltage stimulation. The deposition current density in PPy(DBS) film exhibit less extensive movement, reduced peak separation and less charge transfer per cycle compared to low density current density because high deposition current density are more reluctant to exchange a given amount of charge. Moreover, Han and Shi [19] observe that the bending responses and capacity of tri-layer film are much higher than those of the bi-ionic film. This is as a result of gold nano-film which provided a high conductive layer.

However, actuator operating in air (dry actuator) is achieved by separating two conjugated polymer films by a polymer electrolyte leading to different forms of actuators as mention above. During actuation mechanism, ions are shuttled between the two conjugated polymer films during electrochemical switching [11-12]. The bending mode actuation occurs when one polymer is oxidized; ions are transferred, and the other polymer is reduced at the same time in the switching process.

2.3 Microfabrication Techniques.

2.3.1 Sputtering:
Sputtering is a physical vapor deposition (PVD) method, in which a thin film of a material is deposited on a substrate. The equipment consists of a solid slab of metal, called the target, inside the vacuum chamber, which electrically grounded. Its principle is based on three steps:
1. The material to be deposited is converted into vapor.

2. Transportation of this vapor to a substrate across a low pressure.

3. Condensation of the vapor on a substrate to form a film.

When an argon gas is introduced into the chamber, it is ionized to a positive charge [20]. The positive charged argon atoms are accelerated to the target. The argon atom gains momentum during their acceleration and strike the target (momentum transfer take place at the target) causing its atom to scattered. The sputtered atoms from the target travel into the chamber and deposit on the substrate (see figure 4).

Diode sputtering is one of the methods used in sputtering in which the target is connected to a negative potential. The negative potential charged target ejects electrons that collide with argon gas atom and ionize them [20]. Diode sputtering has a problem of virtual leak. This problem is overcome by placing a small negative bias on the wafer holder. Another method used in sputtering is by connecting the target to a negative side of radio-frequency (RF) generator. This method is useful when sputtering both non-conducting (dielectrics) and conducting materials. Moreover, magnetron sputtering system is use to prevent the escape of electrons into the chamber, which does not contribute to the establishment of the plasma necessary for deposition. This magnetron is designed to confine the plasma at the target face. As a result, it increases the sputtering rate, thickness, uniformity and allowing the plasma to be sustained at lower gas pressure [21].
Figure 4: Shows Magnetron Sputtering (Deposition Mechanism).

2.3.2 Thermal evaporation:
Thermal or vacuum evaporation involves heating the metal to a liquid state so that the atoms can evaporate in a vacuum system. Comparison between sputtering method and its counterpart, vacuum evaporation is that vacuum evaporation method cannot be used to deposit an alloy because each element has a different evaporation rate at a given temperature but in sputtering techniques the atoms or molecules are ejected form a solid target [19, 22]. Secondly, the sputtered material has a composition that is close to source material. A sputtered film has a better adhesion on the substrate than the vacuum evaporated film. Thou, sputtering can lead to contamination because of gases introduced into the deposition chamber.

3.0 Photolithography:
Photolithography is a process of transferring geometric pattern of a mask to the surface of a substrate. The steps involved in the photolithographic process are substrate cleaning, spin coating
a thin layer of resist (the photosensitive film) on a surface, soft bake (i.e. evaporation of resist solvents by heating), alignment, exposure, and development. Now the substrate can be processed, for instance etching a metal layer with the transferred pattern or deposit a layer (see fig 5). After processing the photoresist will be stripped [20]. These processes steps will be discussed further in this report. There are two types of patterned transfer process namely additive and subtractive process.

Figure 5: shows the subtractive and addictive process of photolithography. Adapted from reference [20].

Subtractive is a conventional process that consists of multiple deposition, pattern transfer and removal by etching while in addictive process there may have a reduced process flow [24].

3.1 Spin-coating:
Spin-coating is a process in which a solution of for instance a photoresist is spread evenly over a surface of a substrate using centripetal force. This results in a relatively uniform thin film of a specific thickness. Figure 6 shows a spinner used in spin-coating.

There are two types of photoresist used in photolithography process, namely negative photoresist and positive photoresist. Negative photoresist is a resist in which the polymer changes from unpolymerized to polymerized polymer during exposure to the ultra-violet (UV) light. The polymer forms a cross linked material [20, 22].
Figure 6: Spinner used for spin-coating.

On the other hand, positive photoresist consist of phenol-formaldehyde polymer which is insoluble. When the polymer is exposed to UV light, it undergoes a reaction called photosolubilization and converts to a more soluble state. This photosolubilized part of the resist can be removed by using developer [19, 22]. Figure 6 shows the cross section of positive and negative patterned photoresist.

Figure 7: shows the cross section of positive and negative pattern photoresist. Adapted from reference [20].

Furthermore, the positive photoresist have fair adhesion to substrate, is more expensive and have minimum feature size of 0.5µm and below while negative photoresist have excellent adhesion to the substrate, less expensive and minimum feature size ± 2µm [22]. In addition positive
photoresist has better step coverage with aqueous developer base while negative photoresist has lower step coverage with organic developer base [20, 22].

There are four basic ingredients in photoresist namely: the polymers, sensitizes, solvent and additive. The solvent makes the resist a liquid which can easily apply on a substrate as a thin layer by a spinning. Sensitizers control certain reaction of the resist while additive are used to achieved a particular result, for instance, inhibitor which are present in a positive photoresist are used to inhibit the dissolution of non-exposed portion of the photoresist during development.

3.2 Contact mode:
Contact printing is a form of photolithography whereby the image to be printed is obtained by pressing the mask against coated wafer during exposure. The photomask is in direct contact with the substrate coated with an imaging photoresist layer. The photomask consist of opaque chromium patterns on a transparent glass plate or printed image on a transparent film using a higher resolution printer.

In principle, the substrate is coated with a thin film of photoresist and placed underneath the photomask the sample is also placed in direct contact with the photomask and it is exposed to UV light to become dissolved by developer. The photoresist covered by the pattern is unaffected. A Mask aligner is used to carry out the operation of transfer of pattern from the photomask to the sample. Generally, contact printing has high resolution compared to proximity printing but it is sensitive to the presence of defect on the mask or on the substrate [22]. Proximity printing has a poor resolution compared to contact printing. In contrast with contact printing, a preselected gap is created between the photomask and the sample in proximity printing. The distance between the photomask and the sample determined the resolution. The lower the distance between the photomask and the substrate the higher is the resolution. Furthermore, distance between the photomask and substrate facilitates lower defects on the mask.

3.3 Wet etching:
In wet etching a liquid etchant is used to remove material by immersing the substrate in the tank of the reactant while dry etching is done using a plasma. Basically, we have two types of etch profile namely: isotropic etch profile, which etch equally in all direction. In most cases wet etching gives isotropic profile. Secondly we have anisotropic etch profile, which etched in preferred direction only. Dry etch gives anisotropic profile [20]. Figure 8 shows the diagram of isotropic profile and anisotropic profile.

The liquid etchant used in etching gold consist of potassium iodide, iodine and water.

\[
\text{KI} + \text{I}_2 \rightarrow \text{KI}_3^- \quad (3)
\]

\[
2\text{Au} + \text{I}^- + 2\text{I}_3^- \rightarrow 2\text{AuI}_2^- \quad (4)
\] [22].
Figure 8: Shows a pattern before etching top, the Isotropic etch profile left, Anisotropic etch profile right.

The iodine and potassium iodide combine reversibly to form the complex ion $\text{KI}_3^-$ as shown in the chemical equation above. Etching of gold is due to reduction of iodine complex ion in the presence of potassium iodide [22].

3.4 Resist stripping:
Resist stripping is a process of removing the resist layer that has been acted as an etching barrier. The chemicals used in photoresist stripping are classified according to substrate surface, the polarity of the resist production consideration and condition of the resist [20]. In addition strippers are divided into different types namely: negative resist and positive resist-only strippers, metallized and non-metallized strippers.

According to Zant [20], wet chemical strippers used in metallized surface are phenolic organic strippers (containing a combination of sulfonic acid and chlorinated hydrocarbon solvent) such
as duodexabenzenzene, solvent/amine strippers (e.g. acetone for positive resist stripper) and hydroxylamine (HDA) chemistry.

Photoresist can also be removed by developing exposed substrate coated with photoresist to UV light source using so-called flood exposure.

4.0 Instrument and Material:

4.1 Printed Mask:
A printed mask is an interface between designer and fabrication process, containing a geometrical image of one layer of the process. The image is printed on a transparent film using a higher resolution printer (see figure 9). The photomask may be used many times to reproduce a pattern unto different samples. The printed photomask have a lower minimum resolution than the standard Cr-mask. However, they are normally chosen because they are much cheaper than Cr-masks.

Figure 9: Shows high resolution printed photomask
4.2 Mask Aligner:
The function of a mask aligner is to allow the user to align features of photomask to features on a substrate (see figure 10). The elements of mask aligner are:

- **Microscope:** microscope is one of the components of mask aligner that allow the user to see points on opposite sides of a wafer at the same time. Most mask aligners have at least 20X microscope objective to allow alignment resolution down to 1 micron. The microscope helps in high-resolution alignment.
- **Wafer chuck:** wafer chuck makes use of vacuum holes throughout its surface to hold the wafer in place. It moves up and down to bring the substrate into contact with photomask or pull it away from the photomask.
- **Microscope positioner:** microscope positioner is used to holds the photomask in place. It has a flat surface through which a wafer will be placed in contact with the mask.
- **Wafer/mask positioner:** this enable the substrate to be move to different X-Y directions or different angle rotations in relation to the mask. Movement is done by turning the knob in the desired X-Y directions.
- **Exposure time:** this allows the user to select the exposure time for the mask aligner i.e. how long the sample and photomask will be exposed to ultraviolet light.
- **Contact command:** this command enable the user to bring the sample up into contact with the photomask. This is done before the exposure is taken place and after alignment.
- **Exposure command:** this enables the user to begin the exposure process. Ultraviolet light is flooded over the mask and wafer for the exposure time set by the user [25].

The alignment procedures for aligning the features on a wafer to features on a photomask begin with loading the photomask and sample. Next, is to align microscopic objective to mask alignment marks. When both marks are in view, slight adjustments in X-Y position and rotation angle are made until the mask appear parallel. Finally, the wafer is rotated to approximate alignment (i.e. the photomask alignment marks are in parallel with the substrate alignment marks) and the X-Y positioning of the substrate is adjusted to matched exactly with the alignment marks (see appendix 1). Moreover, when the substrate is aligned with photomask, a contact command button is used to move the substrate into contact with the photomask. The substrate is exposed to UV light by selecting the exposure time and pressing the exposure button.

4.3 Pyrrole:
Pyrrole is one the major compound that is used in this project. Pyrrole (C4H4NH) is a colorless volatile liquid that darkens upon exposure to air. It has a molar mass of 67.09gmol⁻¹ and density of 0.967gcm⁻³. The boiling point of pyrrole is 131⁰C with low melting point of -23⁰C, vapor pressure of 7mmHg at 23⁰C and viscosity of 0.001225Pa s [26].
Figure 10: shows mask aligner used in this experiment (Model: KSM, Kari Suss West-Germany).

Pyrrole is prepared by treatment of furan with ammonia in the presence of acid (see figure 11). Polypyrrole is obtained from electropolymerization of pyrrole monomer and it is a derivative of polyacetylene. Pyrrole is a flammable liquid and can cause severe eye damage when applied to the eye, toxic when swallowed. Inhalation of pyrrole may cause drowsiness and dizziness.

\[
\text{\Large \begin{array}{c}
\text{Furan} \\
\text{\Large + NH}_3 \\
\text{\Large - H}_2\text{O} \\
\text{Pyrrole}
\end{array}}
\]

Figure 11: shows pyrrole synthesis. Copied from reference [26].

First aid measures taken when pyrrole is in contact with the eye is flush the eye continuously with running water. If in contact with skin, flush the skin as well with running water. Pyrrole can be stored in a glass container at a low temperature of about 20 degree.

During electropolymerization of polypyrrole, the pyrrole monomer is dissolved in an appropriate solvent containing the desired anionic doping salt. The monomer is oxidized at the surface of the
electrode by application of an anodic potential. The solvent and the electrolyte selected should be stable at the oxidation potential of the monomer and provides an ionic conductive medium [26]. Organic solvent like propylene carbonate and acetonitrile are normally used because they have large potential windows and high relative permittivity, which allows a good dissociation of electrolyte and thus, a good ionic conductivity [26]. The initial oxidation of the pyrrole causes the radical monomer cations to form and react with other monomers present in the solution to form oligomeric products and then the polymers. The doping and synthesis of polypyrrole are generally done at the same time because the anion is incorporated into the polymer to ensure an electrical neutrality of the film and a polymeric film of controllable thickness is formed at the anode at the end of the reaction. Electropolymerization can be carried out in an aqueous electrolyte because pyrrole has a relatively low oxidation potential compare to thiophene and benzene [26].

4.4 Polypylene carbonate:
Polypylene carbonate is an organic solvent with molecular formula C₄H₆O₃. It is a colorless and odorless liquid with high molecular dipole moment and it is useful as a polar and aprotic solvent. The molar mass of polypylene carbonate is 102.09g/mol with density of 1.205g/cm³, melting point of -55°C, boiling point of 240°C, refractive index of 1.4189 and it is very soluble in water [28]. Polypylene carbonate has large potential window and it is used as a permittivity component of electrolyte. Figure 10 below shows the molecular structure of propylene carbonate.

Figure 12: Molecular structure of propylene carbonate. Copied from reference [28].

Propylene carbonate is obtained as a byproduct of synthesis of polypropylene carbonate from propylene oxide and carbon dioxide [28]. It has no health hazards at 5% concentration according to American collage of toxicology [28]. It is hazardous at concentration of 10% when in with skin, eye contact, ingestion and inhalation.

4.5 Polyvinylidene difluoride (PVDF):
Polyvinylidene fluoride (PVDF) is valued for its toughness, stability, and distinct engineering advantages. For example, if you need a polymer that will withstand exposure to harsh thermal,
chemical, or ultraviolet conditions, PVDF offers superior stability similar to the performance of fluoropolymers in these environments and it offers optimal blotting for protein greater than 20kDa [30].

PVFD is a homopolymer of 1, 1-di-fluoro-ethene. Its highly desirable insolubility and electrical properties result from the polarity of alternating CH2 and CF2 groups on the polymer chain. It is a family of fluoropolymers of Vinylidene. An extremely hard material, PVDF may be used at temperatures from -62 to 149°C. No oxidation or thermal degradation occurs during continuous exposure to 149°C [30, 32]. It is used in western blots for immobilization of proteins, due to its non-specific affinity for amino acids. Moreover, PVDF consist of hydrogen, carbon, and fluorine (see figure 13). It has piezoelectric property with a negative d33 value [32]. This implies that PVDF will be compress instead of expand or expand instead of compress when exposed to the same electrical field with other piezoelectric material like PZT. Immobilon –P Polyvinylidene difluoride membrane, we used in this work, has a pore size of about 0.45µm (see appendix 2) for sample of PVDF membrane.

![Molecular structure of PVDF](image)

**Figure 13:** molecular structure of PVDF. Copied from reference [29].

4.6 Ma –P1275 photoresist:
Ma –P1275 photoresist is a very high viscous positive tone photoresist. It has the following properties according to micro- resist technology processing guidelines sheet [31].

- It has high stability in acid and alkaline plating bath.
- It is well suitable for application as an etch mask exhibiting high dry and wet etch resistance.
- Good thermal stability of the resist patterns.
- Used in an aqueous alkaline development.
- It has thickness of 6-40µm with a single coating, dynamic viscosity of 430± 25mPas and a density of 1.087± 0.003gcm³.

<table>
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<tr>
<td>[min]</td>
<td>30</td>
<td>45</td>
<td>60</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>Relaxation [min]</td>
<td>—</td>
<td>—</td>
<td>20</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Exposure dose (365nm) [mJ cm⁻²]</td>
<td>210 ± 10</td>
<td>430 ± 20</td>
<td>1800 ± 50</td>
<td>2300 ± 100</td>
<td>3400 ± 100</td>
</tr>
<tr>
<td>Development [s]</td>
<td>80 ± 10</td>
<td>80 ± 10</td>
<td>210 ± 30</td>
<td>250 ± 60</td>
<td>720 ± 120</td>
</tr>
<tr>
<td>(ma-D 331)</td>
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<tr>
<td>Development [s]</td>
<td>80 ± 10</td>
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<td>(ma-D 531)</td>
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<tr>
<td>Development [s]</td>
<td>50 ± 10</td>
<td>70 ± 10</td>
<td>90 ± 15</td>
<td>120 ± 20</td>
<td>240 ± 20</td>
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<tr>
<td>(2.38% TMAH)</td>
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</table>

**Table 1**: Processing conditions for different thickness of ma- P 1275. Copied from reference [31].

The unexposed positive photoresist is stored at temperature 18-25°C and in a closed bottle when not in use with a humidity of about 40-50% [31]. In addition, the unexposed photoresist films have to be processed under a yellow light. The processing conditions for different film thickness depends on spin coating speed, prebaked, exposure dose and development time (see table 1). The broad exposure, intensity is measured at wavelength of 365nm.

Prebake process is required to increase the etch resistance and thermal stability of the resist. Increases in prebake temperature within 100-110°C using an oven for 30- 45minutes will increase the etch resistance and thermal stability of the resist. The developing time and required exposure dose will increase as well.
Exposure of photoresist ma-P 1275 to UV light makes it soluble in the developer like any other positive photoresist. The photoresist is effective for broadband, g line, or I line exposure (see figure 14).

**Figure 14:** shows the UV/VIS absorption of unexposed and exposed ma-P1275. Copied from reference [31].

**4.7 Developer:**
The developer used in this experiment is ma-D331. It is a positive photoresist developer adapted for the ma P 1275. According to Dill *et al* [33], in the absence of the photoresist compound, a film composed only of the base resin is moderately soluble in the aqueous alkaline developer, with a removal rate of 15nm/s. The dissolution rate of unexposed photoresist film is reduced to the range of 0.1-0.2nm/s, when the photoactive compound is present. Therefore, photoactive compound acts like an inhibitor, to inhibit the dissolution of photoresist on an unexposed surface area.
What happens during development is that the carboxylic acid formed during exposure of photoresist to UV light, moves from the hydrophobic to the hydrophilic part of the cresol chain and promotes the deprotonization of the OH- group, increasing the resist solubility in an aqueous alkaline developer [33].

The rate of development of ma- D331 developer depends on temperature of the solution, exposure dose and the concentration of the solution. The temperature dependency of the development rate depends on the thermal activation energy of physical transport mechanism of the developer and developed resist, as well as chemical reaction involved in the development and complex formation [33]. The higher the exposure dose the higher the rate of development. Hence, the higher the developer concentration, the higher the development rate at a high selectivity [33].

The optimum temperature for ma- D331 developer is between 20-25°C [31]. The developed resist film should be thoroughly rinsed with deionized water and then dried.

4.8 Ivium Compactstat:
Ivium compactstat consist of a microprocessor and a potentiostat/galvanostat which is used to control the potential or current applied to the electrodes and measures the potential or current response (see figure 15). Ivium software is used as an interface between the computer and the Ivum compactstat instrument.

The rear panel of Ivium compactstat instrument consists of the following according to reference [34]:

- Power connector: fits the supplied 5V power adapter.
- USB connector: fits to supply USB A/B cable which should be connected between instrument and PC.
- Peripheral port: 37p connector that provides access to a range of analog/ digital input/ output signals.

The front panel consists of the following:

- On LED: when the cell is on counter electrode (CE), this LED will light up red.
- Cell connector: 15p connector that fits the supplied electrode cable.
Figure 15: shows Ivium compactstat instrument

Computer is used to specify the parameters of the measurement, to display the measured curves and to calculate the results of the measurement [34].

5.0 Experimental:
This experiment was carried out at the Department of Physics, Chemistry and Biology (IFM) at Linköping University, Sweden. The area of the PVDF was first patterned, followed by electropolymerization of the conducting polymer on this patterned PVDF membrane, activation PPy trilayer of microactuation and characterization of PPy tri-layer microactuator. See figure 16 for graphical representation of the work process for microfabrication of PPy microwalker and characterization.

5.1 Micro-walker Fabrication:
5.1.0 Patterning:

5.1.1 Metallization process:
The PVDF, Immobilon transfer membrane, pore size 0.45μm was sputtered with gold of thickness 200Å with sputtering equipment, ION TECH (see appendix 3). The PVDF was used as
received from Sigma-Aldrich. During sputtering process, the PVDF was mounted on silicon Wafer and loaded inside the sputtering equipment by first turning on the cooling targets for the gold target which is to be used. The chamber was ventilated by turning the load lock switch to vent on the pressure panel and the load lock hatch was removed to let nitrogen in. The pressure in the inner chamber was reduced by pumping down before pushing the sample holder inside the main chamber.

The sputtering process begins after loading the sample by opening the main Argon (Ar) inlet valve to flow position (see section 3 above). The flow and pressure are maintained at 36.6 and 4.6 respectively. The main power supply was connected to the machine and ensured that the plasma is ON position. The current and voltage are set to 2.20mA and 4.20V values respectively. The target shutter was opened for 120 seconds to deposit a layer of 200Å of thickness.

The target shutter was closed when the sputtering time has finished. The power supply and Ar inlet valve were turned off. Hence, the sample was unloaded from the equipment (see appendix 4). The machine was pumped down and the load switch left in an auto position.

After sputtering process, the PVDF/Au was spin coated with positive tone photoresist (mAP1275) to 20µm thickness using Polo’s spinner (see appendix 5). Ma-P1275 photoresist was used as received from Micro-Resist Technology. Program 20 was used with a speed of 500/1800 rpm for 20s. The sample was baked in ovum at a temperature of 105°C for 20 minutes using Heraeus Oven (see appendix 6). The dried sample was exposed to UV light using contact mask aligner (see figure 10). The selected exposure time used was 5 minutes with g line exposure. Furthermore, the sample was developed for 5 minutes. Developer used was ma-P331. The ma-P331 was used as received from Micro-resist technology. The developed resist film was thoroughly rinse with deionized water and then dried. The same process was repeated on the back side of the sample before etching process.
Figure 16: Graphical representation of the work process for fabrication of micro-walker.
5.2 Etching process:
The etching process was done using Au etchant. The etching time was 30 seconds. The sample was rinsed with deionized water and dried after etching.

5.3 Photoresist stripping process:
We used flood exposure for 5 minutes to strip the photoresist. After exposure to UV light, the sample was again developed for 4 minutes in a developer. It was thoroughly rinsed with deionized water and dried. The whole process was done in the clean room.

6.0 Fabrication of PPy tri-layer Microwalker:
The actuators were manufactured using a chronoamperometric polymerization method, which involves electro- deposition of PPy layers on both surface of Au/PVDF membrane (acting as a working electrode) by passing a constant current through a solution containing 0.1M pyrrole monomer dissolved in 0.1M LiTFSi/ PC (1% of water). LiTFSi/ PC was prepared by dissolving 7.17725g of LiTFSi in 250mL of PC and stirred thoroughly. The solution was degassed by passing nitrogen gas for 15 minutes followed by cooling for 15 minutes before the start of electropolymerization.

The polymerization was conducted for 12 and 6 hours for thick and thin film respectively in a freezer and a current density of (0.1 mA/cm$^2$) was applied. Metal mesh was used for two counter electrodes that were parallel to the gold- coated PVDF membrane. An Ivium Compactstat/ Choronoamperometric, interface with Ivium software was used to generate the constant current.

At the end of electropolymerization, the PPy tri-layer microactuation was rinsed with acetone and soaked with 0.1M LiTFSi/ PC solution for 10 minutes (see figure 16 for design layout).

![Cross section](image1)

![Top view](image2)

**Figure 17:** device layout
6.1 Activation of the tri-layer micro-walker:
The device was activated by application of potential using Compactstat/potentiometric. In dry state PPy tri-layer microatuation, electrolyte needed for an ion source/sink is soaked into the pores of the PVDF membrane. There was no electrochemical cell or electrolyte needed to submerge the device during activation of the actuation. The actuation of dry state PPy tri-layer microactuation requires only the control unit and a two electrode mode configuration (the four electrodes of the potentio stat are connected as followed in order to create the two electrode configuration: working electrode connected to the source electrode and the counter electrode connected to the reference electrode).

The potentials were applied at two levels. A constant positive potential that is responsible for the oxidation state of the device and a constant negative potential that is responsible for the reduction state of the device. However, both potentials switch alternatively according to the time interval set by the user at each cycle.

7.0 Characterization:

7.1 Distance as a function of applied voltage
We characterized the distance as a function of applied voltage by measuring the distance covered during oxidation and reduction. Potential differences between 0.6 to 2V were applied to the device and distances covered were measured and recorded.

7.2 Speed as a function of applied Voltage
In characterization of the PPy tri-layer microactuator, the speed was characterized as a function of an applied voltage. A potential different between 0.6 to 2V were applied to the device and distance covered during oxidation and reduction were measured and recorded (see figure 18). The time taken to complete this distance was also recorded. The speed of tri-layer microactuator was evaluated using the ratio of distance covered to the time taken to cover the distance

\[
Speed = \frac{\text{Distance (m)}}{\text{Time (S)}}
\]

The speed obtained was plotted against voltage. At each input potential, we measured two different values of distances and the average was calculated.
Figure 18: Current/time graph showing the oxidation/reduction state of PPy/PVDF actuation at 0.8V.

Figure 19: Measurements of distance during actuation.
7.3 Speed as a function of thickness of the film:
Characterization of the speed of tri-layer microactuator as a function of the thickness of the film was done by electropolymerization of pyrrole monomer on two different Au/PVDF using the same current density of 0.1mA/cm$^2$ and the same 0.1M LiTFSi/PC (1% of water) of a solution but with different time interval of 6 and 12 hours for thin and thick film respectively. The thickness of deposited PPy was measured and recorded after electropolymerization using dektak. Both tri-layer microactuator devices measured 15 and 30µm respectively. Both were activated using potential difference between 0.6 to 2V and the speed was estimated using the formula mention above.

7.5 Work done:
The work done by trilayer microactuator was characterized by using the formula: mass of the object (M) * acceleration due to gravity (g) * distance the object was lifted (h). Potential different between 0.6 and 2V were applied during actuation. The distance covered by the object was recorded at these potentials. An object of mass $1.3 \times 10^{-5}$ kg was attached to the device. The work done by the device was plotted against the input voltage. The simple PPy trilayer microactuator device has a mass of 0.033g and dimensions 30mm*5mm*30µm while the pattern PPy trilayer microactuator has a mass of 0.037g and dimensions 30mm*30mm*30µm.
8.0 Results:
The result obtained shows that pattern dry PPy trilayer microactuator and simple dry PPy trilayer microactuator are working in the same way. We actuated a dry state, pattern PPy trilayer microactuator by cutting the center part of the actuator to enable it have a free movement (see figure (20)).

Figure 20: Actuation of pattern PPy microactuator with its center part cut to enable a free movement. Potential applied from 0 to 1volt.

We also added the same load to both pattern and simple PPy actuator and the current/ time graph obtained in both actuators were overlaid. The overlay graphs shows that both pattern and simple trilayer micro actuator is similar (see figure 22).
**Figure 21:** Pattern PPy trilayer microactuator before cutting from the center part.

**Figure 22:** shows overlay of pattern and simple PPy trilayer microactuator

(Potential applied 1.5V.)
Figure 23: Activation of dry state PPy trilayer microwalker with three legs (Potential applied from 0 to 0.75V).

8.1 Distance as a function of voltage:
The result shows that distance is proportional to input voltage within the range of voltage studied (see figure 24).

Figure 24: shows the graph of distance against input voltage (average values, n=2, measurement error = ± 2 mm).
8.1 Speed as a function of applied voltage:
The curve shows that speed of PPy trilayer microactuation is linearly proportion to the applied voltage within the range of voltage studied (figure 25). This result was in agreement with result obtained by the Gursel and his co-workers [2, 15]. I believe that an increase in an input voltage will cause the ions to gain more energy to transport into PPy layers.

![Graph of speed as a function of applied voltage](image)

Figure 25: graph of speed as a function of applied voltage (measurement error = 0.004(m/s)).

8.3 Speed as a function of thickness of the films:
From the result presented in figure 26, the speed of a thin layer PPy trilayer microactuation increases more than the speed of thick layer PPy trilayer microactuation within the specified voltage. This is because the ion transport into PPy layer is generally rate limited [13].
Figure 26: shows the graph of the speed as a function of thickness of PPy layer (measurement error = 0.0004 m/s).

8.5 Work:
The result presented in figure 27, shows that the work density increases with increase in the input potential difference. This because increase in voltage increase the speed (see section 8.1).

Figure 27: shows the graph of work density as a function of voltage  (measurement error = 2*10^-7 N).

9.0 Discussion:
In this report we have used a standard micro fabrication method called photolithography to patterned PPy on PVDF membrane material. The patterning process was achieved using etching
process. To the best of my knowledge this is the first time this technique has been used to pattern PPY on PVDF membrane to form a PPY trilayer microactuation/microwalker with an individually controllable digits that can operate in air.

There are other technique that could be use like lift- off method [35] and micro contact printing [36] etc. Gursel et al [2], use the excimer laser ablation technique to fabricate conducting polymer microactuation that can work in air. Jager and Krogh [37] cut (out) PPY and entire PPY based devices using laser ablation and punching.

The PVDF coated with photoresist (thickness 10µm) was conducting. Ideally, it should have been non-conducting at this process stage. I believe that reason why the surface layer coated with photoresist was conducting after baking may be due to the absorption of the resist, through the pores of the PVDF layer as well as the very high surface roughness. This effect makes it difficult to pattern a photoresist on a PVDF membrane.

This problem was overcome by increasing the thickness of the photoresist up to 20µm and subsequently, increase the baking time to 20 minutes, exposure time was also increase to 5 minutes and development time was 5 minutes as mention before.

The spinning process was done two times on front side of PVDF with a speed of 1800 rpm to obtain a thickness of 10µm. This could have done once by reducing the spinning speed but the photoresist tends to cluster together after baking causing non-uniform of photoresist layer (see appendix7). The method adopted to solve this problem was to spin the sample with photoresist in two stages using a speed of 1800rpm and baked for 10 minutes each.

Secondly, etching process was done simultaneously on both side of the sample. This is to reduce the effect of etching one side of the surface to the other. After, etching process the photoresist (an etching protection layer) was removed using flood exposure. Flood exposure was used because it is better adapted to PVDF than the use of acetone and photoresist removal. The photoresist pattern is used to define areas of electrodeposition of PPY.

However, PPY trilayer microactuation has five layers (see figure 2 above), it consist of three different material namely: two layers of PPY of about 30µm thickness, two layers of gold of about 150Å and a PVDF membrane (110µm) sandwich in between these two materials. The gold was sputtered on the PVDF to increase the conductivity between the electrolyte (PVDF) and PPY layers [18].

Moreover, we tried other technique, vapor phase polymerization, to enhance the conductivity of the electrolyte (PVDF) and PPY layers. The idea was to replace the Au layer with a PEDOT layer. We used oxidative chemical polymerization of 3, 4- ethylenethiophene (EDOT) with iron (III) tosylate (or Iron(III) p-toluenesulfonate , (CH₃C₆H₄SO₃)₃Fe, FeTos) to enhanced the conductivity. First the PVDF was soaked in a 20% FeTos solution. Next, we heated about 10µl EDOT to a vapor phase in an enclosed container at temperature of 100ºC and mounted the FeTos
soaked PVDF in the container for 4 hours. When the dark blue PEDOT(Tos) film was formed on PVDF, we rinsed thoroughly with butanol and then isopropanol for 5 minutes each and finally with water. After vapor phase polymerization, we found that the resistance of the PVDF is still very high. Next, we tried synthesize PPy on the PEDOT/PVDF layer using the standard electropolymerisation method as described in section 6.1 above.

We did not have a successful PPy electropolymerization as a result of a high resistance (see figure 28).

Figure 28: PEDOT coated PVDF using vapor phase polymerization using EDOT and iron (I) tosylate.

In addition, we also used PEDOT/PSS with ethylene glycol. We soaked PVDF with a solution containing PEDOT/PSS and ethylene glycol in the ratio of 3:1 and heated on a hotplate at a temperature of 100°C for one hour. The result obtained also shows higher resistance (see figure 29).

Figure 29: Coating by soaking with PEDOT/PSS and ethylene glycol.
The PVDF layer is porous polymer with pores of about 0.45µm which serves as reservoir for electrolyte and as a chemical cell separator. The electrolyte used was 250 ml of 0.1M LiTFSi in polypylene carbonate and 1% of water. The dissolved ions (Li\(^+\), TFSi\(^-\)) will serve as dopants.

The electropolymerization of PPy must be done on a conducting surface, known as working electrode, since the method relies on conduction /transfer of electrons [12, 15]. When a constant current is applied, a redox reaction occurs in the PPy layers. In the oxidized state, the PPy attract an anion to balance the electron removed. On the other hand, during reduction state electron are accepted in the polymer and anions are removed when PPy layer are negatively charged. The anion that is transfer during redox reaction in PPy trilayer microactuation is contained in the pore of the PVDF that contains in the electrolyte. In addition the doping rate is control by the current applied [15].

The bending behavior of PPy trilayer microactuation is based on volume expansion and contraction. The volume increases/expands during oxidation because anion is added to the PPy layer and electrons are removed. Likewise, the volume decreases/reduces during reduction state because anions are removed from the PPy layer and electrons are added [1-5, 10, 12, 14, and 15]. The oxidation state is refers as doped PPy while reduction state is refers as undoped state. This bending behavior is utilized during actuation of dry state PPy trilayer.

10.0 Conclusion:
We have for the first time used clean room facility to fabricate a patterned PPy trilayer microactuator /microwalker device that have individually addressable controllable digits that can operate in air. We have characterized the speed, force and work density of the PPy trilayer microactuator. The result presented in this paper shows that the speed of PPy trilayer microactuator increases with increase in the applied voltage within the voltage studied (0.6V-2V). Hence, thin film PPy trilayer microactuator has a higher speed compared to thick PPy trilayer microactuator. Moreover, the distance of PPy trilayer microactuator increase with increase in applied voltage. The results obtained were in agreement with the results obtained with Gursel and his coworkers. Finally, a detailed reproducible fabrication protocol has been developed in this paper.
11.0 Recommendation for future works:

We have fabricated a milimeter size of patterned PPy trilayer microactuator, future work should focus on reducing this size to micro- and nano- scale. Secondly, research is also needs to characterized the life cycle of the PPy trilayer microactuator.

12.0 References:


[32] Applications of active materials, Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 672, ERIK EDQVIST, 2009.


[34] Ivium technologies, user manual, Eindhoven, September 2010

Appendix 1: Top view diagram showing how the wafer is rotated counter-clockwise in order to match the rotation orientation of the wafer and the mask. Part (a) shows the situation before rotation and (b) after the mask and wafers orientations are approximately matched. Copied from reference [25].
Appendix 2: Sample of PVDF mounted on top of Si wafer. Sample before spin coated with photoresist (a), Sample after spin coated with photoresist (b).
Appendix 3: shows sputtering equipment.

Appendix 4: PPy membrane sputtered with Gold.
Appendix 5: Polos spinner.

Appendix 6: Heraeus oven
Appendix 7: Shows Au/PVDF coated with non-uniform photoresist (350 rpm- 60s).

Appendix 8

Fabrication protocol trilayer actuators

1 Cut PVDF (dimensions 5*4 cm)
2 Sputter Au on front sides of PVDF about 200Å
3 Spin photoresist on PVDF/Au surface about 20µm thickness.
4 baked the sample for 20 minutes
5 Exposed the sample to UV light for 5 minutes using g line exposure
6 Developed for 5 minutes
7 rinse thoroughly with deionize water and dried
8 Repeat the same process on the back side of the PVDF starting from number 2
9 Etch both sides of the sample for 30sec with Au etchant
10 strip the photoresist using flood exposure for 5 minutes on both side of the sample
11 Developed the sample again for 4 minutes.
12 rinse thoroughly with deionize water and dried.
Electropolymerization of PPy:

1. Dissolved a solution containing 0.1M pyrrole monomer in solution containing 0.1M LiTFSi/PC (1% of H₂O).

2. Degassed the solution (1 above) with N₂ gas for 15 minutes.

3. Create a two electrode mode configuration of the potentiostat i.e. working electrode connected to source electrode and reference electrode connected to counter electrode.

4. Connect the counter electrode (metal mesh) in parallel to the working electrode.

5. Measure the surface area of the sample and recorded.

6. Polymerization is conducted inside a freezer by applying a constant current density of 0.1mA/cm² for 12 hours.

7. Rinse thoroughly with acetone and then deionize water.

8. Soaked in LiTFSi/PC for 5 minutes before actuating.