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Inkjet printing of resistive-type humidity sensor for harsh environments

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ABSTRACT

INKJET PRINTING OF RESISTIVE-TYPE HUMIDITY SENSOR FOR HARSH ENVIRONMENTS

by
Hamed Kazerani

A flexible resistive-type humidity sensor for harsh environments is successfully designed and fabricated by an inkjet printing method using a Dimatix materials printer (DMP-2800 series from Fujifilm). Construction of the sensors is based on inkjet printed interdigitated silver electrodes on a polyimide flexible substrate along with an inkjet printable polyaniline (PANi) as humidity sensitive material. A copolymer of ethylene and vinyl alcohol (EVOH) is used as sensor protective coating. Double strand water-soluble PANi ink is synthesized by polymerization of aniline monomers with poly(4-styrenesulfonic acid) (PSSA) as a template.

Manufactured devices showed high sensitivity (1% @ 45%RH) to humidity with good linearity (R-squared correlation value of 0.99) and fast absorption and desorption responses over a broad range of humidity (15-95%RH). The response time for the sensors without EVOH coating on top is around 5 and 15 seconds for absorption and desorption, respectively. The response time for the coated sensors is about 40 and 110 seconds for absorption and desorption, respectively. Sensors showed small hysteresis (about 3%) while a protective polymer coating provided a barrier to damage or false signals due to solvents and chemicals.

Fabricated sensors are characterized in order to investigate the structure and morphology of the thin films. UV-Visible spectroscopy is used to obtain information on PANi in solution form and to confirm that PANi in the form of emeraldine salt is

obtained. FT-IR spectroscopy is used to verify the incorporation of the PSSA into PANi. SEM microscopy method is used to characterize the PANi-PSSA in powder form and the AFM method is used to show the morphology of the thin films.

**INKJET PRINTING OF RESISTIVE-TYPE HUMIDITY SENSOR
FOR HARSH ENVIRONMENTS**

**by
Hamed Kazerani**

**A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Materials Science and Engineering
Interdisciplinary Program in Materials Science and Engineering**

May 2012

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APPROVAL PAGE

**INKJET PRINTING OF RESISTIVE-TYPE HUMIDITY SENSOR
FOR HARSH ENVIRONMENTS**

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This dissertation is dedicated to my family, especially my daughter, Atrina.

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CHAPTER 1

INTRODUCTION

1.1 Background

Printed flexible electronics is a new and fast growing industry which is the future of new applications in sensors, displays, power and other fields of research and study. We are now entering the organic age in which the collaboration of nanotechnology, biology and information technologies can be lead to multiple applications in commercial and defense markets. Flexible electronics is a revolution that along with previous electronics industry innovations will be a disruptive technology that will create, change and shift markets. Organic electronics built upon plastic materials offer not only ease of manufacturing and low cost, but also lightweight and mechanical flexibility [1].

As opposed to being restricted to traditional rigid wafer-based circuit boards, the possibility in having electronic devices to be formed into desired shapes and be placed on any type of surface has attracted engineers and scientists alike. Early concepts of flexible electronics go back to the 20th century. Flexible electronics have found application in countless systems where flexibility and space limitations restricted the options for engineering. Nowadays, almost every type of electronic products contains flexible components [2].

Flexible electronics are developing as an alternative to the established silicon electronics for applications such as flexible displays, sensors, solar cells and Radio-frequency identification (RFID) tags. Flexible displays on plastic substrates are much thinner and lighter than the conventional liquid crystal displays (LCD) on glass

substrates. Flexible displays can withstand bending to much smaller radiuses of curvature than be achieved with normal displays. Also, flexible electronics and displays can be manufactured by printing techniques. The production cost of flexible electronics can offer considerable savings over silicon electronics, which require a complex and high expense manufacturing process. High-performance thin film transistor (TFT) displays based on new oxide material consisting of indium, gallium and zinc (known as IGZO) are also overtaking hydrogenated amorphous silicon (a-Si:H) TFTs for three-dimensional (3D) displays [3-5]. With the fast growth of TFT technologies, more applications in displays and smart sensors are now becoming available. New organic thin film transistor (OTFT) technologies such as floating-gate OTFTs allow one to reduce the process variations and understand large-area active-matrix organic light emitting diode (AMOLED) flexible displays [6].

Integrated circuits are not limited to servers and computers anymore. Instead, there is a growing demand and market for embedded systems such as displays, consumer electronics and smart sensors. Flexible electronics on plastic substrates promises to pave the way for the next generation of inexpensive and portable electronic systems that can take advantage from low-cost manufacturing methods such as roll-to-roll and inkjet printing. These devices can tolerate a large amount of mechanical stress that can lead to design electronic systems that can be folded into smaller forms [7].

1.2 Recent Advances in Flexible Electronics

In recent years, several important developments in the improvement and applications of flexible and stretchable electronics have been established. With the need of energy consumption, energy-related applications are clear. The ability to generate materials that can bend, twist and stretch continually, and yet one still able to keep its capability as conductors or electrodes, has led to several efforts in improving flexible and biological devices that are environmentally friendly such as biodegradable materials and devices [8].

A tactic to manufacture printable elastic conductors consisting of single-walled carbon nanotube (SWCNT), which are uniformly dispersed in a fluorinated rubber, has been reported [9]. By using ionic liquid and jet-milling, long and fine SWCNT bundles can form well-developed conducting networks in the rubber. The display could be stretched by 30%–50% and used for connecting light-emitting diodes (LED) over a curved surface without any mechanical or electrical damage. A flexible LED arrays containing up to 50 diodes in which the arrays can survive repeated stretching of about 100,000 cycles, which is able to tightly conform to a human thumb tip, is fabricated [10]. Figure 1.1 (a) is showing a 4.3" flexible display fabricated based on Phosphorescent OLED technology for military use which is four times more efficient than the LED displays. LG Philips 14.1" flexible active-matrix (AM) display that can produce images on bendable screen is shown in Figure 1.1 (b). The display features a 1280x800 resolution with contrast ratio of 10:1 in which the display can be viewed from any angle. An example of full color flexible OLED concept that can be reality in few years is shown in Figure 1.1 (c).

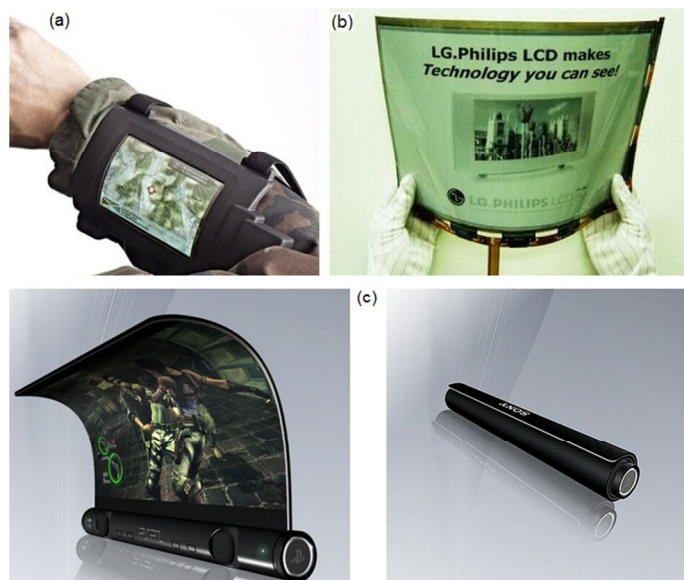


Figure 1.1 (a) 4.3" PHOLED flexible wrist-mounted screen with full motion graphics, (b) 300 μm thick electronic paper and (c) Sony full color flexible OLED [11-13].

Sub-monolayer films of SWCNT that can act as attractive materials for the construction of flexible integrated circuits have been fabricated. A high-performance carbon-based semiconductor consisting of sub-monolayer, random networks of a SWCNT to yield small to medium-scale integrated digital circuits have consequently been manufactured. These circuits are composed of up to 100 transistors on plastic substrates [14].

Integration of ultrathin and flexible silicon nanomembrane transistors into the electrode array has been demonstrated. This technology allows compact collections of thousands of multiplexed sensors that are connected through fewer wires. This is later used to fabricate brain-machine interface devices capable of recording spatial properties of a cat's brain activity *in-vivo*, such as sleep spindles and electrographic seizures [15].

Design and fabricating of different electronics components such as sensors, power supplies and communication elements into an ultrathin, lightweight and stretchable "skin-like" membrane has been reported [16]. The membranes are able to coat onto the surface

of the skin like a temporary tattoo. The devices are then used to measure electrical activity generated by the heart, brain and other organs. A flexible wireless tiny device similar to a temporary tattoo is shown in Figure 1.2. The sensor is thinner than diameter of human hair and can be adhere to skin without adhesive which can be simply peel off like a bandage.

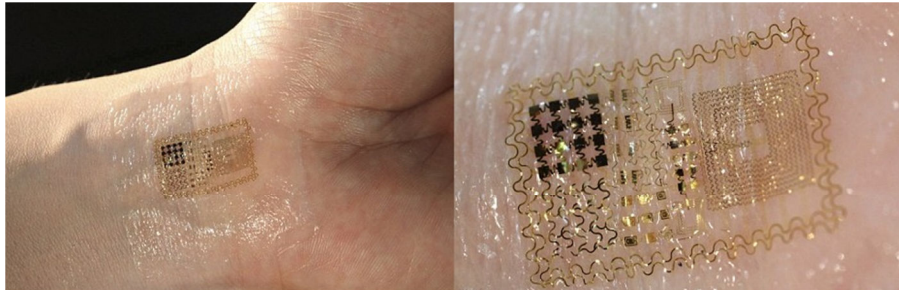


Figure 1.2 Wearable flexible wireless sensor for monitoring patient vital signs [17].

Stretchable and flexible photovoltaic (PV) and photo- electrochemical cells are predicted to be extremely useful as power sources for future technologies such as solar tarps which can be useful for various applications in military, intelligent services and biomedical fields. Figure 1.3 (a) shows a new flexible photovoltaic solar cell with efficiency up to 17.5% that fabricated on a steel foil in Germany. A rollable photovoltaic panel available in the range of 5-20 watts, manufactured by FVG Energy, is shown in Figure 1.3 (b).

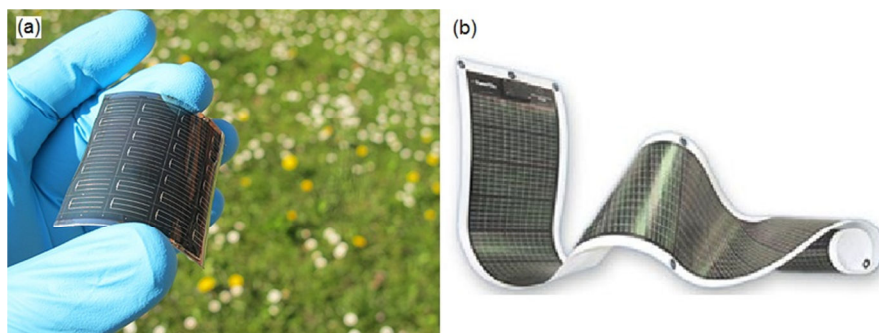


Figure 1.3 (a) Flexible photovoltaic solar cell and (b) Rollable photovoltaic solar panel [18, 19].

In the upcoming years, many efforts and breakthroughs will continue to be made in new materials development, fabrication models and device applications [8]. Based on these examples, it is believed that printed flexible electronics will be a very promising approach to overcome challenges in the future [5].

1.3 Objective

The objective of this dissertation is to design, fabricate and characterize a flexible resistive-type humidity sensor that can be used in harsh environments by using low-cost printing techniques, especially inkjet printing. Inkjet printed silver on top of a flexible substrate acts as sensor electrode. Water-soluble double-strand polyaniline (PANi) is synthesized and used as humidity sensitive material. A special copolymer of ethylene and vinyl alcohol (EVOH) is used as protective coating for the fabricated sensors against harsh environments.

1.4 Overview of Thesis

A brief background of printed and flexible electronics along with some of the most important applications is described in the current chapter. Some of the advancements made in this area in the past few years are summarized as well.

In Chapter 2, printed flexible electronics will be described in more details in terms of different types of substrates and solution processable materials and inks that are being used in this field. Various deposition techniques such as spin and spray coating in addition to inkjet printing methods will be explained. Furthermore, different aspects of

previous research on humidity sensors for harsh environments will be reviewed in details in the next chapter.

In this project, the flexible humidity sensor for harsh environments consists of three parts: electrode, humidity sensitive material and protective coating layer. Chapter 3 details the design, materials synthesis and preparation, and fabrication steps of the device. Different features and parameters of inkjet printing system (a material printer from Fujifilm) that are used for the purpose of fabrication will be discussed in detail.

Organic and structural analysis used to examine the characterization of the materials and fabricated sensors will be discussed in Chapter 4. The experimental setup which is assembled to test the fabricated sensors along with the results and discussion also comes in this chapter.

Finally, Chapter 5 covers the conclusion and the recommendations for further research in this field.

CHAPTER 2

FLEXIBLE ELECTRONICS AND SENSORS

2.1 Flexible Substrates

Many researchers and industries are showing considerable interest in flexible substrates. These substrates are garnering attention in many technical applications and industries nowadays due to their outstanding properties such as light weight, flexibility and stretchability, chemical resistance, low cost and great mechanical properties such as superior dimensional stability over a wide range of temperatures (from -269 °C to 400 °C). Their thicknesses can range from few microns up to 100 microns. The three major groups of flexible substrates are mainly based on plastics, metals and ceramics. Other than conventional substrates available for general purposes, new substrates are being investigated and made for specific applications based on industry needs and requirements. For example, metallic flexible substrates can be plated with different functional surfaces to achieve the favored property. Some of the leading industries that are currently using flexible substrates are automotive, photovoltaic, light-emitting diode (LED), Radio-frequency identification (RFID) and sensors. Substrate properties need to be optimized in order to meet an application requirement. Varieties of methods such as reel-to-reel method are being used to manufacture technological and economical substrates. Micro stamping, etching and micro injection moldings are some of the fabricating technologies in which the device perform better if a special substrates is used. As an example, a specially made substrate coated with gold enables putting LED lens on the substrate along with mini-chips in the smallest possible space [20].

2.1.1 Plastic Substrates

Plastic substrates are mostly polyimide and polyester based. Kapton, manufactured by Dupont, is a well-known plastic substrate that is being synthesized by polymerizing an aromatic dianhydride and an aromatic diamine. These polyimide films can offer a variety of properties that makes them useful for numerous applications in different industries. Aerospace, automotive, bar code labels, photovoltaic, flexible printed circuits and safety industries are already using Kapton plastic substrates for their needs. Different Kapton substrates can offer great electrical and mechanical properties over broad range of temperature from -300 °C to 400 °C with good hydrolytic and dimensional stability, great thermal durability along with low effect on humidity and temperature over long period of time. Thickness of these types of substrates can vary from 7.6 μm up to 100 μm [21]. Some of the features and applications of different types of Kapton flexible polyimide films, obtained from a variety of sources, are listed in Table 2.1.

Table 2.1 Typical Features and Applications of Different Grades of Kapton Polyimide Film

Grade	Features	Applications
B	Excellent balance of physical, chemical, and electrical properties over a wide temperature range – superior dimensional stability at elevated temperatures	Heaters, Antenna, LED circuitry, Applications requiring precision laser ablation
CR	Developed specifically to withstand the damaging effects of partial discharge	Electrical rotating machines, Electrical insulation, Generators, Traction motors, Transformers
FCR	Withstands corona discharge while delivering improved long-term performance – Cost-effective wire insulation that helps reduce thermal upsets and partial discharge – Improves service life and operational efficiency versus conventional insulation	Large industrial motors, Traction motors, Generators
FN	General purpose film that is coated or laminated on one or both sides with Teflon – Imparts heat sealability, provides a moisture barrier, and enhances chemical resistance	Tubing, Heater circuits, Heat sealable bags, Automotive diaphragms and manifolds, Electrical insulation
FPC	Superior dimensional stability and adhesion	Flexible printed circuits, Automotive, Computers, Telecommunications equipment, Military applications, Aerospace, PCB stencils, Screen printing
HN	General-purpose film for applications at temperatures as low as -269°C (-452°F) and as high as 400°C (752°F) – All-polyimide film with an excellent balance of properties over a wide range of temperatures - HN film can be laminated, metallized, punched, formed or adhesive coated	Mechanical and electronic parts, Pressure sensitive tape, Fiber optics cable, Insulation blankets and tubing, Etching, Shims

Polyester films, which can range from 50 μm to 75 μm in thickness, have extremely clean and smooth surfaces along with excellent flatness and registration, which allows the position of the substrate for a multi-pass printing process to be accurately determined prior to each printing pass. These properties in addition to strong stability, resistance to heat, chemicals and moisture make them suitable for indium tin oxide (ITO) sputtering process that can be a great choice for flexible display applications. Also polyethylene naphthalate (PEN) substrates with the ability to withstand extreme heat and harsh chemical and solvents environments are being used in flexible and high-tech OLED and touchscreen displays. Comparisons of different types of plastic substrates are shown in Table 2.2.

Table 2.2 Plastic Film Properties [22]

Film Type	Polyimide Kapton®	Polyester Mylar®	Polyester PEN
Glass Transition Temperature, T_g ($^{\circ}\text{C}$)	410	75	120
Continuous Operation Temperature ($^{\circ}\text{C}$)	240	105	180
Tensile Strength @ 25 $^{\circ}\text{C}$ (Kpsi)	33	30	40
Modulus (Kpsi)	430	550	850
Elongation (%)	70	130	70
Dielectric Strength (Volts/mil)	7000	7000	8000
Dielectric Constant (1kHz)	3.5	3.2	2.9
Heat Shrinkage (%) @ 200 $^{\circ}\text{C}$, 30 min.	0.1	4	1
Moisture Absorption (%)	2.8	0.5	0.4

2.1.2 Metallic Substrates

Metallic substrates are used when higher chemical resistance, temperature tolerance and heat dissipation are desirable. Metallic substrates show higher compatibility for CMOS (Complementary Metal Oxide Semiconductor) processing due to its long term stability for moisture and high thermal shock resistance [2]. Compared to ceramic substrates, metallic substrates have the advantages of higher mechanical and thermal durability, excellent conductivity, which leads to less chance of overheating, and more cost effectiveness.

Also, ultrathin metallic substrates ranging from 2-3 nm are used for Transmission electron microscopy (TEM) grids since they are electron transparent which make them great for TEM examinations. Gold, platinum and palladium are some of the recognized materials in this field that are being used to make thin substrates due to their robustness and electron transparency properties. Titania (TiO_x) substrates are also being used in different types of applications since they are biologically compatible and can be implanted into body tissues. They are also used for making high quality paints that can be used in aerospace and automobile industries [23].

2.1.3 Ceramic Substrates

Very thin flexible ceramic substrates (less than 45 microns) based on Yttria-stabilized zirconia (YSZ) are now commercially available. Figure 2.1 shows a 40 μm thick sheet of 3 mol% Yttria-Stabilized Zirconia (3YSZ). Some of the novel advantages of these types of flexible substrates are high strength at extreme high and low temperatures, high thermal cycling tolerance (more than 2000 hours), low thermal conductivity, high

chemical durability, high physical wear durability and very low weight. These extreme properties makes them perfect to be used in different industries for different types of applications such as military electronics, flexible circuits, pressure and oxygen sensors and extreme high temperature sensors. They are highly durable, flexible and extremely light which also make them suitable for gas separation applications such as carbon dioxide (CO_2), Hydrogen (H_2) and carbon monoxide (CO) in which they can be used as membrane in order to separate gases from an environmental samples [24].

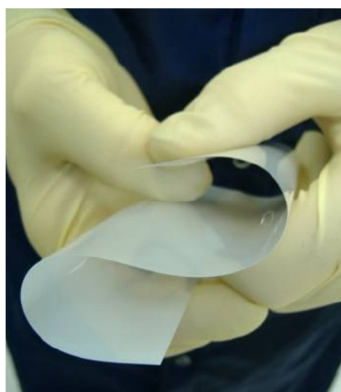


Figure 2.1 40 μm thick sheet of 3 mol% Yttria-Stabilized Zirconia (3YSZ) [25].

2.2 Solution Processable Materials

There are a number of processing techniques that can be used for fabricating thin films from solutions, such as spin and dip coating, stencil, screen and inkjet printing. A particular ink with special properties needs to be formulated and modified depending on the processing technique that is being used for thin film fabrication. Depending on requirements for each fabricating method, it is necessary for the inks to have correct specifications, such as viscosity and surface tension, in order to be processable. Typical types of inks can be categorized in two major types of conducting and insulating.

2.2.1 Conductive Materials

Conducting materials can be metallic or polymeric based. Solution preparation from nanomaterials is a major area of research and study. Making nanoparticles can be done by chemical reduction in which the metal in the form of salt is reduced with solvents, or it can be done by physical methods such as laser ablation. There are number of metallic inks commercially available for printing purposes. Sun chemical Inc. makes stable silver nanoparticle solution for inkjet printing purposes. Sigma-Aldrich is another well-known company for making gold functional inks for the purpose of inkjet printing and spin coating techniques. A numbers of studies are being conducted with the focus on making other metallic solutions to be suitable for different fabrication methods. Table 2.3 shows list of some of the conductive inks that are available commercially for different processing methods.

Table 2.3 Commercially Available Conductive Inks

Name	Manufacturer	Printing Method	Ink Type
NanoGold	Sigma Aldrich	Inkjet Printing	Nanoparticle Dispersion
Clevios TM PH 500	Heraeus	Spin Coating Dip Coating	PEDOT/PSS
NanoSilver	Sun Chemical	Inkjet Printing	Nanoparticle Dispersion
Clevios TM PH 1000	Heraeus	Various Printing Techniques	PEDOT/PSS
Polyaniline (Emeraldine salt)	Sigma Aldrich	Spin Coating Inkjet Printing	Nanoparticle Dispersion

Other types of conductive inks are based on intrinsically conducting polymers (ICPs). These are form of polymers in which the charges in these types of polymers are transported between molecules via charge carriers such as electrons and protons. They are composed of molecules that have conjugated sequences of double bonds along their chains and their conductivities are due to delocalization of the π -bonded electrons in this conjugated bonds [2, 26]. Polyacetylene, polythiophene, polypyrrole and polyaniline are some examples of conductive polymers. Major families of conducting polymers are shown in Figure 2.2. These polymers can be synthesized and formulated or they can be obtained commercially. Conductive polymers have been widely used in various industries for difference purposes such as in sensing, photovoltaic and OLED applications.

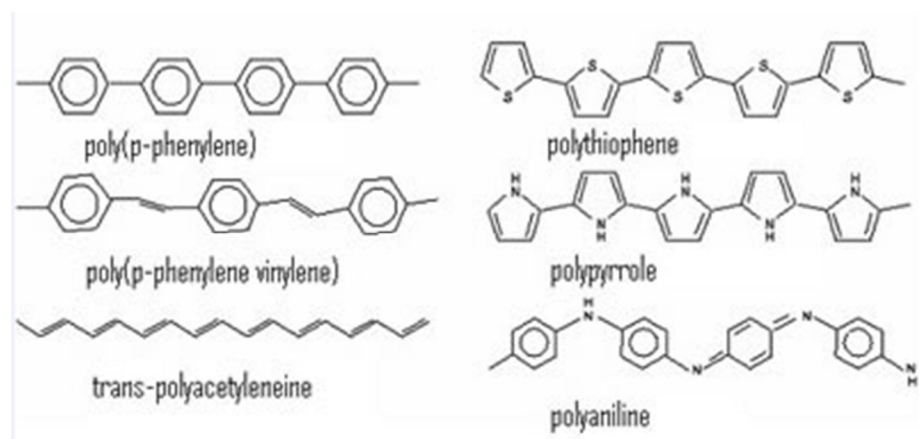


Figure 2.2 Major families of conducting polymers [27].

Ngamna et al. [28] synthesized aqueous polyaniline nanodispersions doped with dodecylbenzenesulfonic acid (DBSA). A piezoelectric desktop printer is used to inkjet the aqueous polyaniline. The synthesis is optimized in terms of the ratio of monomer to oxidant and dopant and surface tension analysis show that the aqueous nanodispersions are suitable for inkjet printing.

2.3 Deposition Method

Spin coating, spray and dip coating, stencil, screen and inkjet printing are some of inexpensive methods that can be used for fabricating thin films. Since the purpose of this study is to fabricate a flexible humidity sensor for harsh environment based on printing methods, some of these methods which are used for this study will be reviewed in this section.

2.3.1 Spin Coating

Spin coating is a recognized non-vacuum process that is used to deposit uniform thin films onto substrates. The process generally involves depositing a known amount of a fluid onto a substrate. The substrate is rotated at a high speed which eventually causes the fluid to spread over the substrate due to centripetal acceleration. The initial amount of fluid required for deposition is determined by the properties of the ink such as viscosity and surface tension as well as by the area that is needed to be coated. Final thickness of the coating can be determined and calculated by the spinning speed, acceleration and other ink parameters such as drying rate, viscosity and surface tension.

Two methods of dispensing the fluid onto the substrate are static and dynamic. Static dispensing is when drops of ink placed onto the center of the substrate that are stationary and will follow by rotation. Dynamic method on the other hand is depositing the ink onto a rotating substrate at low speed followed by spinning at higher speeds. Acceleration to high speed (about 1500 to 6000 rpm) is usually required as the final step in order to form a film with the desired thickness. Usually higher speeds will lead to thinner film thicknesses. A separate curing process might be required after spin coating in

order to make a uniform and high quality film without any flaws or defects such as pinholes [29, 30]. A schematic of spin coating process is depicted in Figure 2.3.

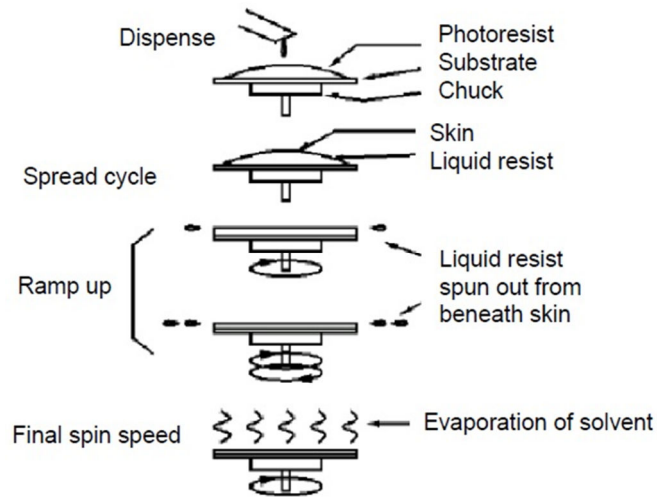


Figure 2.3 Schematic of spin coating process [30].

2.3.2 Spray Coating

Spray coating is a process that uses a compressed form of a gas in order to increase the velocity of particle to be deposited onto a substrate. A high kinetic energy of particles caused them to collide with the substrate and form a uniform coat on the substrate. The compressed gas can be helium or air at some cases. Particle size and density as well as the temperature and velocity are the key points to control in order to achieve a uniform and flawless coating. The cold spray method, as shown in Figure 2.4, is a mask-free process that achieves low defect coatings at low temperature as well as enabling thicker coatings.

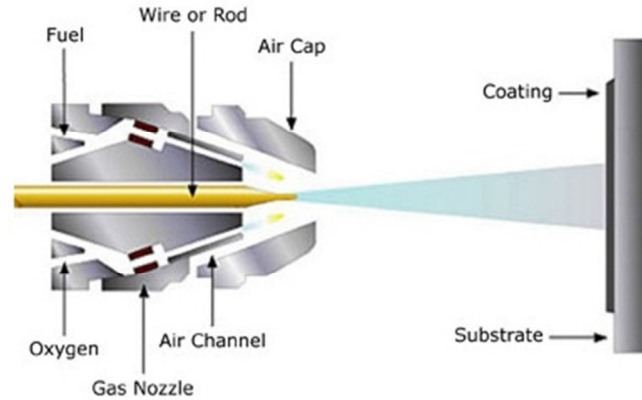


Figure 2.4 Schematic of cold spray coating process [31].

Some of the disadvantages of this method are that it is limited to ductile materials and cannot be used for brittle substances like ceramics and glasses. Also, the substrate has to be able to accept the coating since not all the materials accept coating because of their properties such as surface energy [32].

2.3.3 Inkjet Printing

Inkjet printing is one of the methods that enable deposition of materials with any geometry on different types of substrate. Conducting polymers, metallic and bio materials are a few examples of materials that have been printed by inkjet printing method. Devices such as batteries, fuel cells and polymer light emitted diode (PLED) have been fabricated using conducting polymers. Some of the important advantages of inkjet printing method that makes inkjet printing as an alternative to photolithography and other fabrication methods in fabricating micro and nanoelectronic devices are as follows [33-36]:

- Compatibility with various substrates
- Ability to deposit precise amount of materials in a quick and reproducible manner
- Computer controlled ability to print on specific locations
- Low temperature processing with no need to vacuum
- Non-contact and low cost method of fabrication
- Possibility of finer design and details than screen printing
- Printing more than one material simultaneously

One of the most usual modes of inkjet printing is drop-on-demand. Figure 2.5 shows a schematic view of how a drop-on-demand system works. In a typical process a voltage is applied to a piezoelectric material that is coupled with a pumping chamber that holds the ink. The piezoelectric material reacts in shear mode and will cause the ink to be jetted onto a moving substrate [37].

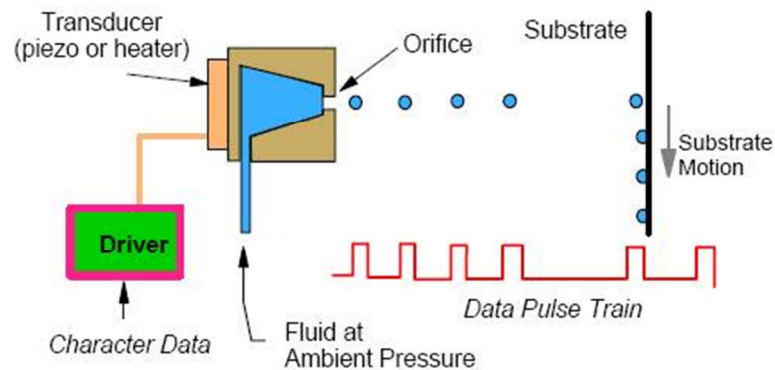


Figure 2.5 Schematic of a drop-on-demand [37].

2.4 Literature Review

There are various studies conducted in the areas of humidity sensing. Two major aspects of studies include studying different types of humidity sensitive materials and methods of fabrication of humidity sensors. Protective layers in general have been another area of interest for researchers. In this section major works and studies that is done previously on

humidity sensors, polyaniline and different fabrication methods as well as inkjet printing is summarized.

2.4.1 Humidity Sensors and Polyaniline

Humidity sensors are one of the important categories in sensing. The importance of humidity and humidity sensing can be seen in different areas such as moisture sensitive products, food industry, storage etc. Humidity sensors fabricated from polymeric materials also have been used for environmental monitoring in different industries such as hospitals, museums, libraries etc.

There are different kinds of humidity sensors based on ceramics and glasses available in the market. People have also shown interest in organic materials and conducting polymers as humidity sensing substances since polymeric materials are flexible, light weight and cost effective. Also, polymeric materials are easy to work with and the sensors are simple to fabricate. Different methods of fabrication of polymeric sensors include electrochemical polymerization, chemical/electrochemical deposition, spin coating etc.

Polyaniline is one of inherently conducting polymers (ICPs) that have been studied due to its special properties such as H switching properties, ease of synthesis and wide range of potential applications in sensing and other electronic devices. Nano-electronic circuitry and nanosensors are few examples of promising applications of Polyaniline nanoparticles. Some of the methods that have been used for fabrication of ultra-thin conducting polymers are spin coating, casting, self-assembly and Langmuir-

Blodgett (LB) methods. Screen and inkjet printing are other methods of fabrication of polymers that have been used more recently [28, 38-40].

2.4.2 Inkjet Printing of Polyaniline

Fabrication and performance of an ammonia gas sensor by using inkjet printing deposition method has been reported by Crowley et al. [36]. Polyaniline (PANI) nanoparticles are used as sensing material and the results show stable logarithmic response in the range of 1-100 ppm to ammonia gas.

Morrin et al. [41] reported on Polyaniline (PANI) deposition onto screen-printed carbonpaste electrodes (SPE), polyethylene terephthalate (PET) and gold-PET by using a desktop inkjet printer. Morphology of the films is studied by profilometry, scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods. Printed films show smooth morphology at micro-dimensional scale.

Ngamna et al. [28] synthesized aqueous polyaniline (PANI) nanodispersions doped with dodecylbenzenesulfonic acid (DBSA). A piezoelectric desktop printer is used to inkjet the aqueous Polyaniline (PANI). The synthesis is optimized in terms of the ratio of monomer to oxidant and dopant and surface tension analysis shows that the aqueous nanodispersions are suitable for inkjet printing.

Loffredo et al. [33] reported on fabrication of an ammonia sensing device by inkjet printing of Polyaniline suspension on alumina substrates. Some of the printer parameters such as amplitude and duration of jetting impulse, jetting frequency and substrate velocity are optimized in order to fabricate thin polyaniline lines. Also,

fabrication of water dispersible Polyaniline-Poly(4-styrenesulfonate) nanoparticles for inkjet printing of ammonia sensor are reported by Jang et al. [35].

Shim et al. [42] reported on inkjet printing of an electrochromic devices using polyaniline-silica and poly(3,4-ethylenedioxythiophene)-silica colloidal composite particles. Also, synthesis and inkjet printing of water dispersable polyaniline/carbon nanotube composite are reported by Small et al. [43]. Fabricated films show good optical transparency, sheet resistance and electrochromic behavior.

2.4.3 Inkjet Printing of Humidity Sensor

Nam et al. [40] reported on fabrication of humidity sensitive using an inkjet printer equipped with a UV lamp system. Photo-curable electrolyte inks are prepared by dissolving the following in methanol/2-methoxyethanol: [2-[(methacryloyloxy)ethyl]dimethyl]propyl ammonium bromide (MEPAB), 1,5-[bis(2-methacryloxyethyl)dimethylammono]pentane dibromide (MDAPD), a multifunctional reactive oligomer (SP1013), trimethylolpropane triacrylate (TMPTA), and photo-initiators. Different ratios of MEPAB/MDAPD/SP1013/TMPTA are used for optimization of the ink.

An inkjet printer with 15 microns diameter nozzle driven by a piezoelectric mechanism has been used by Chil et al. [34] to fabricate a humidity sensitive membrane on electrode-Alumina substrates using polyelectrolyte solution containing ionene oligomer and cross-linking agent. Fabricated sensor impedance characteristics are in close agreement with that of dip-coating method.

2.4.4 Polyaniline Humidity Sensor

A humidity sensor based on Cobalt-Polyaniline nanocomposite is reported by spin coating method in Toluene medium by Fuke et al. [44]. Fabricated sensor shows a fast response and recovery time with good repeatability, reproducibility and low hysteresis effect in the range of 20–95 %RH. Material characterization is done by X-ray diffraction (XRD), scanning electron micrograph (SEM) and Fourier transform infrared spectroscopy (FTIR).

Layer-by-layer (LbL) nano-assembly is used by Nohria et al. [39] for making thin poly(anilinesulfonic acid) (SPANI) films in order to be used as humidity sensors. For comparison purposes, spin coating is also used as another method of fabrication.

McGovern et al. [45] synthesized copolymer of Polyaniline with polyvinyl alcohol and also with butyl acrylate/vinyl acetate. The copolymers are used as sensing material of a resistive-type humidity sensor which is fabricated by dip-coating method on polyesterinsulated platinum wire as electrodes. Final thickness of the film is about 150 microns. Sensor show high sensitivity, low resistance, and good reversibility without hysteresis.

2.4.5 Other Resistive-type Humidity Sensors

A Resistive-type relative humidity sensor based on plasma-treated multiwall carbon nanotube/polyimide (p-MWCNT/PI) composite films reported by Yoo et al. [46]. Beyond the percolation threshold, which was reported to be 0.05 wt%, the sensor shows good linearity over the entire humidity range. A humidity sensing mechanism of the composite

is proposed based on charge transfer between adsorbed water molecules and the p-MWCNTs.

Humidity sensitive films are prepared by Chen et al. [47] through simultaneous quaternization and crosslinking of poly(4-vinylpyridine) and poly(glycidyl methacrylate) with 1,4-dibromobutane and diethyltriamine, respectively. The prepared humidity sensors show less than 1% RH (relative humidity) hysteresis with fast adsorption and desorption response.

2.4.6 Coatings and Ethylene Vinyl Alcohol (EVOH)

One use of coating layers is to protect the coated surfaces or materials from outside environments. Coatings can be formed through a diffusion bond between the coating material and the surface which the coating is applied to, or it can be a mechanical adhesion between the two surfaces. Some of the properties of materials and devices that can be improved by coating layers are optical, magnetic, electrical, thermal attack, corrosion and barrier properties. Copolymers of ethylene and vinyl alcohol are distinguished by their great processability and barrier properties. The resistance of these copolymers to oils and other organic solvents are very good. EVAL™ (trade name for Ethylene Vinyl Alcohol copolymers) resins, which are available commercially, show high resistance to weather effects such as retaining their colors and minimal changes to mechanical properties. Proper copolymerization ratio of ethylene to vinyl alcohol, selected degree of polymerization and specifically manufacturing process used in the making of EVAL™ copolymers are the key factors to their special properties [48, 49].

2.4.7 Humidity Sensors for Harsh Environments

Most of the reported papers on humidity sensor for harsh environment are based on ceramics and ceramic composites and there are not too many papers on polymer-based humidity sensor designed for harsh environments.

Neumeier et al. [50] presented a humidity sensor based on H-ZSM-5 type zeolite can detect traces of humidity (~10-110 ppmV) under harsh conditions such as high temperature.

Connolly et al. [51] reported on a relative humidity sensor based on a porous SiC membrane with Aluminum electrodes. Using SiC allowed the fabricated sensor to be stable in harsh environments. Some of the environments that the sensor are tested and effects of those environments investigated under those conditions are outlet of a car exhaust, 85°C operating oven and an ammonia atmosphere for 5 days.

Fabrications of crosslinked polyimide and fluorinated polyimide-based humidity sensors are reported by Matsuguchi et al. [52] The crosslinked polyimide sensor shows good resistance to chemicals and the crosslinked fluorinated polyimide shows long-term stability in harsh environments.

2.4.8 Ethylene Vinyl Alcohol and Other Coatings

Marais et al. [53] characterized the effects of CF₄ microwave plasma treatments on water vapor transportation through the Poly(ethylene-co-vinyl alcohol) and polyethylene films. The barrier effect to water in plasma treated layers of Ethylene Vinyl Alcohol (EVOH) is improved significantly.

In Oksuz et al. [48] work, an ethylene vinyl alcohol copolymer powder is coated using flame spraying method with oxygen and acetylene gases. The bond strengths and microstructures of the coatings are determined with tensile testing, scanning electron microscopy and Fourier transform infrared.

Ranucci et al. [54] used Poly(ethyleneglycol)s (PEG)-based crosslinked resins as hydrophilic coating for relative humidity (RH) sensors. Fast and reversible sorption behavior is observed.

2.4.9 Conclusion and Motivation

As a summary of the literature review section, it is found that there are several works on using polyaniline as humidity sensor by fabrication methods such as spin-coating, nano-assembly and other methods but not inkjet printing. Also, Ink jet printing of humidity sensors based on other polymers such as photo-curable polymers and polypyrrole has been reported, but there has not been any work on ink jet printing of polyaniline acting as humidity sensor. On the other hand, humidity sensors for harsh environments are mostly based on different kinds of ceramics, ceramic composites, fiber optics etc. and there are no studies that can be found on resistive-type humidity sensor based on polymeric materials. Most importantly, there has not been any work or study on inkjet printing of EVAL™ copolymers for coating or for other purposes.

For these reasons, the primary motivation of this study is to design and fabricate a resistive-type humidity sensor that can withstand harsh environments by using simple and low-cost fabrication methods like printing methods, especially inkjet printing.

CHAPTER 3

FABRICATION

3.1 Introduction

Conventional methods of fabrication such as lithography, both micro and nano lithography, have advantages and disadvantages. Ability to fabricate very small features is one of the main advantages of the lithography. Micro and nano lithography methods are complex processes that involve multiple time-consuming procedures. Also, since the fabrication method is based on material removal by etching processes, it is clear that it is not an economical method of fabrication. One-time masks and etching chemicals are examples of consumable supplies and waste in this process that makes the method inefficient and hazardous to the environment. Because of the nature of the fabrication method, it is required for the process to be conducted in extremely clean environments; thus, an advanced cleanroom is a necessity for this manufacturing technique.

On the other hand, variety of substrates such as glass, metallic and polymeric as well as paper and even cloth can be used in inkjet printing process. Since this technique does not involve any mask or etching steps, it makes it a very fast and especially cost-effective compare to the conventional methods. One of the biggest advantages of this method is that it does not require cleanroom facilities for manufacturing process. The final spatial resolution or printed structures depends on the inks and their properties. Poor spatial resolution, compared to the nanolithography, is the major disadvantage of this method. Also, extensive research on fluid properties is required in order to optimize the quality of the fabricating features [55].

3.2 Dimatix System Description

Dimatix materials printer (DMP-2800 series) is an easy to use and cost-effective fabrication tool for material deposition. Piezoelectric cartridges, with the choice of 1 and 10 picoliter drop volume, enable this device to construct feature sizes as small as 9 microns. Computer-controllability coupled with the ability of inspecting the printed pattern during processing makes the DMP perfect for fluid/substrate interaction evaluation, product development and material assessment purposes. Use of the supplied software allows one to generate desired patterns as well as ability to modify them for features optimization. It also makes it possible to import designs from some other external programs such as CAD as a patterns for inkjet printing. Figure 3.1 shows the Dimatix printer used for the purpose of fabrication.

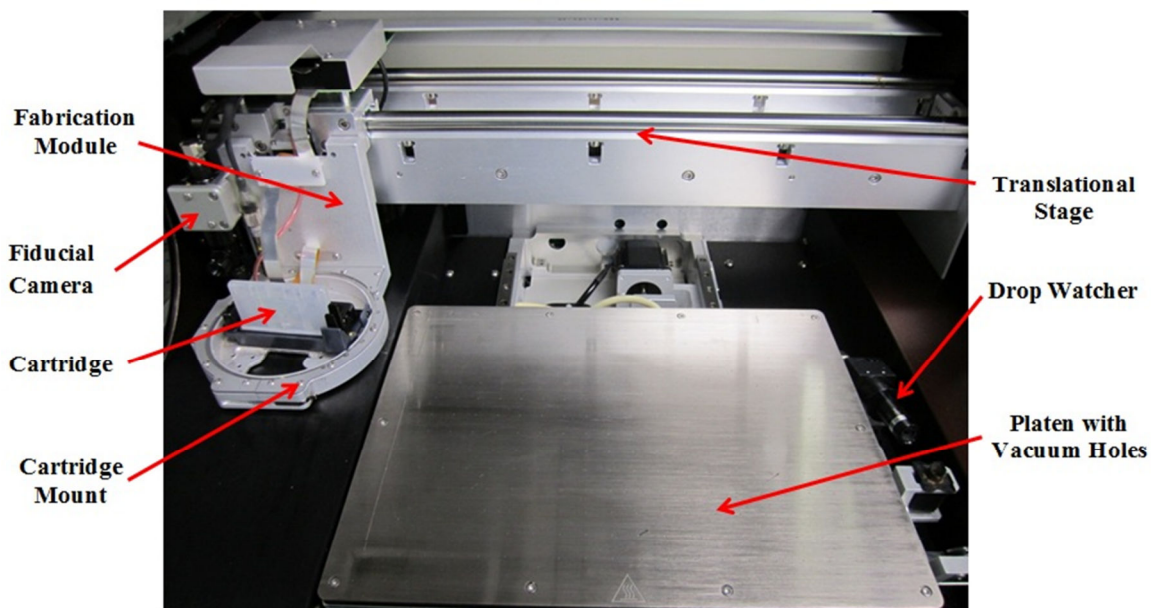


Figure 3.1 Dimatix Material Printer (DMP-2800 series).

The DMP-2800 series allows printing on a maximum of 8x11 inches substrates in which the thickness of the substrates can be up to 25 mm by controlling the z height of the printer head above the substrate. The platen with vacuum holes holds the substrate in place during printing. The platen temperature can be varied from ambient temperature to 60 °C if necessary. Also, DMP's waveform editor permits optimization of the piezoelectric jetting device by controlling the pulse to the device. A built-in fiducial camera allows substrate alignment as well as positioning of the print origin. It also provides measurement of features and well as ability to capture pictures. The printhead uses a MEMS-based technology with 16 nozzles spaced over 254 μm , as shown in Figure 3.2 (a), with the ability to hold 1.5 ml of fluid. It allows for the user to fill their own inks and different fluids into the cartridge for various fabrication purposes [37, 55]. Image of two nozzles, nozzles number 9 and 10, taken with an optical microscope is shown in Figure 3.2 (b).

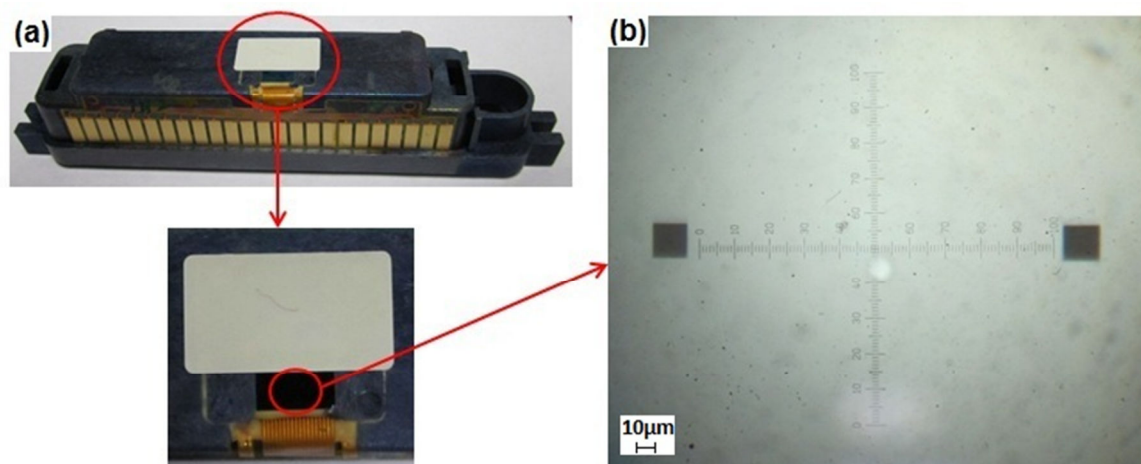


Figure 3.2 Image of a Dimatix printhead and nozzles.

Figure 3.3 shows part of a waveform setting page that can be modified based on fluid properties to achieve the optimum jetting results by controlling the pulses and other parameters. Schematic of four stages in the waveform editor is shown in Figure 3.4.

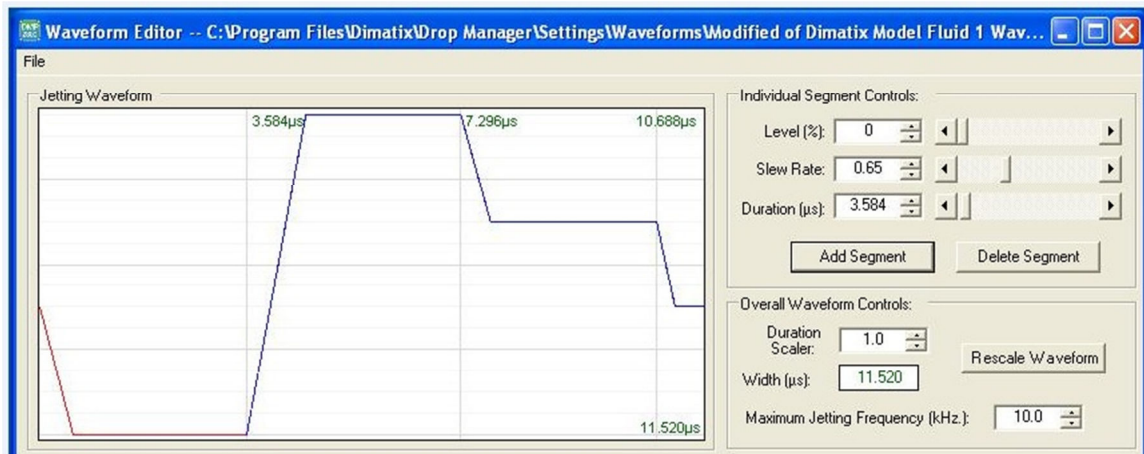


Figure 3.3 Portion of waveform editor of Dimatix printer.

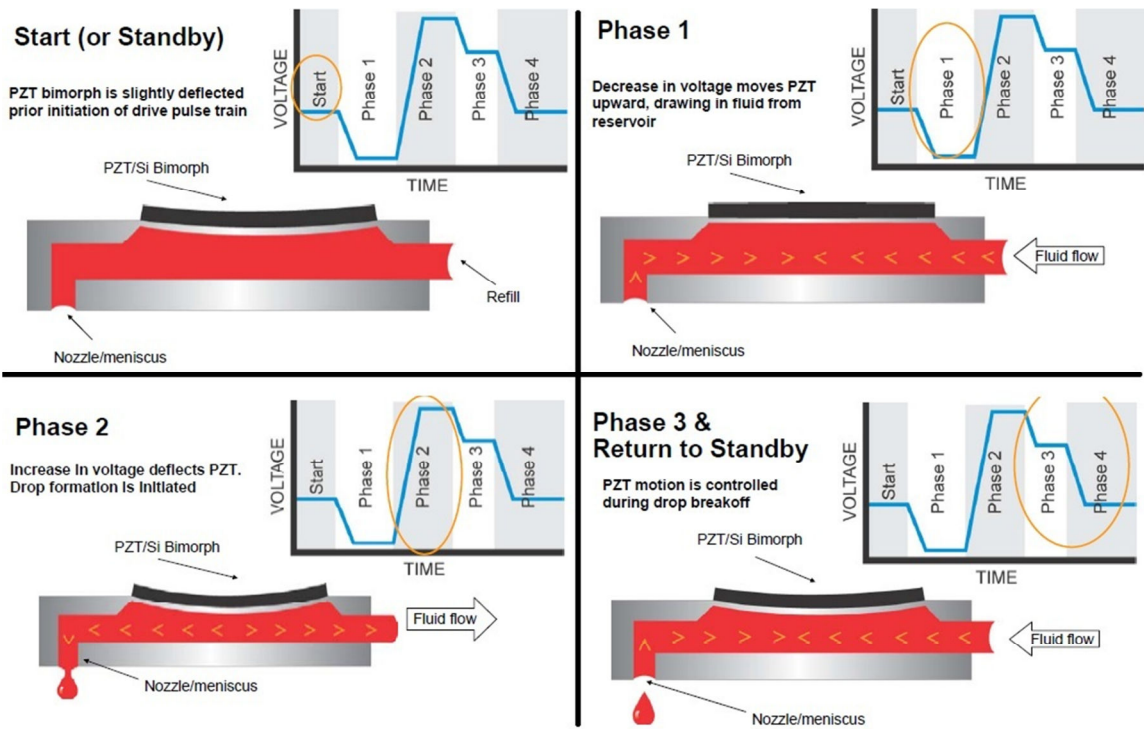


Figure 3.4 Schematic of four waveform stages [56].

3.3 Synthesis and Ink Preparation

3.3.1 Materials

Polyimide flexible film (Dupont Pyralux® AP grade) is purchased from Insulectro. Silver ink (20 and 40 wt. %) is obtained from Sun Chemical Co. Aniline (99.5%), poly(4-styrenesulfonic acid) (PSSA) (Mw ca. 75,000, 18 wt. % in water), ammonium persulfate (APS) (98.0%), 1-propanol (n-PrOH) (99.5%) and acetone (Semiconductor grade, 99.5%) are purchased from Sigma Aldrich. Ethylene vinyl alcohol copolymer (EVOH) (ethylene content: 32 mol.%) pellets are supplied by Kuraray America, Inc. All chemicals, except noted otherwise, are reagent grade.

3.3.2 PANI-PSSA Synthesis

Preparation of water-soluble PANi by chemical-oxide polymerization is described previously [57]. In order to synthesize PANi-PSSA with molar ratio of 6:1 PSSA: PANi which is determined to have the optimum property for humidity sensing purposes, 12.5 g of PSSA is diluted with 20 ml of deionized (DI) water in a 50 ml glass bottle. 0.2 ml of aniline monomers is then added to the PSSA solution. The solution is stirred, by using a magnetic spin rod, at around 400 rpm for 1 hour at room temperature. A 0.05 g/ml solution of APS in DI water is prepared separately and 10 ml of the prepared APS solution is then added to the aniline-PSSA mixture and stirred for 5 min in the same way explained above. The resulting mixture is left at room conditions for 12 hours in order for the polymerization to take place. Polymerization steps to synthesize a double-strand PANi-PSSA powder is illustrated in Figure 3.5. Every 5 ml of PANi-PSSA solution, after

completion of polymerization, is mixed in 25 ml of acetone. The precipitated powders are separated and collected by filtering the powder-acetone mixture.

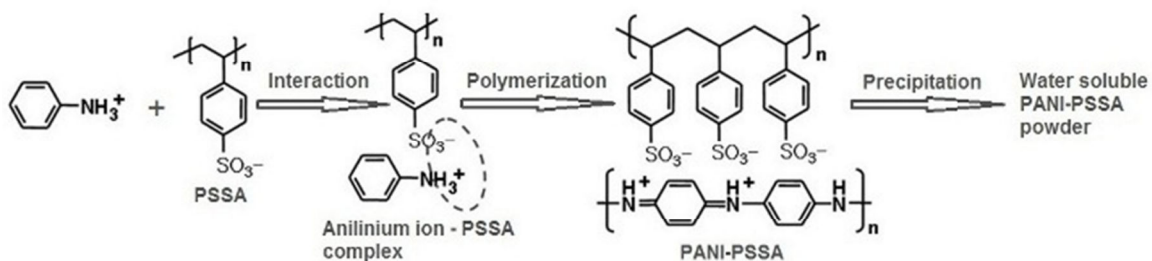


Figure 3.5 Preparation of water-soluble PANi-PSSA powder.

The resulting powder is vacuum dried for 24 hours and dark green PANi-PSSA powders are obtained after drying process as shown in Figure 3.6. The prepared powders are completely water soluble with no precipitation after leaving the solution aside for a long period of time (over two months).



Figure 3.6 PANi-PSSA powders with its solution in water after two months.

3.3.3 EVOH Solution Preparation

A 5 wt. % EVOH solution is prepared by mixing EVOH, n-PrOH and DI water together in a vial with magnetic stir bar with ratio of 5 wt. %, 61.75 wt. % and 33.25 wt. %, respectively. The mixture is placed in water bath at 60 C on a hot plate with magnetic stirring capability. Temperature of the water bath is then raised to water boiling point gradually and the mixture is stirred at around 400 rpm for 3 hours in order for the pellets to dissolve completely. The solution is left at room temperature for 5 h to stabilize before use.

3.4 Humidity Sensor Design

Overall design of the resistive-type humidity sensor is shown in Figure 3.7. The sensor consists of silver electrode inkjet printed on top of the polyimide flexible substrate along with PANi as sensing material and EVOH as protective coating material. The details of the design of all the components (interdigitated silver electrode, PANi and EVOH) patterned with Dimatix printer software along with fabricating parameters will be explained later in this section.

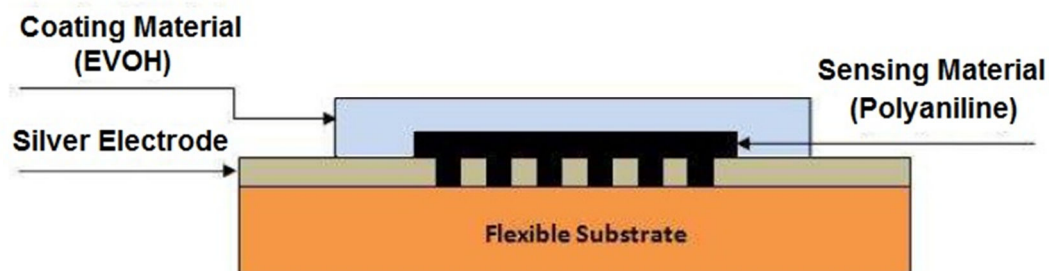


Figure 3.7 Schematic view of the resistive-type humidity sensor.

3.5 Fabrication Steps

3.5.1 Substrate Preparation

It is very important for the substrate to be clean and free of any particles such as dust. Even though the feature size mostly depends on fluid properties such as surface tension and liquid volume, but substrates that are not cleaned properly can affect the deposited fluids by changing the fluid's surface tension and also causing the fluid to spread unequally in different directions which will cause the pattern to smear. Cleaning procedure for Kapton substrates include a pre-cleaning process consist of acetone cleaning followed by isopropanol (IPA) cleaning and finally blow drying the substrate. The substrate then needs to be boiled with distilled water and three drops of D-91 cleaning agent for about one hour followed by one hour of ultrasonication. Rinsing with acetone then isopropanol followed by air blow drying will be the final step of cleaning procedure. In case of using copper-cladded Kapton, one step of wiping the surface with acetone and isopropanol would suffice. The reason of using IPA is to remove any residue left from acetone on the surface [55].

3.5.2 Silver Electrode

3.5.2.1 Design Layout Silver ink, both 20% and 40% content from Sun Chemical Inc. is chosen to be used as a material for humidity sensor electrode and it is used as received without any further modifications. Dimatix printer software is used in order to design the electrode. The electrode design consists of interdigitated comb-shape with five legs of 2.750 mm and 0.250 mm in length and thickness, respectively. The spaces between the legs are intended to be 0.5 mm and two contact pads of 1 mm by 1 mm are

considered for contacting the sensor to outside and other electronics. The complete design of the electrode, as shown in Figure 3.8, is described in detail in Appendix B.

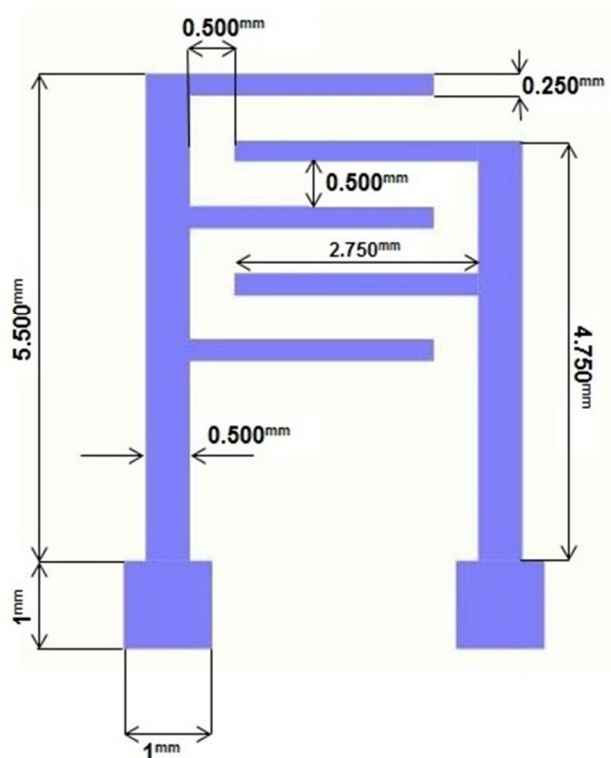


Figure 3.8 Design of the silver electrode.

3.5.2.2 Cartridge and Waveform Settings There are number of settings that are needed to be modified in order to have an optimum deposited film quality. Jetting waveform, voltages applied to nozzles, cartridge temperatures and cleaning cycles are some of the main features in “Cartridge Settings” section in the printer interface that can be defined and modified. In order to fabricate the best quality of film, for each ink and substrate combinations, these settings need to be adjusted. Modified model fluid 1 waveform as shown in Figure 3.9 is used for inkjet printing of silver.



Figure 3.9 Waveform setting for silver ink.

For example, the firing voltage of 24 volts is chosen as best voltage to obtain the best quality of film. Summary of cartridge settings as well as cleaning cycle are listed in Table 3.1.

Table 3.1 Silver Ink Cartridge Settings

	Task	Time	Frequency	Post Delay
Cleaning Cycle	Spit	500ms	2KHz	1s
	Purge	0.5s	-	1s
	Spit	500ms	2KHz	1s
Firing Voltage	24 Volts			
Meniscus Vacuum	4.0 inches H ₂ O			
Cartridge Print Height	1.000mm			
Cleaning During Printing	Run every 15 bands OR 300 seconds			

3.5.2.3 Curing Process The ink that is used for inkjet printing the electrode contains 20 % or 40 % silver content. It is not possible to get a conductive line without annealing or curing the printed ink since the silver nanoparticles are not in contact with each other due to the polymer encapsulations surrounding the silver nanoparticles. Thus, it is necessary for the ink, after deposition, to be cured by evaporating the solvents and other chemicals such as binders and encapsulations at elevated temperatures in order to obtain the highest conductivity of silver. Choosing a temperature between 150-200 °C will eventually cause the silver nanoparticles to join and form shiny conductive lines. Figure 3.10 shows inkjet printed silver electrodes during curing, on a hot plate, by evaporation of the solvents chemicals (dark color).



Figure 3.10 Inkjet printed silver electrodes during (right) and after complete (left) curing.

The quality of inkjet printed silver is inspected by the printed fiducial camera. Printed lines are smooth with sharp edges as shown in Figure 3.11.

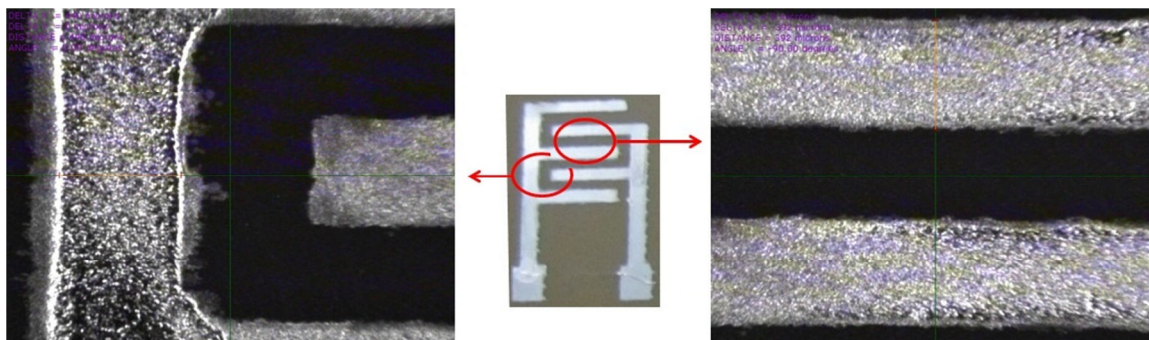


Figure 3.11 Images of different parts of an inkjet printed silver electrode.

3.5.3 Humidity Sensitive Material (PANI-PSSA)

3.5.3.1 Design Layout

A simple square shape is designed with the Dimatix software in order to cover the interdigitated silver electrode by inkjet printing of prepared conductive PANI-PSSA on top of the electrode. This will cause for legs of the silver electrode to be in contact with each other with this conductive layer on top of them. Any change in resistance of the PANI-PSSA sensitive material will eventually lead to change in overall resistance over the two contact pads of the electrode. The humidity sensitive material design along with an inkjet printed sensor is shown in the Figure 3.12.

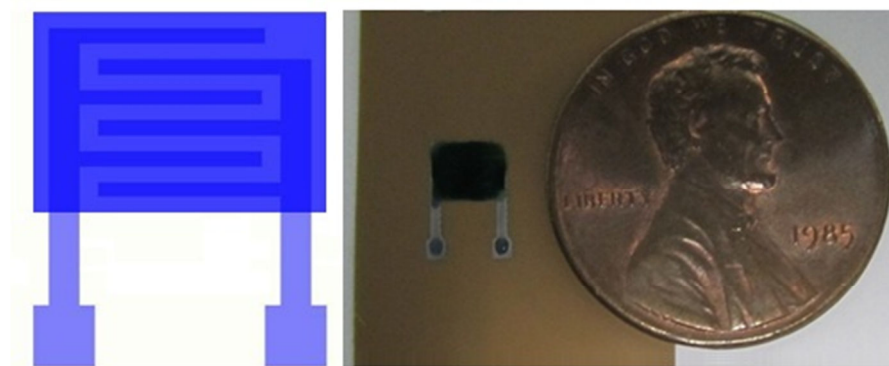


Figure 3.12 Design of PANi-PSSA (left) and inkjet printed version of the sensor (right).

A 6 wt. % solution of PANI-PSSA in DI-water is prepared from powders by dissolving them in DI-water followed by physical shaking and ultrasonication for 15 min. for complete dispersion of the powders in water.

3.5.3.2 Cartridge and Waveform Settings The same waveform that is used to inkjet print the silver electrode is utilized and worked perfectly for the PANi-PSSA material. Since the ink properties are different from the silver ink, especially the viscosity of the prepared solution, slight changes are made to the firing voltage and cleaning cycles. The detailed cartridge settings are outlined in table 3.2.

Table 3.2 PANi-PSSA Ink Cartridge Settings

	Task	Time	Frequency	Post Delay
Cleaning Cycle	Spit	100ms	1.5KHz	1s
	Purge	0.1s	-	1s
	Spit	100ms	1.5KHz	1s
Firing Voltage	12 Volts			
Meniscus Vacuum	4.0 inches H ₂ O			
Cartridge Print Height	1.000mm			
Cleaning During Printing	None			

3.5.3.3 Curing Process Since almost every conductive polymer is very sensitive to high temperatures that can lead to permanent damage on the electrical properties, it is better to evaporate the solvents under vacuum at low temperature after deposition of these materials. Since the solvent used for PANi-PSSA is water, it can be either air dried or for faster curing process, it can be cured under vacuum at room temperature. Both methods are tested on curing the PANi-PSSA and the results are the same in terms of quality of the films and their properties after curing.

3.5.4 Protective Layer Coating Material (EVAL™)

Two methods is proposed and performed in order to deposit the protective coating on top of the fabricated sensors; inkjet printing and spin-coating method.

3.5.4.1 Inkjet Printing Different concentrations of EVAL™ ink are prepared and tested for inkjet printing. Optimum concentration for the purpose of inkjet printing is chosen to be in the range of 0.8-1.5 wt. %. The same waveform as explained from the previous sections is used for the waveform setting. Modifications, to the cartridge settings, that are made in order to get the best quality of the fabricated film are shown in Table 3.3. 60 layers of material is deposited on top the fabricated humidity sensors. The completed sensors then cured under vacuum at room temperature to evaporate the EVAL™ solvents and to avoid damaging the temperature sensitive PANi-PSSA.

Table 3.3 EVAL™ Ink Cartridge Settings

	Task	Time	Frequency	Post Delay
Cleaning Cycle	Spit	500ms	2KHz	1s
	Purge	0.5s	-	1s
	Spit	500ms	2KHz	1s
Firing Voltage	32 Volts			
Meniscus Vacuum	5.0 inches H ₂ O			
Cartridge Print Height	1.000mm			
Cleaning During Printing	Run every 10 bands OR 300 seconds			

3.5.4.2 Spin Coating Method A spin coater from MTI corporation (Model: TC100) is used for the purpose of the spin coating. 5-10 wt. % solution is used for spin coating the protective coating layer on top of the fabricated humidity sensors. The humidity sensors fabricated by inkjet printing method are removed and taped onto the spin coater's rotating disc using a double-sided tape. Silver electrode contact pads are covered by a soft tape to protect them against covering by EVAL™ solution. Few drops of prepared ink is deposited on top of the sensor and the rotating disc speed is set to 40-50 rpm for spreading the ink over the sensor for 5-10 seconds followed by ramping up the speed between 2000-5000 rpm, depending on the thickness required, for 30-60 seconds. Completed sensors are finally cured under vacuum at room temperature.

Because of the high molecular weight of EVAL™ polymer as well as clogging issue, which will lead to formation of pinholes in the fabricated films, successful inkjet printing of EVAL™ ink requires a significant effort. Few numbers of print heads are needed in order to make a perfect and flawless film which makes the inkjet printing more time consuming and less economical compare to the spin coating method. For these

reasons, spin coating technique is used as a dominant method for fabricating the protective layers for the humidity sensors.

3.6 Print Quality and Troubleshooting

There are several factors when using the material inkjet printer that need to be taken into consideration in order to improve the quality of the printed films. Accuracy in drop placement and modifying alignments parameters are some of these factors. In this section, some of the possible issues that can lead to poor quality films as well as suggested solutions are described.

3.6.1 Droplet Ejection Accuracy

One of the most important factors needed in order to print a uniform design is the placement of each firing drop accurately where it belongs. Misdirected drops, as shown in Figure 3.13, are the most common problem that causes the drops deposit where they do not belong. There are few factors that cause the droplets to be misdirected. Nozzle contamination by dust or any kind of external particle during printing will cause the drops to fire in angle and not straight. This problem can be inspected by pattern observation and it can be fixed by modifying the cleaning cycle settings in order to keep the drops pathway clean and free of debris. Also, proper filtering and ultrasonication can break and remove the large particles from the ink which will lead to better quality ink that will eventually avoid partial clogging of the nozzles due to big particles.

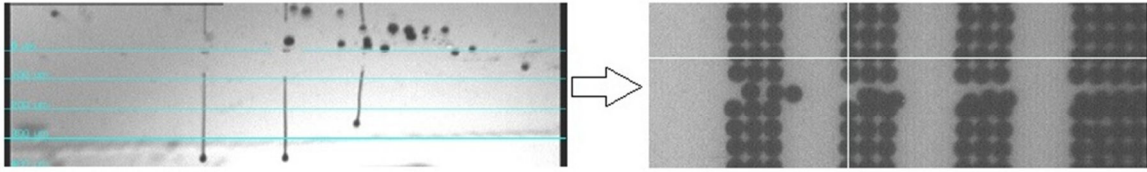


Figure 3.13 Image of off-axis jet firing (left) that leads to disrupted pattern (right).

Imperfect and damaged nozzles can also lead to misdirect firing. Sometimes due to the nature of some of the solvents or the ink itself, it is possible that part of the nozzle get etched away by the ink or its solvents over time. This can lead to jetting the ink in an angle direction rather than straight. This problem can be detected by the built-in camera on the printer which will allow inspecting each nozzle and can be eliminated by removing the specific nozzle from the printing process. In some cases that the misdirecting cannot be eliminated completely, the problem can be reduced by adjusting the space between the nozzles and the substrate.

3.6.2 Cartridge Alignment

Since drop sizes are varied from ink to ink, the printer software relies on the user to adjust the print cartridge angle based on the drop size of the printing ink. The print head needs to be physically rotated to a proper angle to avoid improper alignment. After the drop size is determined for a specific fluid and by knowing the spacing between the nozzles, the rotation angle of the cartridge head can simply calculated by $\theta = \text{Sin}^{-1}(d/s)$ as shown in Figure 3.14, Where “s” is nozzle spacing and “d” is vertical spacing between the nozzles due to print head rotation.

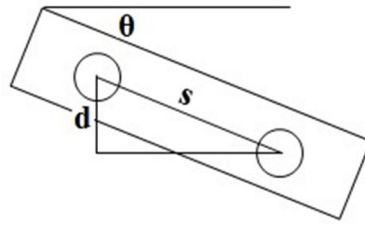


Figure 3.14 Diagram of tilted cartridge.

Rotation of the cartridge more than calculated angle will cause gaps between the printed lines in vertical direction. On the other hand, tilting of the cartridge less than calculated angle can cause overlapping the drops which will lead to overflowing the fluid. This will cause the stepping problem in the printed pattern.

3.6.3 Non-firing Nozzles and Non-matched Velocities

Individual nozzles can get clogged and stop the jetting due to several reasons such as bubble formation at the nozzle and big particles in the ink. Non-firing nozzle will cause the pattern to be discontinued in vertical direction which eventually causes the pattern to be separated from top and bottom. Disrupted pattern due to a non-firing nozzle is shown in Figure 3.15.

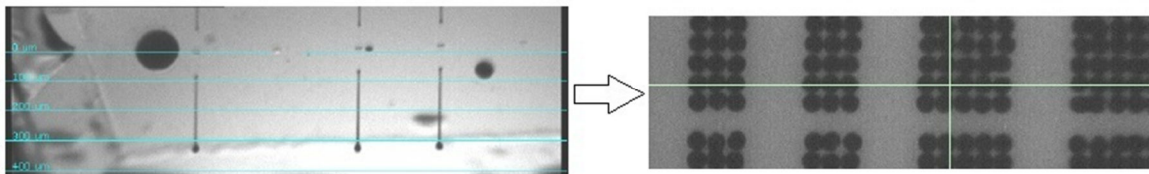


Figure 3.15 Non-firing nozzles.

Also, nozzles jetting with different velocities will directly impact on the quality and overall line fidelity. These problems can be inspected by using the drop watcher and can be eliminated by proper adjustment in jetting velocities and nozzle selections.

3.6.4 Incorrect Waveform

Two types of problem can occur by having an incorrect waveform. One is that a drop will break up and leave the nozzle before the complete drop ejected from the nozzle and left a meniscus ink behind at the surface of nozzle. This is because there is not enough pressure applied to the nozzle to remove the drop completely from the nozzle. This will affect the next drops that are firing out and will affect the quality of the deposited film. The second effect of an incorrect waveform setting is that the tail of a drop breaks and forms a secondary droplet and will follow the main drop to the substrate. Since the velocity of the broke up tail is slightly different that the main drop, it will cause the pattern not to be perfect and it leads to smearing. Both of these problems can be illuminated by accurate manipulation of jetting waveform settings for each ink.

3.6.5 Other Effects

For situations in which substrates need to be heated, the heat arising from the substrate can cause partial evaporation of the inks' solvents before firing. Since the velocity is inversely proportional to the viscosity and surface tension, substrate temperature can eventually reduce the viscosity and surface tension which will lead to increase in speed of the jetting inks which will affect the quality of the printed films.

Humidity is one of the biggest issues in microfluidic deposition. The solvent of the ink can absorb water from space around the nozzles which will change the viscosity and surface tension of the droplets and eventually affect the jetting performance. Thus, it is recommended that printing to be done in a low humidity conditions.

CHAPTER 4

CHARACTERIZATION

4.1 Introduction

The purpose of this section is to characterize the films fabricated in the previous chapter in order to understand the structure and morphology of the films. Four methods are described in this section to characterize the films. UV-Visible spectroscopy is used to obtaining information on PANi in solution form and to confirm that PANi in the form of emeraldine salt is obtained. FT-IR spectroscopy is used to see the incorporation of the PSSA into PANi. SEM microscopy method is used to characterize the PANi-PSSA in powder form and AFM method is used to characterize the morphology of the thin films.

4.1.1 UV-visible Spectroscopy

Ultraviolet-Visible (UV-vis) spectrometer is an analytical device that uses ultraviolet and visible spectral to determine presence of substances by interacting with samples and measuring the absorption of samples radiation as a function of frequency.

A Hewlett Packard (Model 8453) spectrophotometer with wavelength range of 190 - 1100 nm is used for measuring the absorbance of a sample, in aqueous solution, as a function of the wavelength. A sample of PANi in DI-water is prepared and diluted to a concentration in order to get an absorption spectrum in the wavelength range of 200-800 nm. Figure 4.1 shows the absorption spectra of the sample.

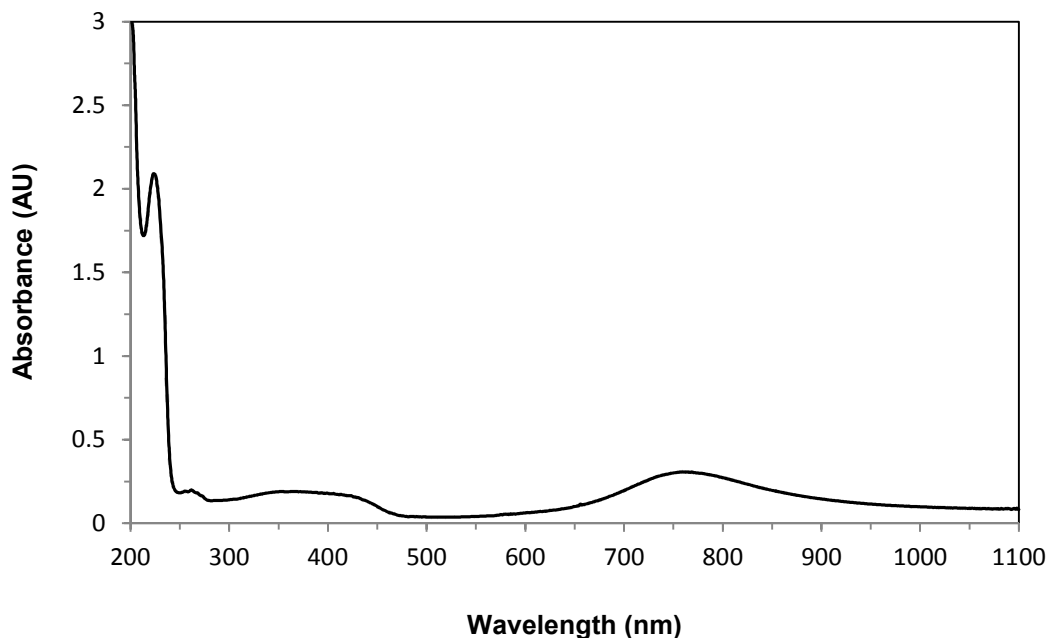


Figure 4.1 Absorbance spectra of PANi-PSSA solution.

The absorption peak at 224 nm can be assigned to the absorption peak of the benzene ring in PSSA [57]. The peak at around 310-350 nm can be ascribed to $\pi-\pi^*$ transition of the benzenoid rings. Two peaks at around 400–420 and 760 nm can be attributed to polaron- π^* and π -polaron transitions, respectively, which are related to doping level and formation of polarons. These data indicate that the polyaniline in the form of emeraldine salt (conductive form of polyaniline) is successfully attained. Ratio of absorbances at 760 and 400-420 nm can approximately indicate the doping level of polyaniline. The calculated ratio of 1.6 suggests a high doping level of PANi-PSSA [58].

4.1.2 Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) is a technique that is being used to measure light absorption of a sample in a range of frequencies. The wide infrared wavelength range is used to obtain infrared spectrum of absorption of a material.

A Mattson infrared spectrometer is used to attain basic information about the composition and structure of the fabricated films. A thin film of PANi-PSSA from solution is cast onto an IR sample card (real crystal KBr card) to obtain the FT-IR transmittance spectra of the film as shown in Figure 4.2.

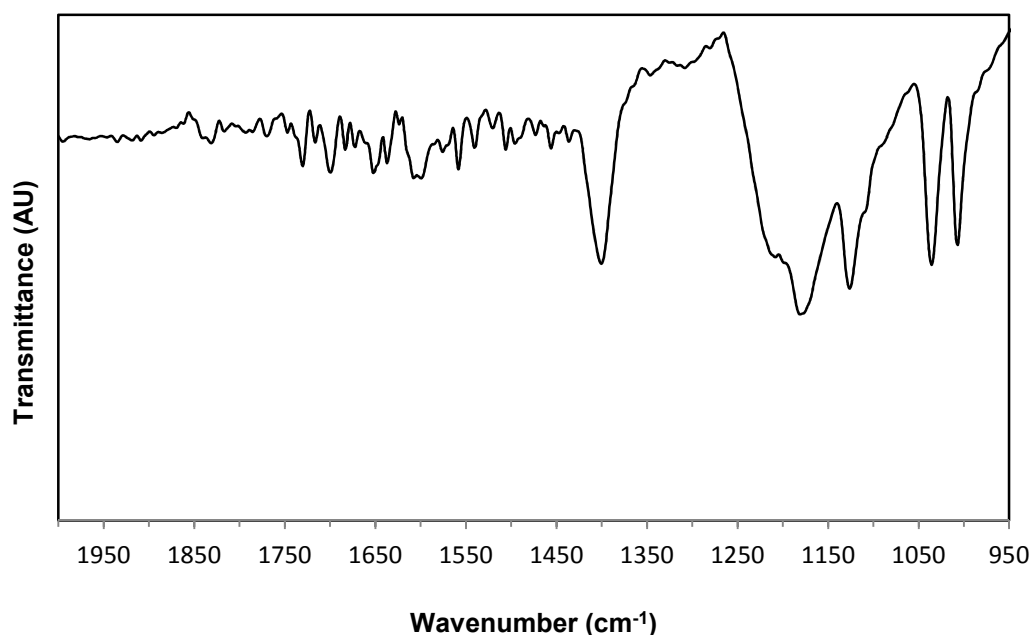


Figure 4.2 FT-IR spectra of PANi-PSSA film.

The peaks around 1560-1595 and 1487-1510 cm^{-1} correspond to the benzene and quinone ring deformation, while the weak absorption peaks at 1290-1300 cm^{-1} are due to the C=N stretching of a secondary aromatic amine. The peak at 1130 cm^{-1} is due to in-plane skeleton vibrations of the benzene ring. The two peaks at 1007 and 1036 cm^{-1} are ascribed to the vibration of sulfonic salts which shows the incorporation of styrenesulfonic acid in the PANi film [57, 59].

4.1.3 Electron Microscopy

SEM is a microscopy technique that is used to obtain information on surface topography of a sample. An image is produced by scanning the sample surface with electrons in which the electrons interact with the sample atoms. TEM is another similar microscopy technique that uses a beam of electrons which passes through a very thin sample. An image forms by the interaction of electrons with the sample while passing through the sample. TEM can give a much higher resolution image compare to SEM.

A LEO 1530VP Field Emission Scanning Electron Microscope with Oxford EDS Detector (FESEM-EDS) is used to examine the surface of the synthesized PANi-PSSA powders. Figure 4.3 shows SEM image of PANi powders in two magnifications. At lower magnification (10 μm) it can be seen the agglomeration of powders about 15 μm . A higher magnification (2 μm) shows that these clusters are composed of nanometer size particles. Breaking down the powders mechanically and investigating the surface of the powders shows more uniformity in the PANi powders which can be seen in Figure 4.4.

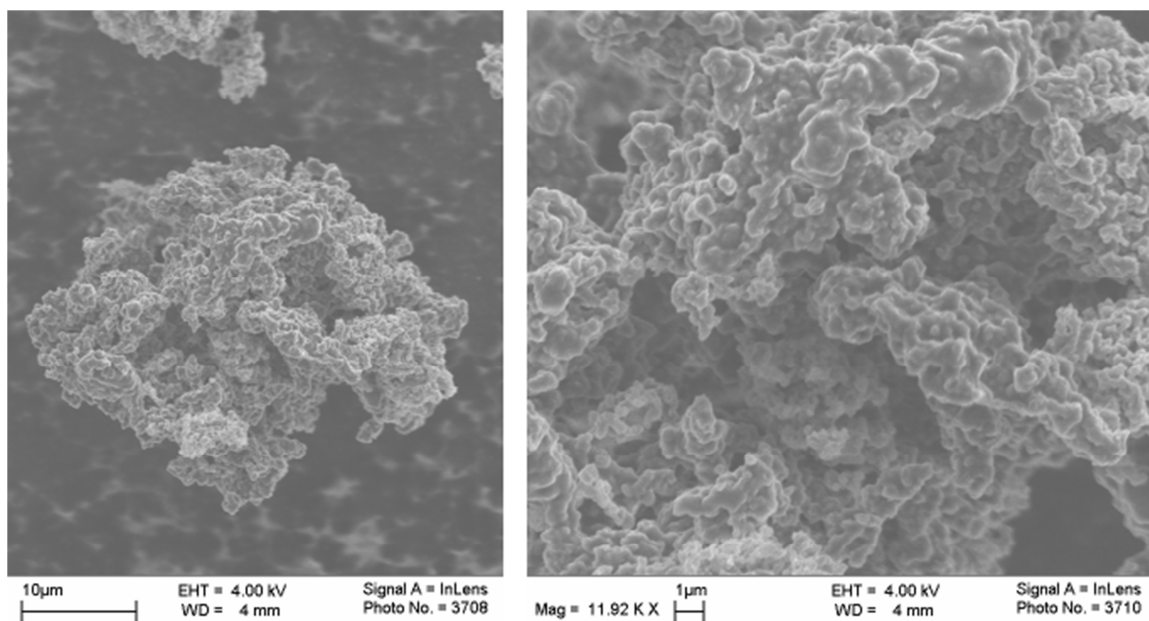


Figure 4.3 SEM image of PANi-PSSA powders in low and higher magnifications.

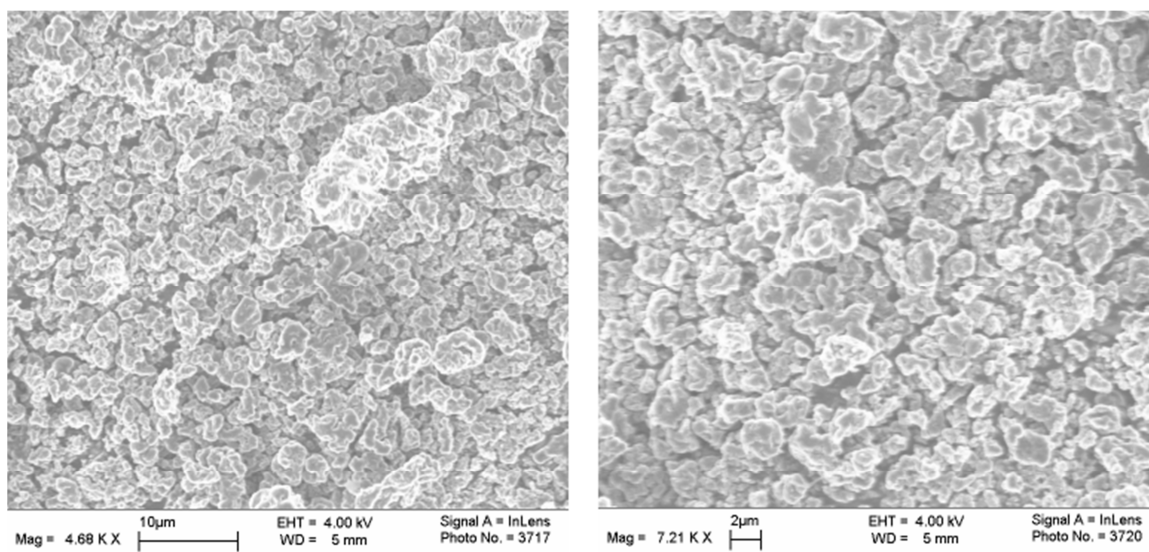


Figure 4.4 SEM micrographs of PANi-PSSA powders after mechanical breakdown.

4.1.4 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a very high resolution (on the nanometer range) type of scanning probe microscopy (SPM). A cantilever with a sharp tip is used as a mechanical probe to scan the surface of a sample in order to reconstruct an image of the specimen surface by measuring the deflection of the cantilever with laser.

A Digital Instrument Nanoscope III MultiMode Scanning Probe Microscope (SPM/AFM) is used to look at the surface of the polyaniline films. Figure 4.5 shows morphology of the fabricated thin film. It can be seen that the PANi-PSSA film is composed of nanoparticles with some fluctuations in height, that are in the range of 5-30 nm, without any distinguishable phase separation in the composite. Also, porous structure in the fabricated film, which facilitates the water molecules absorption that eventually leads to faster response to humidity, can be observed in AFM image as expected.

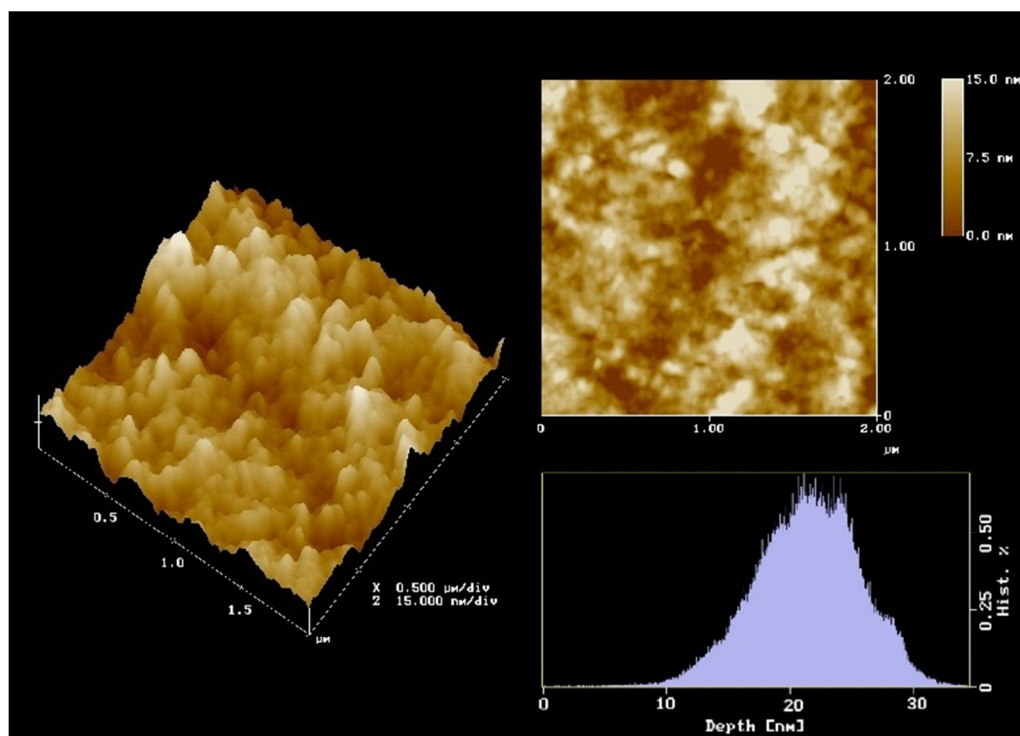


Figure 4.5 AFM image of PANi-PSSA film.

4.2 Experimental Setup

A humidity chamber with built-in humidity and temperature control system (ETS Inc. Model: 5518), capable of maintaining the humidity level from 10 %RH to 98 %RH and temperature from 0 °C to 55 °C is used to investigate the behavior of the fabricated sensors. An alternating current (AC) signal generator from Wavetek (model: 148) is used in order to power the sensors. Digital multimeters (Fluke model: 8520A) are used to record the sensor's voltage and current. An AC source is used instead of direct current (DC) source since it is observed that the sensors did not exhibit a stable resistance when probed with a DC power source. This behavior could possibly be due to some long term polarization effect due to applied direct current through the PANi film. When an alternating current is applied, any long term polarization effect is eliminated resulting in stable sensor voltage and current values for fixed humidity and temperature.

An AC circuit is built in order to test the sensors accurately. The test circuit consists of an AC power source along with a known resistor (10.8 M Ω) connected in series with the humidity sensor. Two digital multimeters are connected in parallel to the sensor and the known resistance in order to record the voltages across them. The voltage-current (V-I) curve and frequency-voltage for the sensor are shown in Figure 4.6.

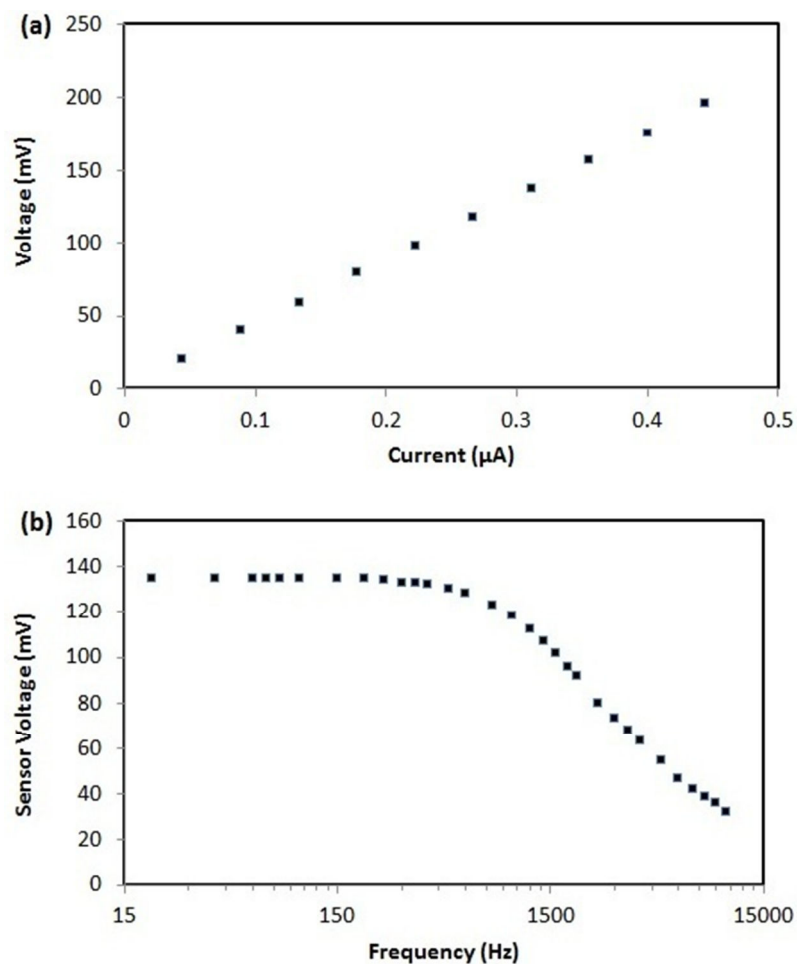


Figure 4.6 (a) V-I curve and (b) Freq.-Voltage of the humidity sensor.

Linear V-I curve proved that the sensors behave as a typical ohmic device while the frequency-voltage curve illustrates the presence of a cut-off frequency around 400 Hz. The frequency dependent response shows that the resistive sensor also exhibits a capacitance in parallel with the resistive element.

The resistance of the sensor is determined by the slope of the V-I curve of the device since $V = R \times I$. The capacitance of the sensor could then easily be estimated by using $f_{\text{cut-off}} = 1 / (2\pi RC)$ in which $f_{\text{cut-off}}$ is the cut-off frequency and R and C are the resistance and capacitance of the sensor, respectively. As an example the capacitance of a sensor with resistance of 470 K Ω will be 0.85 nF.

4.3 Results and Discussion

The known series resistor and resistive humidity sensor are connected in series in the circuit. The known resistor is chosen to be much higher than the sensor resistance so that the current in the circuit would be nearly constant as the resistance of the sensor varied with humidity and temperature. The known resistor is approximately 20 times the sensor's resistance at room temperature while the peak voltage from the AC signals generator is 5 V. The current (I) through the circuit is determined by measuring the potential difference (V) across the known resistor and using Ohm's law $I = V / R$ in which R is the resistance of the known resistor. The resistance of the sensor could then easily be determined by Ohm's law using the current in the circuit and measured voltage across the sensor. As an example when the humidity changes from 67.5 %RH to 29.1 %RH the corresponding voltage change of a sensor is 1.3 mV to 20 mV, corresponding to a sensor resistance change of 4 K Ω to 83 K Ω .

4.3.1 Humidity Response of the Sensors

Fabricated humidity sensors show a linear response over broad range of humidity from 13 %RH to 88 %RH. The humidity response of the sensors over this range is linear with R-squared correlation value of 0.99. The sensors then are tested under a humidification and dehumidification process in order to assess the hysteresis of the sensors. Sensors show a small hysteresis from 0.3-0.5 %. A typical response of the sensor to humidity and its hysteresis is shown in Figure 4.7.

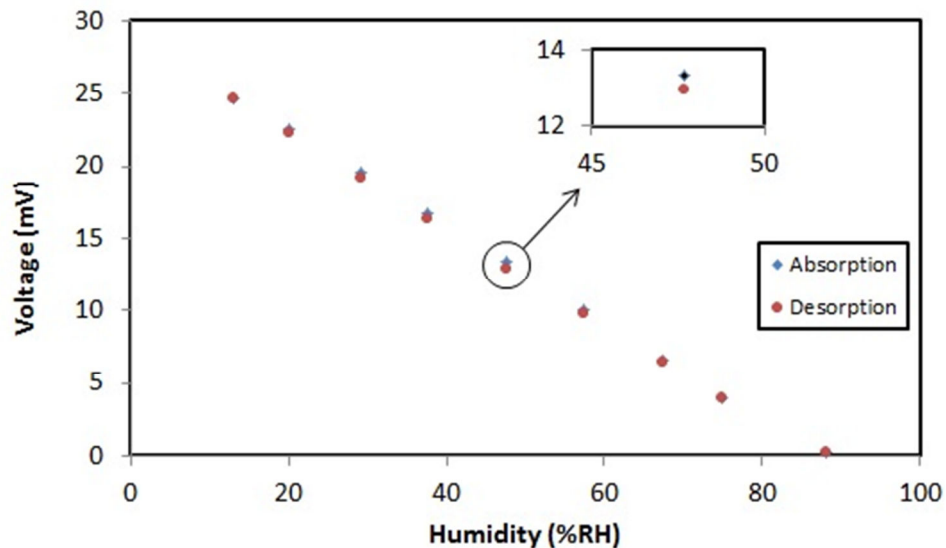


Figure 4.7 Humidity response and hysteresis of the sensors.

For the purpose of determining the sensors stability over time, sensors are held at different humidity levels from 25 %RH to 80 %RH for 48 hours to observe any changes in response after exposure. Sensors show about 1% change in output voltage after exposing to high humidity for 48 hours. Figure 4.8 shows the stability of the sensors before and after they are exposed to different levels of humidity for a long period of time.

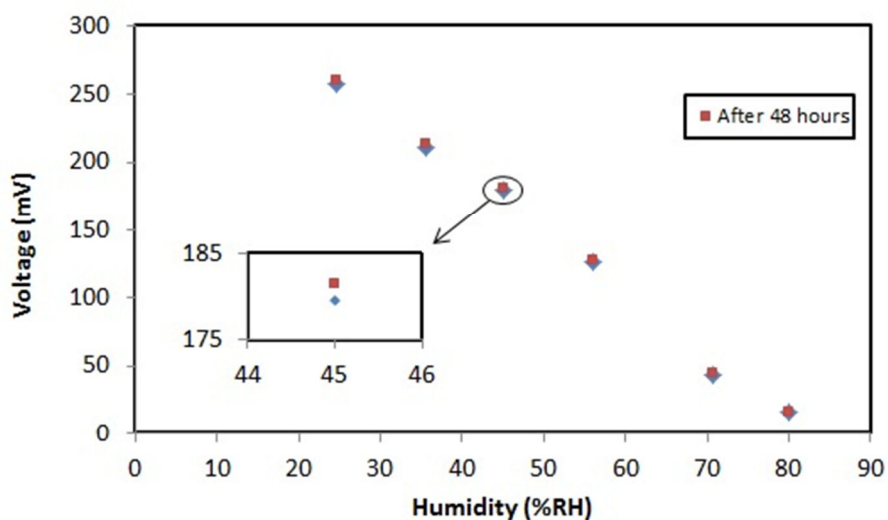


Figure 4.8 Stability of the sensors after exposure to high humidity (70-80 %RH).

4.3.2 Effects of Harsh Environments on Humidity Sensors

A common difficulty with PANi sensors is that the presence of chemicals and solvents normally can damage the PANi sensing material. The presence of an acid will change the chemical structure of PANI resulting in a different oxidation state and permanently change the resistivity of the material. If neither acidic nor alkaline chemicals such as ethanol are present, the oxygenation state of PANi is not permanently altered, but the resistance of the PANi will vary in proportion to the concentration of the ethanol. Essentially, PANi by itself does not exhibit specificity to the presence of humidity. Therefore one must deposit a protective coating on top of the PANi sensing layer to (a) protect the PANi from chemicals which may permanently alter the oxidation state of the material and (b) permit the transmission of only water vapor so that the PANi detection is selective.

In the sensor design, the EVOH coating on top of the humidity sensor blocks chemicals and solvents which normally damage the PANi sensing material, and yet allows water vapor to permeate through for humidity sensing purposes. A few solvents are tested on the capped humidity sensors to determine if they have any effect on the sensors. Methanol, methylene chloride, methyl ethyl ketone and toluene are some of the solvents that are tested on the sensors. The method of testing is to simply put drops of different solvents at room temperature for 24-48 hours on different parts of the EVOH film on top of the sensor and monitor the resistance of the sensor during this process. The results are compared to sensors with no coating covered the sensors. None of the solvents mentioned above have any effect on resistance of the sensor when they are applied to the EVOH coating films. The effect of methanol, methylene chloride and acetic acid in gas

phase on the sensors is tested as well with no effect on the sensors. Depending on thickness of the EVOH films, some of the solvents can have an effect on the sensors. Acetic acid and some of the other solvents in liquid phase can easily dissolve the coating films less than 1 μm and change the sensor resistance permanently. The thickness of the film that is used in this paper is from 11-12 μm in order to protect the sensors from solvents in both liquid and gas phases. By increasing the thickness of the EVOH layer to 11-12 μm the effect of solvents in liquid form on thicker coats of EVOH is reduced and the effect of same solvents in gas phase is eliminated completely.

4.3.3 Effects of Temperature on Humidity Sensors

Polyaniline films are too sensitive to temperature and temperatures above 40 $^{\circ}\text{C}$ can damage the humidity sensors permanently. The effect of temperature on conductive polymeric materials has been investigated and well-described in literatures. At high temperatures, charge carriers scatter due to increase in occupation of phonon modes which results in decrease of the charge carrier mobility as well as slower polaron-band conduction. Carrier concentration can also be reduced due to trapping of charges into states that lie in the band gap which eventually lead to lower charge carrier effective mobility.

Response of the fabricated humidity sensors are monitored from room temperature (around 26 $^{\circ}\text{C}$) up to 40 $^{\circ}\text{C}$ at a fixed humidity and a permanent change in resistance of about 0.05%/ $^{\circ}\text{C}$ is observed. Due to temperature sensitivity of the sensors, all the measurements are carried out at a fixed temperature (room condition).

4.3.4 Humidity Sensor Response Time

In order to determine the response time of the sensors for absorption response, humidity level inside the test chamber is brought from 18%RH to 95%RH. Sensors, which are kept at 18%RH, are exposed to the higher humidity level (95%RH) instantly and the response of the sensors is recorded. The reverse process is performed by exposing the sensors which are initially maintained at higher humidity level (95%RH) to a sudden decrease in humidity level (18%RH) in order to determine the response time for desorption process. The time at which the sensors reached the 90% of their final value ($t_{90\%}$) is stated as response time of the sensors. Sensors both with and without protective coating are tested for response time as explained above in order to compare the difference in response times between coated and un-coated sensors. The time response of the sensors with and without coating is shown in Figure 4.9. The response time for the sensors without EVOH coating on top is around 5 seconds and 15 seconds for absorption and desorption, respectively and the response time for the sensors with coating is about 40 seconds for absorption process and 110 seconds for desorption.

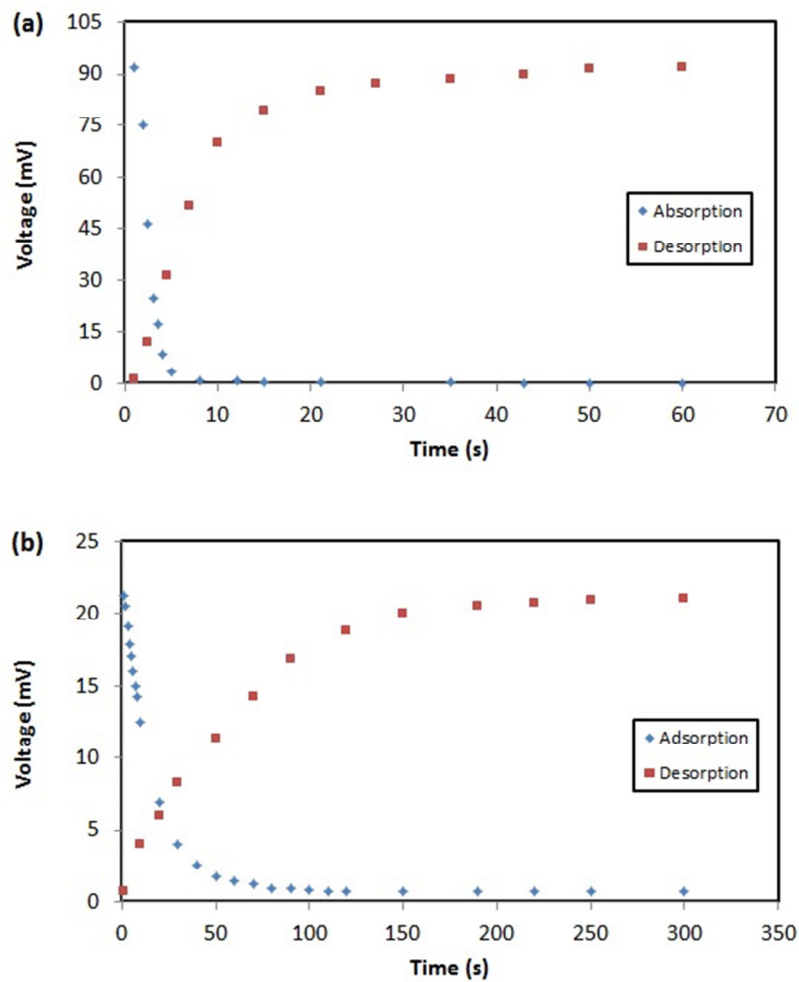


Figure 4.9 Response time of humidity sensors (a) without and (b) with protective coating.

CHAPTER 5

CONCLUSION AND FUTURE WORK

5.1 Conclusion

A resistive-type humidity sensor for harsh environments is successfully designed and fabricated by inkjet printing method on a flexible substrate. A double strand water-soluble PANIPSSA ink is synthesized and the ink is prepared and modified for inkjet printing purposes. An ink from a copolymer of ethylene and vinyl alcohol is prepared for sensor protection against harsh environments. Fabricated sensors show linear response over broad range of humidity (15-90 %RH) with good sensitivity, small hysteresis and fast response. Sensors show great resistivity to solvents and other chemicals which normally damage the PANi.

5.2 Future Work

The purpose of this project is to design and fabricate a resistive-type and flexible humidity sensor for harsh environments. Some suggestions for further research with reference to this dissertation are presented below. The goal is to provoke researches to continue to develop advance flexible thin films not only for sensor application but for other uses such as in display and energy harvesting technologies.

Fabricated sensors in this study are based on polymers that are too sensitive to temperature. Further investigation into proposing other materials especially ceramic and ceramic composites with polymers that can be flexible in order to reduce or eliminate the temperature sensitivity would be innovative.

The proposed material in this dissertation shows that some polarizations take place by using a direct current through the material. Isolating the source of polarization by change the fabrication method, fabrication condition or development of other conductive materials for flexible electronics and sensors that are insensitive to direct current would be novel. Also, development of other inks especially composite inks to improve the sensor performance in terms of linearity and response time can be done in the future.

Lastly, further parameter modifications of material printers can improve the overall performance of printing systems which lead to increase in inkjet printers' utilization as an alternate method for device fabrication.

APPENDIX A

INK FORMULATION FOR INKJET PRINTING AND SPIN COATING

All inks, solutions and materials have to be at room temperature before reformulation to eliminate condensation in the source.

PANi-PSSA Ink Formulation

Powder synthesis:

1. Place a 50 ml flat bottom vial on a digital scale and tare the scale.
2. With a new syringe remove 12.5 gr of Poly(4-styrenesulfonic acid), PSSA, solution (18 wt.% in water solution) and dilute it with 20 ml of DI-water. (This will give 2.25 gr of pure PSSA)
3. With a new syringe remove 0.2 ml of aniline monomer and it add to the solution.
4. Introduce a new magnetic spin rod into the ink vial, cap, and stir at 300-500 rpm at room temperature for 1 hour. (The ink should be stirring level flat with the magnetic stirrer lying in the ink. The stirrer should not be violently rotating if the stirrer is lower the sped or move the beaker to a different spot on the hotplate)
5. Prepare a 0.05 gr/ml Ammonium persulfate (APS) solution in DI-water and remove 10 ml of the prepared solution and add it to the vial and stir for 5 min.
6. Leave the vial at room conditions for at least 12 hours in order for the polymerization to take place.
7. Precipitate the resulting products in large amount of Acetone (25 ml of Acetone for every 5 ml of the results from step 6) and wash with Acetone for 1 to 2 times in order to get Polyaniline-Poly(4-styrenesulfonic acid), PANI-PSSA, in the form of powder.
8. Collect the powders from the mixture by filtering the mixture of the powder/Acetone.
9. Vacuum dry the collected powders for 12-48 hours. (Depending on the amount of powders that are being dried)
10. The results will be dark green PANI-PSSA powders with the molar ratio of 6:1 (PSSA:Aniline).

Ink preparation:

1. Weigh 0.3 grams of PANI-PSSA powders and place it in a 25 ml vial.
2. With a new syringe add 10 grams of DI-water to the vial (this will give 3 wt.% PANI-PSSA ink)
3. Shake the vial for 10-30 seconds by hand and ultrasonicate the solution for at least 15 minutes.
4. Use a new syringe to remove the approximately 1.5 ml ink from the vial and dispense into the Dimatix print cartridge.

Purchasing information:

Aniline – ACS reagent, >99.5%

Part number: 242284

Company: Sigma-Aldrich

Phone: 800-325-3010

Fax: 800-325-5052

Poly(4-styrenesulfonic acid) solution – Mw ~ 75,000, 18 wt. % in H₂O

Part number: 561223

Company: Sigma-Aldrich

Phone: 800-325-3010

Fax: 800-325-5052

Ammonium persulfate – ACS reagent, >98.0%

Part number: 248614

Company: Sigma-Aldrich

Phone: 800-325-3010

Fax: 800-325-5052

Silver (Ag) Ink Formulation

Silver inks will be used as received and no additional modifications are needed for ink jet printing purposes.

1. Shake the original silver ink bottle by hand for 10-20 seconds.
2. Use a new syringe to remove the approximately 1.5 ml ink from the bottle and dispense into the Dimatix print cartridge.

Purchasing information:

Silver Ink

Part number: U5714 (40 wt. % content), U5603 (20 wt. % content)

Company: Sun Chemical Corporation

35 Waterview Boulevard

Parsippany, NJ 07054-1285

Tel: 973 404 6000

Fax: 973 404 6001

EVAL™ Ink Formulation for Spin Coating and Casting

1. Mix EVAL™ pellets with n-PrOH and DI-water in a 25 ml vial with the following ratios at room temperature:
 - a. EVAL™ pellets: 5 wt.%
 - b. n-PrOH: 61.75 wt.%
 - c. DI-Water: 33.25 wt.%
2. Place a magnetic spin bar into the vial
3. Make a water bath at 60 °C on top of a hotplate with stirring capability.
4. Place the vial in the water bath and raise the temperature of the bath to the water boiling point gradually with stirring the solution at 300-500 rpm.
5. Keep stirring the solution at boiling temperature of the bath for about 3 hours or until the pellets dissolved completely.
6. Remove the vial from the water bath and leave it at room condition to stabilize.

EVAL™ Ink Formulation for Inkjet Printing

1. Mix EVAL™ pellets with n-PrOH and DI-water in a 25 ml vial with the following ratios at room temperature:
 - a. EVAL™ pellets: 3 wt.%
 - b. n-PrOH: 63.05 wt.%
 - c. DI-Water: 33.95 wt.%
2. Place a magnetic spin bar into the vial
3. Make a water bath at 60 °C on top of a hotplate with stirring capability.
4. Place the vial in the water bath and raise the temperature of the bath to the water boiling point gradually with stirring the solution at 300-500 rpm.

5. Keep stirring the solution at boiling temperature of the bath for about 3 hours or until the pellets dissolved completely.
6. Remove the vial from the water bath and leave it at room condition to stabilize.
7. Use a new syringe to remove approximately 1.5 ml ink from the vial and dispense into Dimatix print cartridge.

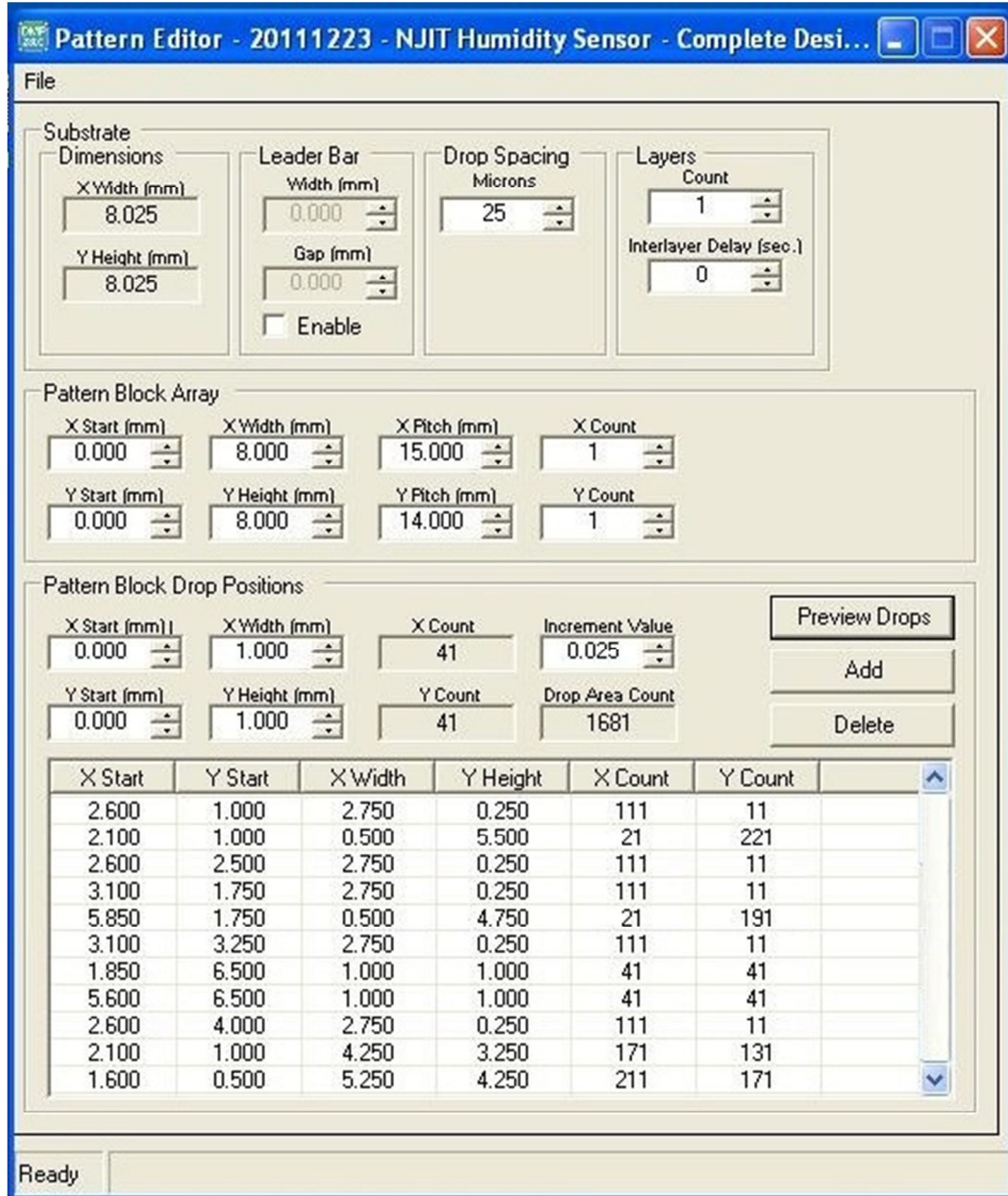
Purchasing information:

EVAL™ Pellets
Type: F101B
Company: Kuraray America, Inc.
EVAL™ Business Unit
2625 Bay Area Blvd., Suite 300
Houston, TX 77058
Tel: (800) 423-9762
Fax: (281) 204-4622
www.evalca.com

APPENDIX B

FUJIFILM DIMATIX (DMP-2800 SERIES) MATERIAL PRINTER SETTINGS

Figures B.1 to B.6 show printer settings for inkjet printing humidity sensor.



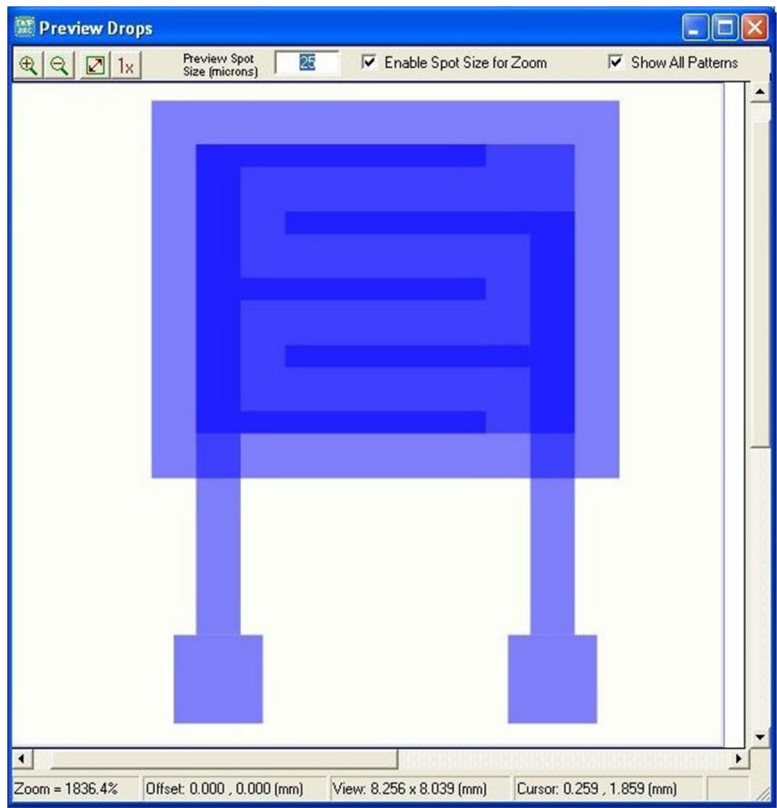


Figure B.1 Complete design of humidity sensor (electrode, sensing and coating material).

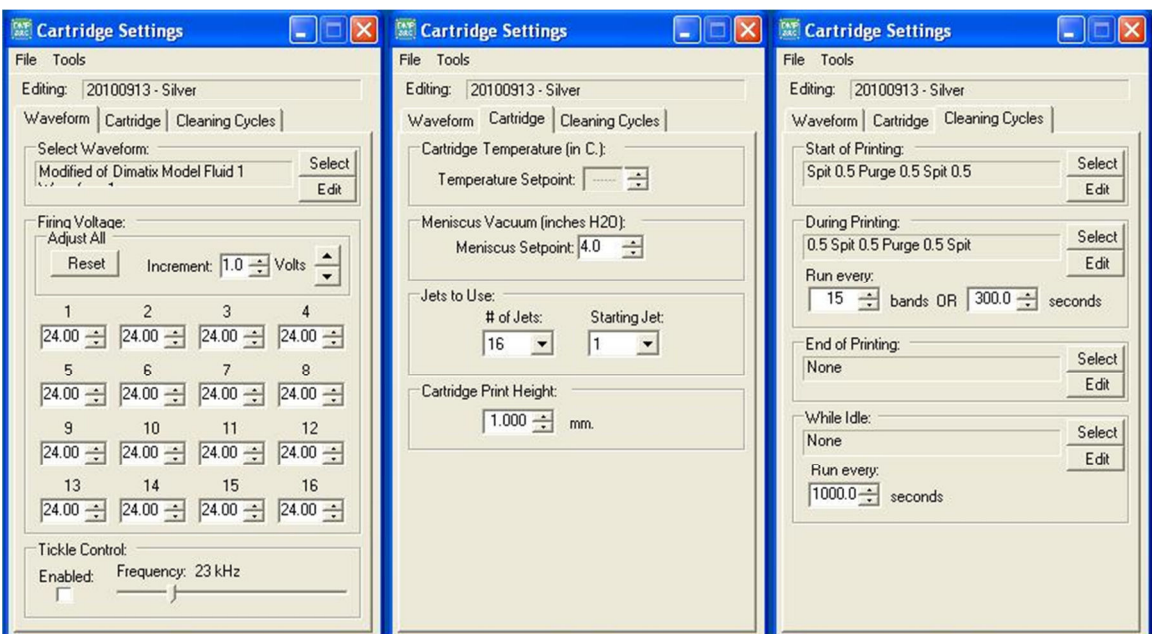


Figure B.2 Cartridge settings for inkjet printing silver electrode.

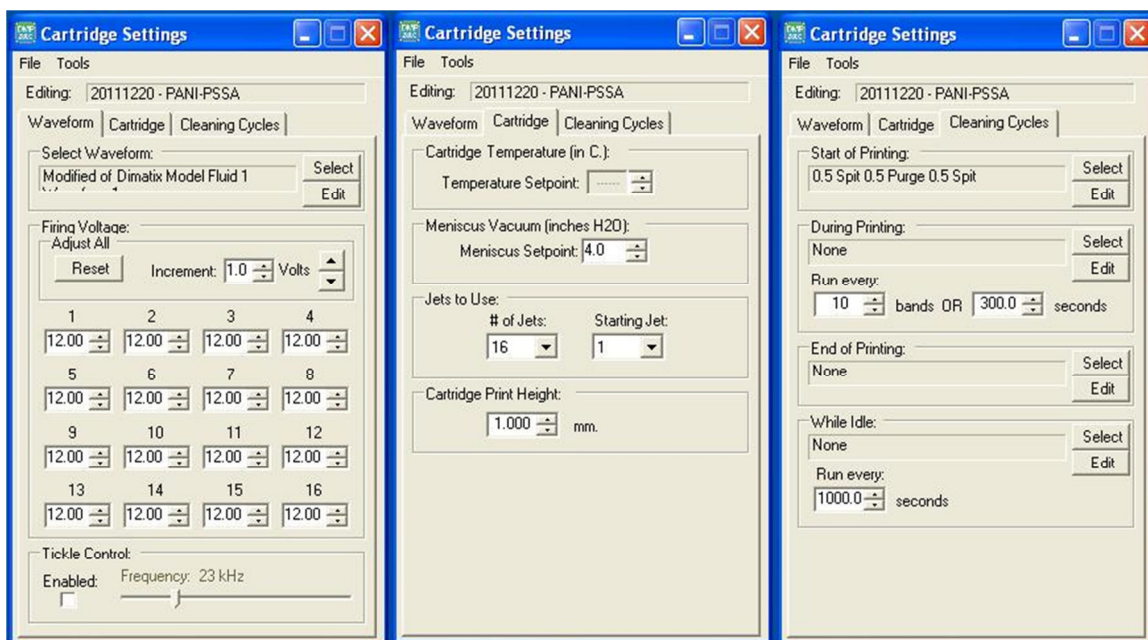


Figure B.3 Cartridge settings for inkjet printing PANi-PSSA.

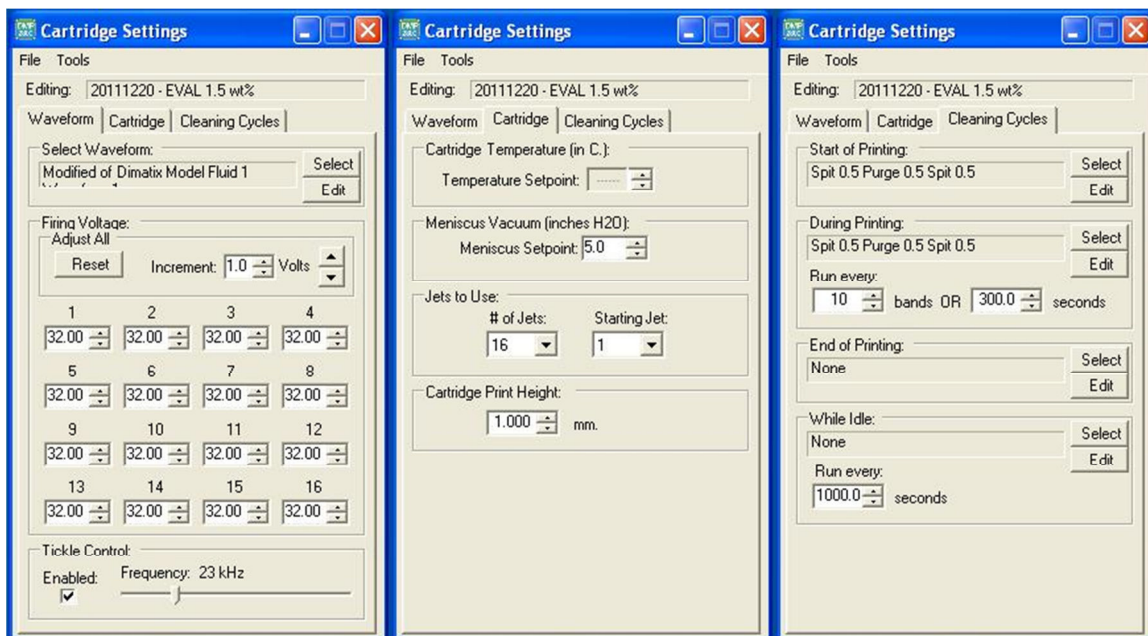


Figure B.4 Cartridge settings for inkjet printing EVAL™ protective coating.

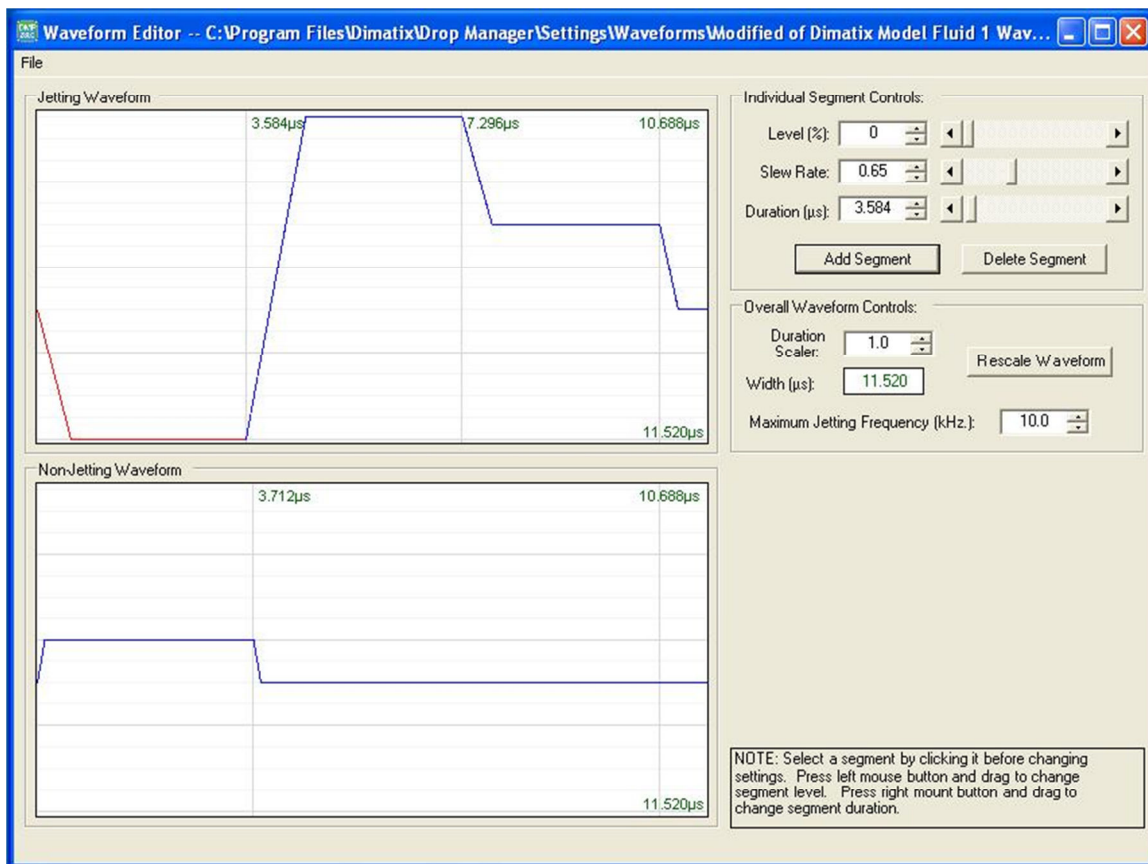


Figure B.5 Waveform settings.

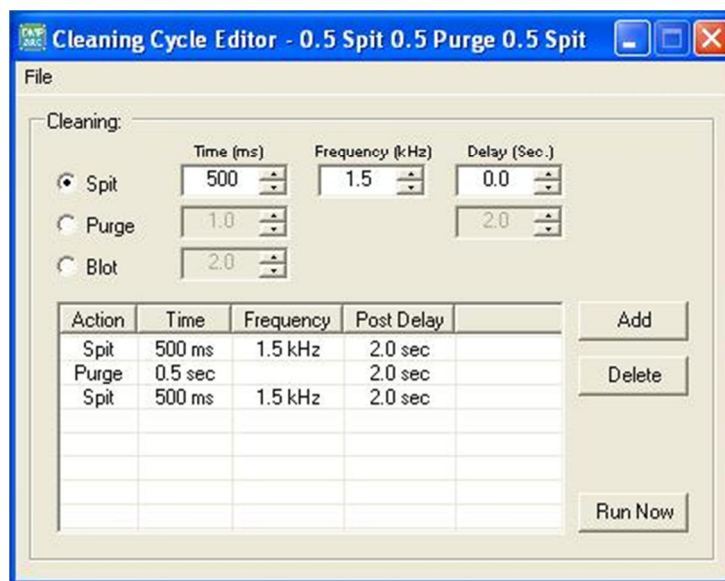


Figure B.6 Cleaning cycle setting.

APPENDIX C

HUMIDITY SENSOR FABRICATION METHOD

All inks and materials have to be at room temperature before reformulation to eliminate condensation in the source.

Silver (electrode) deposition:

Silver (Ag) Ink Formulation (from Appendix A)

Number of layers: 1 layer

Waveform (from Appendix B)

Cartridge settings for inkjet printing silver electrode (from Appendix B)

Platen temp: lab condition

Cleaning cycle: Cleaning cycle setting (from Appendix B)

Curing: 150-200 °C for 1-3 minutes

PANi-PSSA (sensing Material) deposition:

PANi-PSSA Ink Formulation (from Appendix A)

Number of layers: 30 layers

Waveform (from Appendix B)

Cartridge settings for inkjet printing PANi-PSSA (from Appendix B)

Platen temp: lab condition

Cleaning cycle: Cleaning cycle setting (from Appendix B)

Curing: Vacuum dry for 3-5 hours

EVAL™ (coating material) deposition (Inkjet Printing):

EVAL™ Ink Formulation for Inkjet Printing (from Appendix A)

Number of layers: 60 layers and higher (depending on thickness requirements)

Waveform (from Appendix B)

Cartridge settings for inkjet printing EVAL™ protective coating (from Appendix B)

Platen temp: lab condition

Cleaning cycle: Cleaning cycle setting (from Appendix B)

Curing: Vacuum dry for 3-5 hours

EVAL™ (coating material) deposition (Spin Coating):

Inks Formulation/EVAL™ Ink Formulation.doc

40-50 rpm for 5-10 seconds (in order to spread the ink on top of the sensor)

2000-5000 rpm (depending on thickness requirements) for 30-60 seconds

Curing: Vacuum dry for 3-5 hours

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