TAMPERE UNIVERSITY OF TECHNOLOGY

TANVIR AHMED

DEPOSITION OF GALLIUM BASED LIQUID METAL ALLOY ON PLASMA TREATED PDMS SUBSTRATE FOR BIOMEDICAL AND RF APPLICATIONS

Master of Science Thesis

Examiners:
Prof. Donald Lupo
Assoc. Prof. Doc. Matti Mäntysalo
Examiners and topic approved by the Computing and Electrical engineering faculty council on January 21, 2016

ABSTRACT

TANVIR AHMED: Deposition of Gallium based liquid metal alloy on plasma treated PDMS substrate for biomedical and RF applications.
Tampere University of Technology
Master of Science thesis, 53 pages, 6 Appendix pages
October 2016
Master of Science (Technology) in Electrical Engineering
Major: Electronics
Examiners: Prof. Donald Lupo, Assoc. Prof. Doc. Matti Mäntysalo
Keywords: Stretchable Electronics, Microfluidic approach, Galinstan, PDMS, Plasma treatment, Oxidation process.

Printed stretchable Electronics has appeared into the Electronics manufacturing industry only within last few decades. It has provided a new era in electronics especially; medical technology has been enriched with various electronic circuits consisting of conductors with other active and passive components such as transistors, resistors, capacitors etc. printed on top of flexible substrate. This new technique has replaced the traditional manufacturing process through introduction of more efficient and simpler methods. Microfluidic approach is the process, where very highly conductive liquid alloy based electronic components are placed inside flexible encapsulated platforms. In this method low impedance in large areal electronics can be achieved through combining rigid active components into the same area.

This research focuses mainly on the introduction of a new approach using Gallium (Ga) – Indium (In) – based liquid metal alloy. There are a few similar types of previous research works were studied and a less complicated method with fewer processing steps was investigated during this work. Galinstan was used here as the liquid metal alloy, it has very high conductivity and the ability to maintain its performance in mechanical stretch. The characteristics of Galinstan were analyzed by depositing it on top of PDMS substrate. Plasma treatment process is one of the main features of this research. It was used to complete the fabrication method with fewer steps. Different image patterns were mounted on the PDMS surface through the plasma activation. Effect of air plasma and nitrogen plasma on PDMS was analyzed for different patterns. Rapid oxidation of the Galinstan was observed and upon observation it was proved to limit the applicability of the proposed approach unless oxygen can be excluded from the process. Different HCl treatment seemed to be the most effective ways to solve this problem. Other Possible solutions with proper encapsulation processes to remove the oxidized layer were also introduced in this work.

PREFACE

The work for this master’s thesis was performed in the Organic and Nano Electronics group in the Department of Electronics and Communications Engineering at Tampere university of Technology. Originally, the research work was done during the spring and summer of 2016.

I wish to express my gratefulness to my Supervisor, Professor Donald Lupo for his support and guidance throughout this work and I want to thank my colleagues at Tampere University of technology. I also wish to show my gratitude to Associate prof. Matti Mäntysalo for his valuable advice in this work.

I would like to thank Mika-Matti Laurila, M.Sc for his guidance in using Plasma print station. I am also thankful to Miao Li, M.Sc., Arash Nassajy M.Sc. and Dr. Thomas kraft for their valuable comments and suggestions.

I am grateful to the Almighty for everything that I have achieved in my life. Special thanks go to my parents for guiding me through the walk of my life. Finally, I would like to thank Natasha for her love and support.

Tampere, September, 2016

Tanvir Ahmed

CONTENTS

List of Symbols and Abbreviations

3D	Three-dimensional
AF	Amorphous fluoroplastics
Au	Gold
CCD	Charge Coupled Device
Co	Cobalt
Cr	Chromium
EGaIn	Gallium Indium Eutectic
FC	Fluorocarbon
Fe	Iron
Ga	Gallium
GND	Ground
h	Height
HCl	Hydrochloric Acid
HV	High voltage
IC	Integrated Circuit
In	Indium
IP	Internet protocol
l	Lenght
LAN	Local Area Network

LED	Light-Emitting Diode
P	Line Spacing
PAA	Poly Acrylic Acid
PCB	Printed Circuit Board
PDMS	Polydimethylsiloxane
PE	Polyethylene
PNG	Portable Network Graphics
PTFE	Polytetrafluoroethylene
Q	Flow rate
RF	Radio Frequency
Sn	Tin
V	Writing speed
VDC	VoltageDC
W	Width

Chapter 1

Introduction

Flexible electronics has flourished in new medical technology by introducing modern electronic systems attached to skin or different part of organs. The main applications of these devices are in wireless sensing and communication. [1] The wide research areas of the flexible electronics is providing new information about this technology and enriching the integrated circuit technology on thin film applications. It has become more popular by providing good user experience in bio medical applications.

The idea of flexible electronics was introduced by Dr. Ken Gilleo Ph.D. In early 1900s, industrial electronic technologist Thomas Edison provided the method for manufacturing conductors on linen paper. In 1947, "Printed Circuit Techniques" published by Cledo Brunetti and Roger W. Curtis provided the information about fabricating circuits on flexible materials which latterly implemented by Victor Dahlgren and the sanders company founder Royden Sander in 1950s. [2] They have shown very significant breakthrough by developing printed conductors on flexible materials.

In modern day, stretchable electronic circuit technology has mainly developed through the determined attempt of Japanese electronics packaging engineers.[2] It has become top interest for the electronic research field by including active and passive functions in the integration process.[3] Still, the flexible electronic systems have few limitations in their IC(Integrated Circuit) implementing. The main concerns are the cost and higher impedance in large scale fabrication. In this case, printed circuit technology can solve the limitations of this technology by assembling printed circuits with rigid active materials. [4]

1.1 Scope and objective of the thesis

In this work, one simpler way is introduced on a PDMS platform by using the plasma treatment method. One recent study was found similar to this work where tape transfer technique was used to deposit Galinstan (Gallium based liquid metal alloy) on top of stretchable substrate. However, the pattern transferring technique made the method complex and less efficient. [5] To overcome these difficult steps plasma treatment method is used for patterning the expected images on PDMS substrate. The plasma activation process is a new technology through which patterns can be mounted on substrate through high voltage generation. [6] After providing the effective plasma to the substrate, high conductive Galinstan is blade coated on top of it.

The effect of plasma is one of the main features of this thesis work. The main objective of the thesis was to introduce a simpler path in patterning different images through modification of PDMS surface energy. It is done by applying the plasma treatment process on top of PDMS. Several types of pattern are made to observe any difference in plasma activation process. The time gap between plasma treatment and Galinstan deposition is kept very low to provide more effective plasma. Both the nitrogen and oxygen plasma is applied on stretchable platforms and the stability of plasma power is observed during the plasma activation process through the change of plasma power generation. Also, contact angle of Galinstan droplet is measured for analyzing the wetting behavior. The process has the ability to make huge impact in changing the wetting behavior of Gallium based liquid metal alloy.

By combining plasma treatment processes, higher cost and time consuming steps are replaced and a new fabrication method for microfluidic stretchable electronic device is introduced in this work. This type of technique is very feasible and quick patterning technique. Use of plasma print stations can be a new step towards a new fast prototyping technique for stretchable electronics manufacturing. In this work a simple one-step process is introduced using Gallium based liquid metal alloy. At the same time, some limitations of this process are explained briefly after depositing the Galinstan on plasma treated PDMS substrate.

1.2 Structure of the thesis –

The thesis consists of five chapters. Chapter 1 provides a short introduction to stretchable electronics and the main objectives of the thesis. Chapter 2 describes the theoretical background of the thesis. It also shows the advantages of this new patterning technique over the available methods for plasma deposition. Chapter 3 discusses the experimental setup for Galinstan deposition and plasma treatment process. This chapter provides detailed information about materials and the plasma print station that was used in this process. Chapter 4 shows the results found from Galinstan deposition on plasma treated PDMS. Few limitations and possible approaches to overcome the problems of this method are also explained briefly in the same chapter. The final chapter summarizes the most important outcomes of the entire thesis work. There are a few other results found from liquid alloy deposition on PDMS are appended to the end of the thesis.

Chapter 2

Stretchable electronics

Stretchable electronics are based on the materials which can be utilized to fabricate wearable microcomputers, well scale displays, biomedical devices and other systems which are not easily achievable with traditional wafer based technologies. These devices can be implemented on human skin and other soft bases of organs. [7] By utilizing these characteristics, different methods have broadly analyzed in the recent years to improve an efficient system with a self-powered energy source. [8] To make highly stretchable small impedence RF electronic devices with large cross section areas, liquid alloy based microfluidic stretchable electronic system provides identical platforms to put together different sensors on human skin surface or other organs. [9] This printed electronics technology has provided user friendly approach to communicate with the external world remotely with excellent stability during higher stretch within attached active electronic components. [10]

Microfluidic technique is one of the most popular sections of modern electronic research fields.[1] In this approach different liquid metal alloy which has very high conductivity is placed on top of stretchable PDMS substrate and rigid active electronic materials are assembled with the other components through encapsulating PDMS layer on the whole integrated system. Also, these types of alloys have the ability to provide the higher stability during mechanical stress. [11]

Introduction of highly conductive liquids has given the opportunity to fabricate the soft electronic materials from liquids. [12] Targeted thickness and resistant conductors are also achievable from these stretchable electronic materials. The interest on this particular alloy has already developed a few interesting devices and applications. [12] Although, most of them had the limitations in large areal processing, parallel processing and cost effectiveness. [13]

2.1 Gallium based liquid metal alloy in stretchable electronics –

Several previous studies were found on liquid metal alloy. The main concentration of this type of printing technology provides direct printing techniques. Among them, dispensing, 3D-printing, ball point writing and micro contact printing etc. are very recent topics. Molding of liquid alloys, laser printing system also includes for soft electronics device manufacturing process. [14] That said, these techniques have many restrictions that result in higher costs and a less effective system. In very recent times, similar kinds of work were done using the same liquid metal alloy. It was observed on a semi cured PDMS. This work though, has shown many demerits on stencil mask transferring. [5] Several studies were carried out to develop a less complex method for this particular type of printing technology. Most of them were too difficult to implement due to their increasing number of steps.

Generally, in the case of stretchable electronics, liquid alloy based stretchable electronic components are deposited into flexible polymer substrate and then other active electronic components are integrated with them. Here, Gallium (Ga) Indium (In) based very highly conductive liquid metal alloy is deposited on to PDMS substrate. The Gallium (Ga) Indium (In) based liquid metal alloy, Galinstan (Geratherm Medical AG, Geschwenda, Germany) is used in this work. It is the composition of Gallium (Ga), Indium (In), Tin (Sn). Galinstan is a eutectic metal. [15] In liquid state, the Galinstan (68.5% Ga, 21.5% In, 10% Sn) is a nontoxic low viscosity material. [5] It can be produced in very easily. Gallium, Indium, and Tin are melted and mixed together according to the appropriate ratio to produce this liquid alloy. It shows very high electrical conductivity ($3.46*10^6$ S/m at 20°C) and it is able to maintain its original form in minus temperatures. It is non-toxic and has a very low vapor pressure. [16] In some cases it can be used as the ideal replacement for mercury. [15]

Figure 1. *Galinstan.* [15]

Micro channels provided by attaching Galinstan with stretchable platforms are highly stretchable and they can maintain their stability under mechanical stress. It has a very low melting temperature which means it can remain in its liquid state when the temperature is below room temperature. [17] PDMS is treated before alloy deposition according to different pattern sizes.

The prime work of this thesis is focused on developing a less complicated patterning technique for stretchable printed circuits using liquid metal alloy printing process. Significant inspiration came after analyzing research work done by Jeong, Seung Hee, Klas Hjort, and Zhigang Wu recently. [5] This particular work involved a tape transferring technique to improve the printing method with a different way of masking. By forming molds in usual soft lithography, this prototyping technique has made a more advantageous method over the time destructive photolithography method. In this method, shadow mask was designed using vinyl tape on a wax coated paper liner by cutting plotter. [5] Transfer tape was used to transfer it to PDMS. The liquid alloy (Galinstan) is patterned through the atomization of alloy and putting it in a nitrogen gas chamber. [5] The alloy is then sprayed into semi cured PDMS substrate through manual art airbrush. After that, different active components were mounted followed by encapsulation with another layer of PDMS. Finally, Designed mask was removed manually from PDMS to get liquid alloy pattern. [5] Figure below shows the process steps in brief.

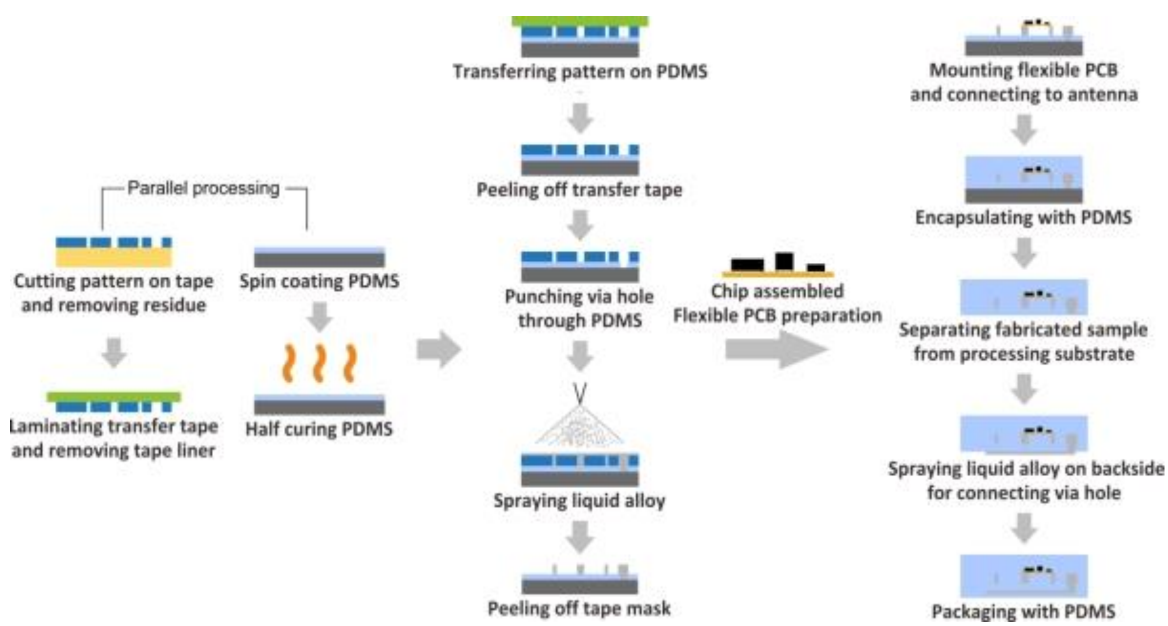


Figure 2*. Tape transfer fabrication process of the integrated stretchable electronic device use.* [5]

A Stretchable liquid alloy coil was created from this work which demonstrates mechanical stability up to 50% strain. When hybrid integrated circuit was included in localized stiff cell the stretchability was decreased to 25%. 10% Power efficiency was found from this liquid alloy coil. 0.47 W power was received by this coil at 140 KHz for 4.6 W transmitted power.

There are several limitations and some complicated steps involved with this tape transfer technique. Especially, Steps that are involved in transferring pattern on PDMS, spraying liquid alloy (twice in this process) and the method of mounting flexible PCB has made the process more complex and time consuming.

This thesis work was done to introduce a new method to fabricate stretchable electronic circuit printing processes in fewer steps using liquid metal alloy. Prime concentration was given to ease the liquid alloy patterning and plasma treatment on PDMS surface to provide less complexity in transferring pattern. The tape transfer fabrication process involved some steps in transferring pattern on PDMS using tape vinyl tape such as: cutting pattern on tape and removing residue, laminating transfer tape and removing tape liner, transferring pattern on PDMS, peeling off the tape, hole punching through PDMS and spraying liquid alloy. These steps made this process very complicated. In this work, these were completed in just a one step process. Pattern was transferred through PDMS surface energy modification. Here, Plasma was generated through strong electric field which was done in plasma print station. Then, Galinstan was blade coated on top of plasma treated PDMS. This method provides rapid prototyping technology for microfluidic electronics. It provides a simple one step masking process with good printing quality and removes limitations of other fabrication methods. Figure below shows the Process flow of Galinstan deposition on Plasma treated PDMS substrate.

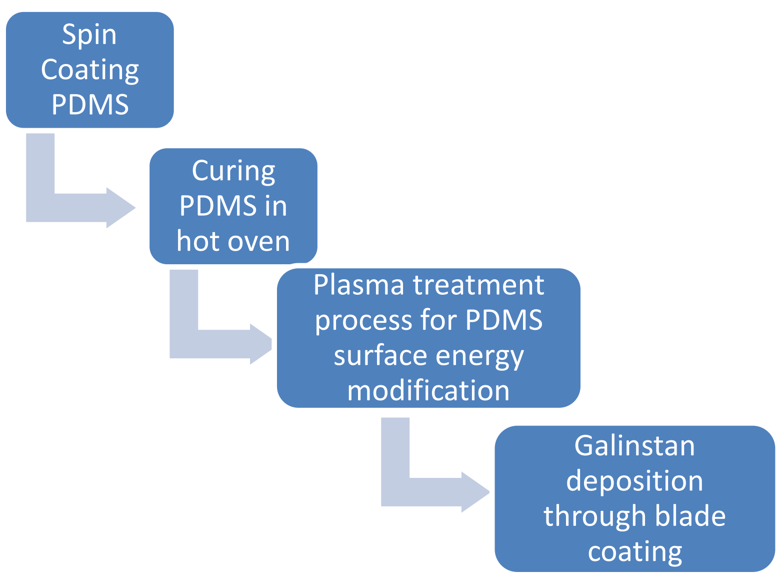


Figure 3. *Process flow of Galinstan deposition on Plasma treated PDMS substrate.*

2.2 Other previous methods –

Previously, some other fabrication methods were introduced related to that work. Among them, masked deposition of Gallium indium alloys for liquid embedded elastomer conductors was done where Galinstan deposition can be found using a different approach. There, thin film is attached with micro channels of Gallium indium alloy to produce flexible electronic circuits. It provides elimination of manual needle injection filling and makes an easy process through musk pattering method to fabricate flexible electronic circuit.[18] Figure below shows the schematic process flow of masked deposition method using Gallium indium alloy

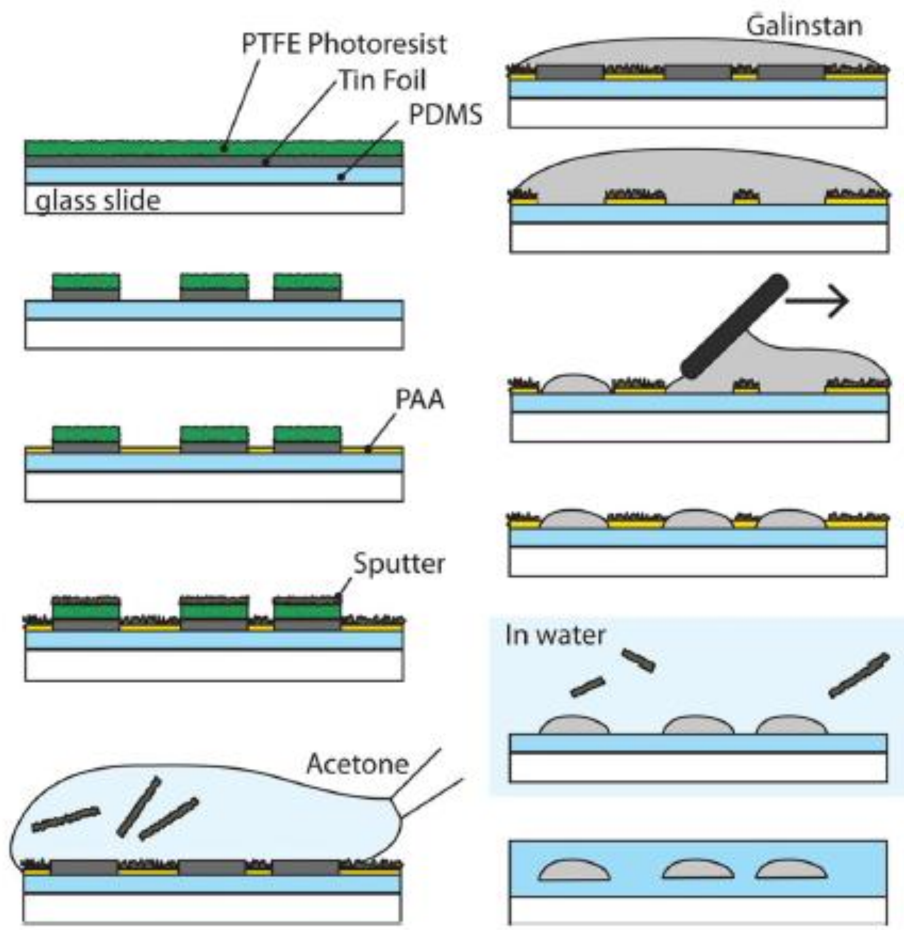


Figure 4. *The process flow of masked deposition method using Gallium indium alloy*. [18]

First, the PDMS was spin coated on a glass slide. Then, using photolithography, Tin foil was patterned on top of PDMS. PAA (Poly (acrylic acid)) release layer was spin coated on top of it. Then indium drops are spitted on the surface while there was photoresist protection, Tin foil was protected from indium. [18] Surface was lifted off after washing it with Acetone. After that, Galinstan was deposited on top where Tin foil gets reactively wetted and extra Galinstan droplets were removed using thin film applicator. Using PAA (Poly (acrylic acid)) release layer, the mask is erased from the surface in water. Then the whole feature was kept at a freezing temperature before going through the final encapsulation process with another layer of elastomer. [18]

In this work, tin foil was patterned and metal films were sputter coated to attain the selective wetting of Galinstan. Wetting behavior of Galinstan was also studied there. It was found that, Galinstan did not wet the PDMS but non uniform distribution of liquid alloy was found with a contact angle of 130°. Another important result found from this study, was the equilibrium state of Galinstan and Tin foil. Over a time period these two materials reacted together and produced a stable alloy of new composition. The average composition (57.63% ± 0.24% Gallium, 22.69% ± 0.09% Indium, 19.68% ± 0.20% Tin) was analyzed using energy dispersive spectroscopy. The fabrication method has the ability to pattern liquid Galinstan on PDMS surface without molding, bonding or other complicated steps such as syringe filling.

In another study a direct writing method of Gallium indium alloy was also studied which seemed to be a complex method because of its experimental set up. Rather, it is a maskless method to provide an identical and continuous writing process. [14] It is the experiment was done by filling the syringe needle with Gallium based liquid metal alloy and putting it close to the moving substrate. [14] Figure below shows the direct writing process using Gallium based liquid metal alloy. The syringe pump was used here to control the flow rate of liquid alloy.

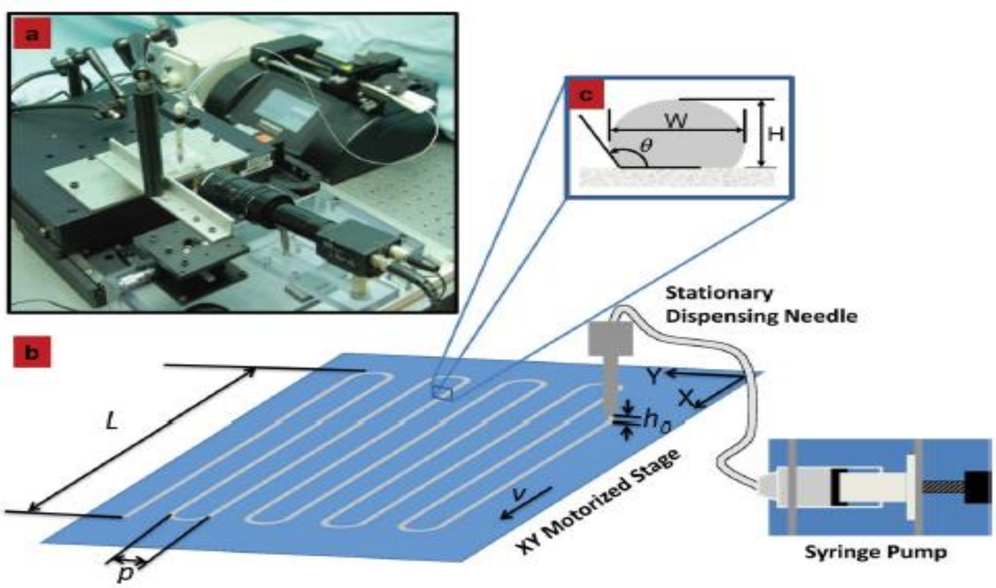


Figure 5. *The direct writing process using Gallium based liquid metal alloy.* [14]

In this method, the lines of Gallium indium alloy can be directly written through the syringe needle. First, the substrate was prepared by spin coating PDMS on top of glass substrate. The syringe needle was coupled with syringe pump and an optical imaging camera. [14] The gallium indium alloy was served through the syringe needle with a constant flow rate each time. Flow rate was maintained by the syringe pump and tubing. The height between the syringe needle and the used moving substrate was kept the same each time. The height was adjusted using the camera together with the system. In the beginning of the writing process the XY motorized stage was moved to the starting point of the pattern. At this point the XY motorized stage was set to zero. [14] After giving certain value the motion of the stage was activated and the motion was controlled remotely. The syringe pump was then turned on and the syringe needle was activated at the end part of the session. The Syringe needle worked at the same flow rate value until the last part of the stage motion. [14] Gallium based liquid alloy was removed after increasing the distance between syringe needle and substrate using the XY stage motion. In the end the process was completed after encapsulating the whole thing with another layer of PDMS. For this, PDMS was spin coated on top of the device. [14]

Contact angle of liquid alloy on glass and PDMS was measured in this work. Similarity in advancing contact angle between glass ($153.4° \pm 3°$) and PDMS ($157.6° \pm 3°$) indicated the similar spreading behavior of glass and PDMS when liquid alloy came into the contact with the surfaces. Then, difference in static contact angle between glass ($128.6° \pm 1.3°$) and PDMS ($150° \pm 2°$) indicated more effective wetting behavior with glass than PDMS. Overall, low wettability was found between liquid alloy and both substrates. The receding angle was found to be $<10°$ for both glass and PDMS. This method is a rapid, repeatable, maskless, one step additive method for fabricating films without any interruption. It has the ability to directly write Gallium based liquid metal alloy which shows non-printable characteristics in case of other printing technology such as inkjet printing. Lower amount of control on needle standoff distance is one of the limitations of this method which reduces the system to a single layer.

In a recent study, soft flexion sensor was integrated on a stretchable silicone substrate for smart glove applications. In that application Gallium indium alloy was used to produce sensory skin for detection of finger curvature. [19] The sensory skin was implemented on textile glove to perform the finger motion. Gallium indium alloy was used here for its effective performance for soft strain sensors. [19] Figure below shows the design and principle of soft flexion sensor using Gallium indium alloy on finger.

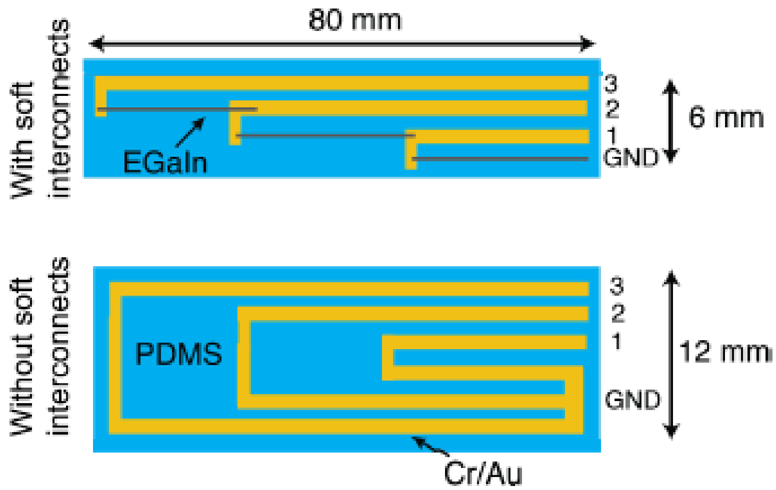


Figure 6. *Design and principle of soft flexion sensor using Gallium indium alloy on finger.* [19]

Here, Gold thin film was coated on stretchable PDMS surface to deposit the Gallium indium alloy on top of it as interconnects. [19] Flexion sensors were integrated on the soft rubbery substrate for static and dynamic testing to be observed. To do this, first the PDMS were spin coated on top of glass slide for approximately two hours. 5/25 nm Chromium/Gold thin films were evaporated thermally to define the pattern. [19] Then, the syringe filled with Gallium indium alloy was kept on top of it to place the liquid on a particular position where the deposition starts. Figure below shows the process flow for fabricating soft flexion sensor on the finger. The Syringe was attached to X-Y-Z stage and a predefined constant pressure (approximately 0.02 bars) was applied to the syringe for applying controlled force to the Gallium indium alloy inside. [19] The tip of the syringe's inner diameter was 360 µm. The distance between the syringe and the substrate was kept at a certain distance (70 µm) to provide constant flow during liquid alloy deposition. Then, wires were connected externally to interconnect by adding small liquid droplets. Finally, the process was completed by providing encapsulation layer through spin coating PDMS at 250 RPM. [19]

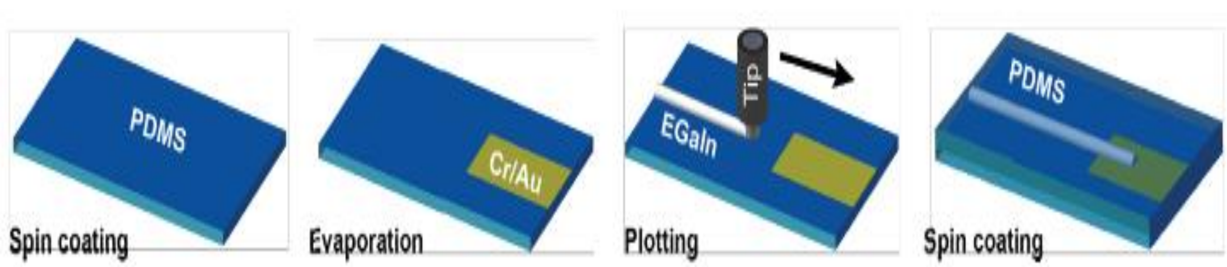


Figure 7. *Process flow for fabricating soft flexion sensor on finger.* [19]

After the fabrication the strip was attached to a textile glove (Eco flex). Then, the glove was then worn by a robot to observe its finger rotation. All finger joints rotated perfectly during the test. In this work, micro cracked structure in the gold film was observed on PDMS. It had the ability to maintain high mechanical deformation and finite electrical resistance. The combination of Gold and Gallium made electrically conductive alloy which was visible around the interconnection area. This method involved only four steps, where interconnects were patterned using maskless, moldless process. A calibration algorithm was also provided to overcome some design problems. Long term response and fatigue resistance of the sensing skin are among the few hindrances involved in this method.

Chapter 3

Experiment

Fluids in flexible micro channels are stable in different levels of deformity without any disturbance or permanent damage in the channel. [20] Since, there is no discontinuation of stream or mechanical disturbance in fluids; it provides a continuous path flow for any particular pattern. [20] Introduction of conductive liquids in soft electronic materials has provided a new way to fabricate stretchable electronics. These types of fabrication process are able to produce low resistant and large areal electronic devices. The principle of this fabrication process has exhibited new ideas of fabrication and more new electronic applications have unfolded. [21] In this thesis work, the principle of conductive liquid was used to fabricate stretchable RF interconnects on a soft electronic materials.

Gallium based liquid metal alloy was used in polydimethylsiloxane (PDMS) to exhibit RF interconnectors. Usage of Plasma print stations has introduced a new type of fabrication process for stretchable electronics. PDMS was plasma treated using both Air plasma and nitrogen plasma through the print station. Different patterns were analyzed through this plasma treatment. Both the air plasma and nitrogen plasma behavior was investigated in this work. The plasma treated area was then blade coated in the laboratory using Gallium based liquid metal alloy. First of all, different line patterns and square patterns were plasma treated to see the behavior of alloy. Then, different RF interconnector characteristics were also demonstrated in this work. Alloy deposition on PDMS was done under room temperature and the alloy behavior and fabrication details were added later. This fabrication method has provided a less complex step-by-step approach in stretchable electronic fabrication using liquid metal alloy. Especially, the use of Plasma print station is a unique approach to fabricate stretchable interconnects on PDMS. The difficulties and complexity of recent studies similar to this work were taken into consideration before starting the thesis work. This Gallium alloy based stretchable electronics fabrication method should eliminate these difficulties found in other manufacturing processes.

3.1 Materials –

Galinstan, that was used as the Gallium based liquid metal alloy, was purchased from Geratherm Medical AG. The Galinstan fluid came in a small PE-bottle measuring 108g. Special care was taken to clean the Galinstan in the laboratory after every use. Though it is a nontoxic liquid, it can still stick to surrounding surfaces. To avoid interaction with other chemicals in the laboratory, special attention is required during its deposition. [22] Surfactant (detergent) /water solution for hard surfaces were used as the cleaning agent during work. Rubber protective gloves and eye protective glasses were used for protection while working with this alloy. [23]

Table 1 below shows the physical and chemical properties of Galinstan

Solubility	Insoluble in water and organic slovents
Melting point	-19°C
Boiling point	Above 1300°C
Density	6.44 g/cm^3 at 20°C
Viscosity	0.0024 pa-s at 20°C
Thermal conductivity	16.5 w m^{-1} k^{-1}
Electrical conductivity	3.46*10^6 S/m at 20°C
Surface tension	0.718 N/m at 20°C

Table 1. *Properties of Galinstan.* [16]

Though Galinstan has very high electrical conductivity, one of the remarkable limitations that affected this thesis work is the very fast oxidizing process of this liquid alloy. Drops of Galinstan can be instantly oxidized. It has the ability to form oxide skin immediately. [24] Special arrangements must be taken to prevent its oxidizing process. More details about its oxidizing prevention will be added in the later part of thesis.

The PDMS **(**Polydimethylsiloxane) substrate used here, SYLGARD 184 was purchased as from Sigma Aldrich. It came in a small 5gm clip pack. Both the base and curing agent came in the same pack. Each pack contained the base and curing agent in 10:1 weight ratio. The base and curing agent were mixed up manually every time. [25]

The Teflon used here in this work was Polytetrafluoroethylene (PTFE), film, thickness 0.2 mm, L 0.5 m. It was ordered through Sigma Aldrich.

The size of glass slides where the PDMS was spin coated were 25*25 mm. Propanol and Acetone was used to clean the glass slides. Before spin coating the glass slides were cleaned with di-ionized water and then dried properly with a blow dryer.

Acetone was used as the cleaning material after spin coating PDMS. Normal foil paper was also used to cover up the spin coating walls as the protection and the spin coater was cleaned properly after every use. After every Galinstan deposition session, the checking of the plasma printing station and contact angle measurement device were carefully done to avoid any mess in the area with the liquid alloy.Cleaning was done by using detergent and normal water.

3.2 Plasma print station –

Plasma print station has one of the most significant roles in this work. It is a compact platform for digital plasma printing which consists of the settings required for patterned plasma treatment. [26] In this work it is used to activate the patterned area. Different types of patterns can be treated using both air plasma and nitrogen plasma. Cold atmospheric pressure is used to treat the surface of PDMS. [27] Repetition of plasma treatment in the same pattern is required to provide better plasma activation. Thus, more effective plasma activation can be achieved by this process. It is also dependent on the substrate type and gas formation. After plasma treatment Galinstan is blade coated on top of PDMS. The effect of plasma treatment is checked by observing the Galinstan spreading dimension on activated pattern area of PDMS. Remarkable effects are shown by varying surface energy of the surface material. As a result, Better wetting ability is found in the treated area.

System components

Figure 8 shows the experimental set up of plasma print station. The most significant system components are print head, power supply, gas controller and substrate table.

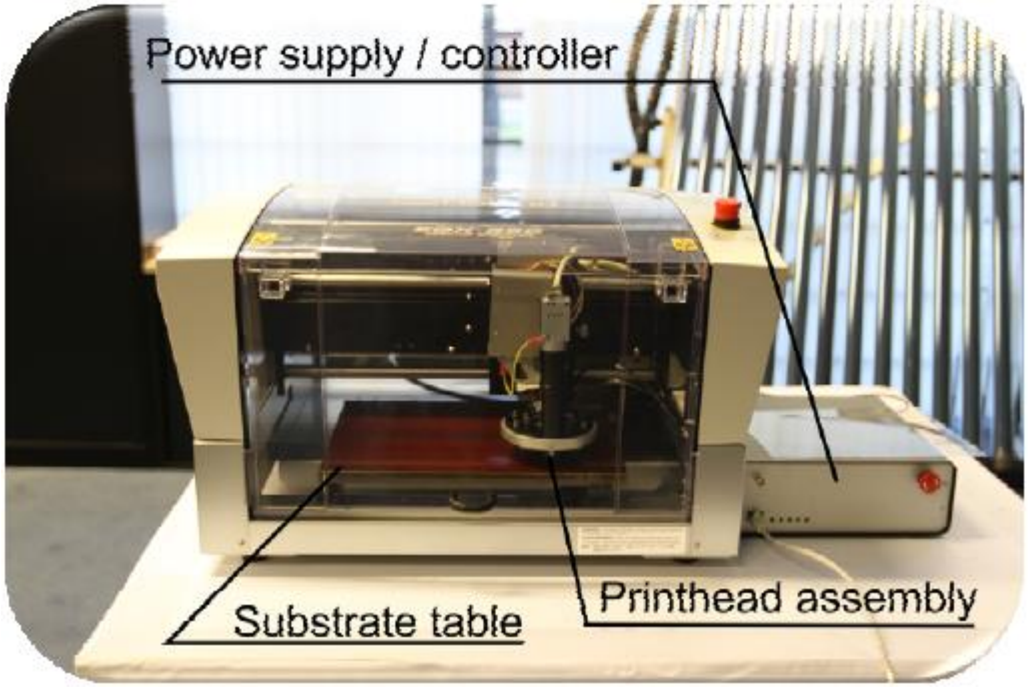


Figure 8. *Experimental set up of plasma print station.* [26]

3.2.1 Print head assembly –

Print head assembly is ascended on the plasma print station. It can be placed in both X and Y direction. The print head height can be adjusted by moving up and down in Z direction. [26] Print head assembly is the combination of different parts. Among them print head, gas nozzle and optical path and camera are most important. [26]

Print head is the most important part of this system. It is a compact system integrated inside the assembly. The whole thing is automatically adjusted with needle electrodes. No other settings are required for this part. [26] Under this setting the print head is able to move in any direction on substrate table. Figure 9 shows the combination of needle electrodes in print head.

- Number of needle electrodes - 24
- Operating frequency (Max.) - 400 Hz
- Operating voltage - 40VDC , ±10%
- Needle electrode size (diameter) - 30 μm

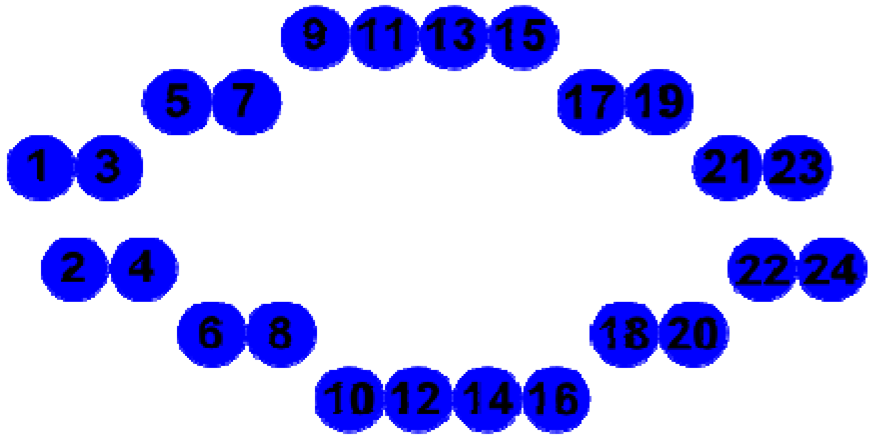


Figure 9. *Combination of needle electrodes in print head.* [26]

A Gas flow nozzle provides gas flow in this system. It is done between the surface and print head. Gas inlet and gas outlet helps to in the gas supply connection. Both the nitrogen and oxygen gas plasma treatment effect is observed in this work.

An optical path or camera is installed in the print head assembly. It is one of the most useful additions in this device. Actually it is a plasma monitoring system during printing. The Camera is placed into an appropriate position and height to observe efficient plasma generation for any particular substrate. It is helpful to select the print origin during the printing process. [26]

3.2.2 Power supply and controller –

The Controller is used to supply low voltage power. It is then converted to high voltage power using the transformer in high voltage box. It is controlled by a microprocessor. The high voltage box is connected to the substrate table through a cable to supply the high voltage to substrate table. [26] The controller is attached to the computer through an Ethernet cable. High voltage plasma can be monitored through the camera. There is an emergency switch to stop the high voltage plasma generation which turns off the power supply of the controller. [26] Figure 10 shows Power supply and controller device of the plasma print station

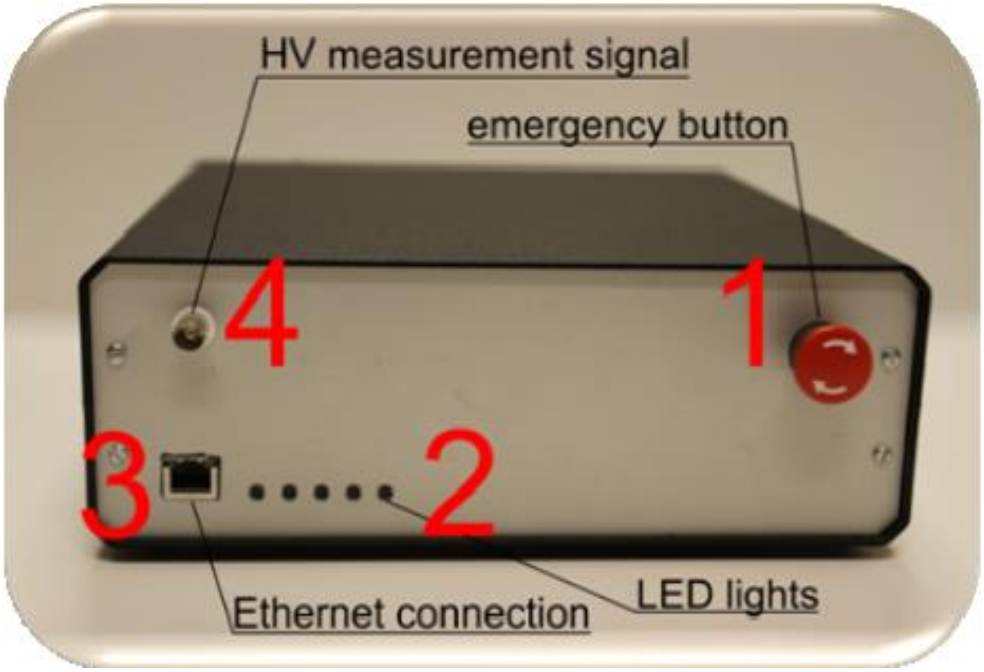


Figure 10. *Power supply and controller device of plasma print station.* [26]

3.2.3 Substrate table –

The Substrate table is the platform where PDMS is placed for plasma activation. Glass base is the basic element of the substrate table. A Conductor and dielectric sheet is also laminated with it. [26] A high voltage cable is connected between electrode table and high voltage box connector. During the high voltage operating mode, the conducting sheet voltage is increased compare to ground. But, in this case, only electrode voltage is increased and the voltage nonmetal part in not changed. For direct flash over prevention, dielectric shield is provided on top of the surface. [26] Figure 11 shows the connection between high voltage box and electrode table.

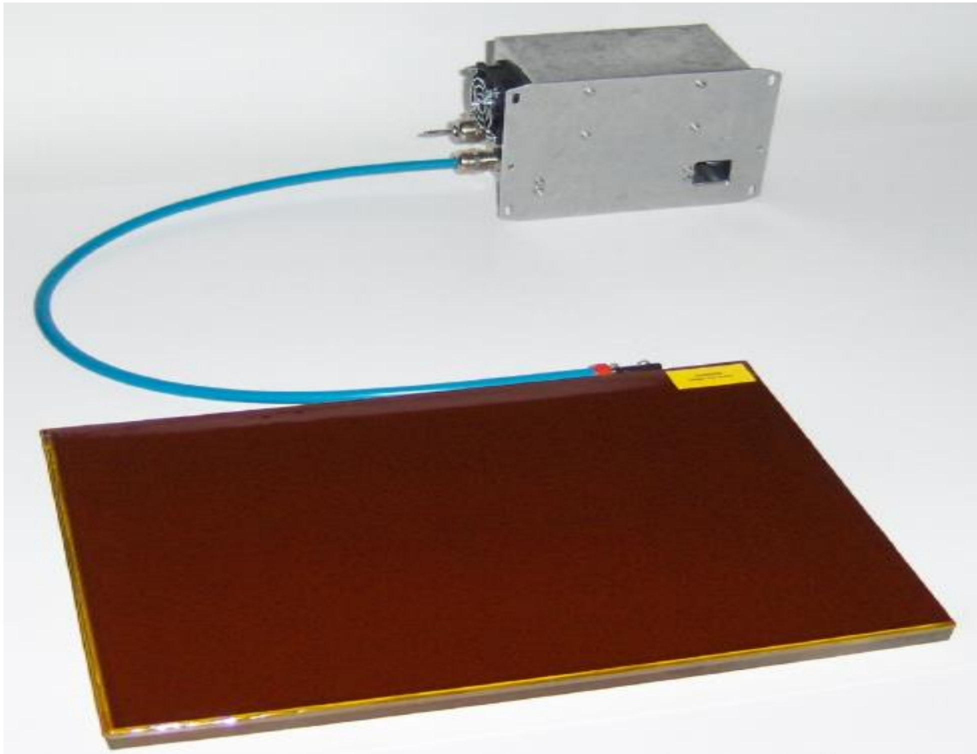


Figure 11. Connection between high voltage box and electrode table. [26]

3.3 Methodology –

3.3.1 Spin coating PDMS –

In the beginning of laboratory work, silicone based organic polymer is deposited on to a clean and flat 25mm*25mm glass slide in clean room. First of all, Polydimethylsiloxane (PDMS, Sylgard 184) and curing agent attached in the same package are mixed. The mixing is done manually in 10:1 ratio. Then, Acetone is used to clean the glass slide.

Acetone, glass slide is cleaned with Isopropanol followed by de-ionized water. The cleaned glass slide is the dried properly with a blow drier. After that, the oven is turned on to 100°C heat before starting the rest of the process.

Secondly, PDMS is spin coated in a spin coater. The Spinner pump and clean air switch is turned on before spin coating PDMS. An Adapter is used on top of spinner to fit the small glass slide. Spin coating process flow is shown below.

Spin coating process flow -

Apply PDMS on glass substrate → Turn on spin coater → Edit mode →

Set time (1 minute) Speed (2500 rpm) Acceleration (250)

The vacuum chamber button is turned on (approximately 21) before putting the slide on to spinner. After placing the glass slide, a very small portion of PDMS and curing agent mixer is dropped on to the glass slide using pipette. Then, the run button is pushed to start spinning.

After spin coating, PDMS is cured on a hotplate inside the oven. The Oven is heated up to a certain temperature. In this case, PDMS is cured at 100°C for 35 minutes inside the oven. [28] Finally, smooth PDMS substrate is readied for the plasma activation process. Figure 12 shows Spin coated PDMS after curing process.

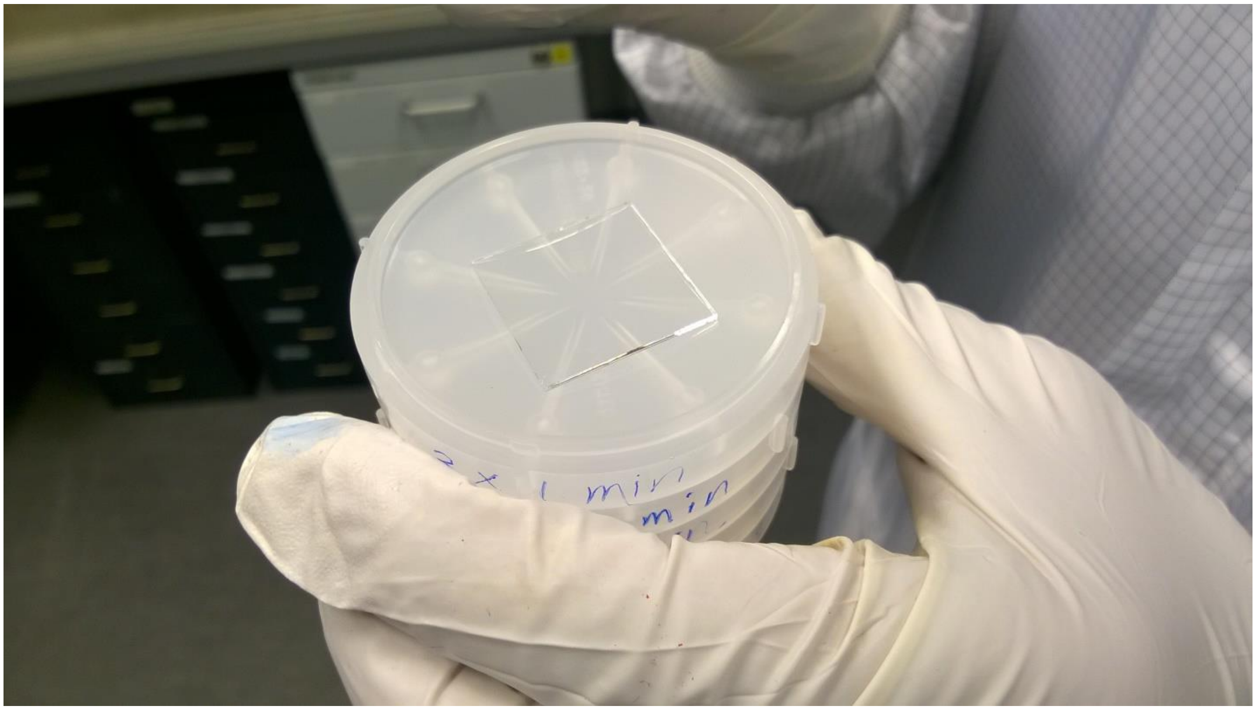


Figure 12. *Spin coated PDMS after curing process.*

3.3.2 Plasma treatment process –

Plasma treatment of PDMS is the most significant part of this thesis work. The plasma is created through strong electric field and the PDMS surface is modified by plasma to change the surface energy. Thus, better wetting ability is found by this process.

In the beginning of the process, all the switches including the print station switch, emergency button, high voltage switch is turned on. LAN Ethernet connection to desktop is provided through IP set up. The same thing is done to turn on the print head camera. Through this camera the plasma generation is observed on the computer screen. Voltage is changed after observing plasma sparks on the screen.

First, Spin coated PDMS is placed on top of substrate plate inside the print station. Then the print station door is closed and the plasma user interface in opened. To operate the system, printing data in generated using this interface and also it is used to send data to system. Figure 13 shows the user interface of the system.

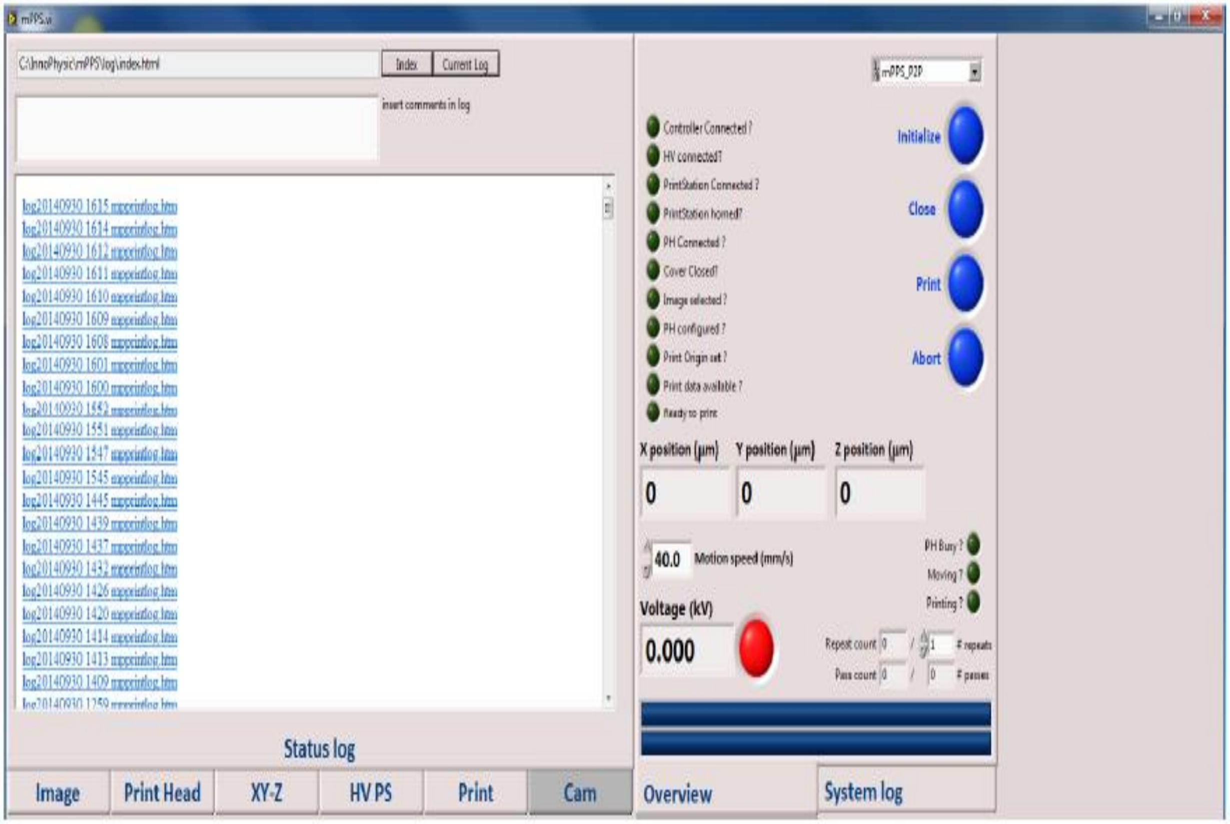


Figure 13. *User interface of the plasma print station.* [26]

Secondly, the system is initialized first to start the user interface connection to the system. After initializing the system, the controller, high voltage box, and print station homed; print head and print station itself is connected. Print station homed position is the initial position of the print head. In this position the print head is not ready yet and printing data is not yet generated.

In the next step, an image is selected from computer. There are different types of patterns tested in this work. The software supports different formats of images including bitmap image, and PNG format. After uploading image the X and Y steps are selected according to the PDMS size. Figure 14 shows the image selecting window of the system interface.

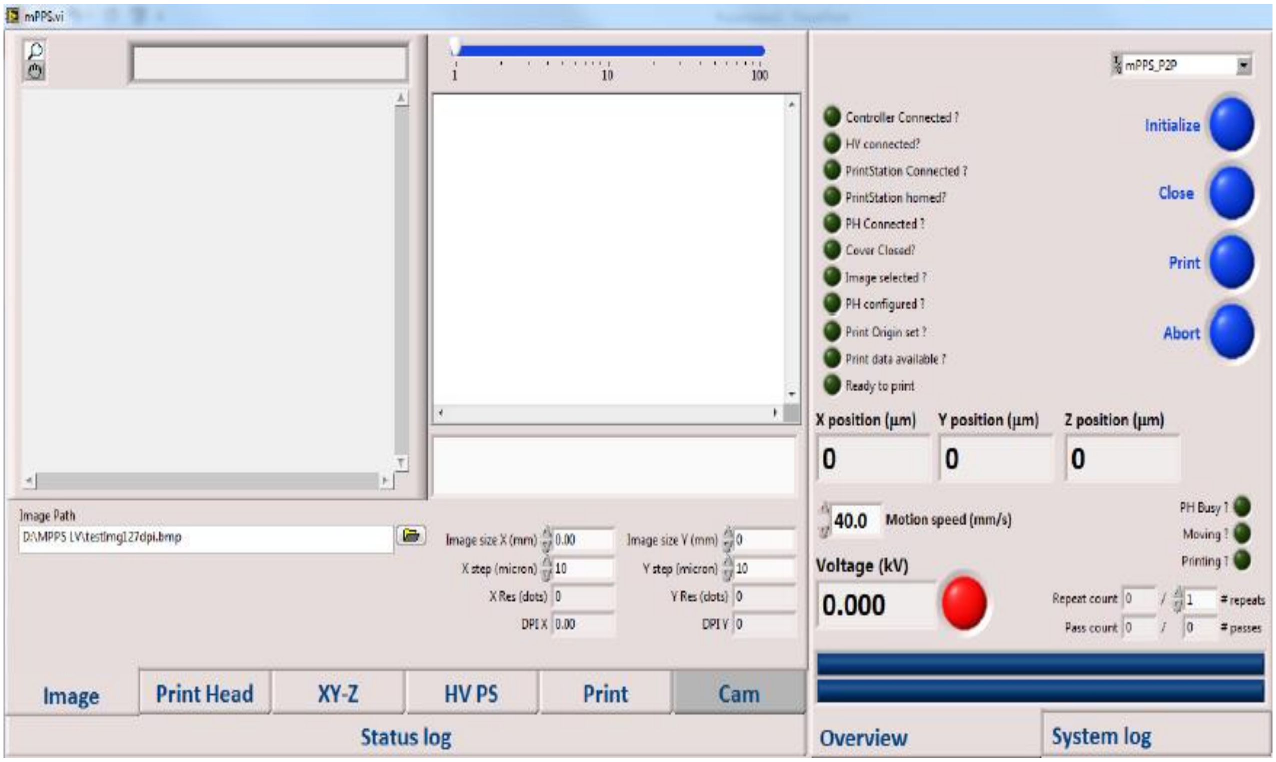


Figure 14. The image selecting window of the system interface. [26]

After selecting image, the print head is configured by choosing one of the needle lines among two rows of needles in print head assembly. Then, the print head is positioned to select the print origin where the system will start printing according to the selected pattern. It is done by selecting platform motion tab (XY-Z). By changing X, Y, Z positions print head is moved from its initial position to exact print position of PDMS that is placed on top of substrate table. The maximum range limit for X, Y, Z is selected carefully to avoid conflict between print head and substrate table. Most importantly, the Z range limit is selected properly. Because, it is the lowest point the print head can move. Touching of needles is avoided by choosing this Z range limit. This range is set by following the PDMS thickness too. Thus, the print head alignment is done using the print head alignment camera. Print origin is selected by following the same alignment camera. Figure 15 shows the platform motion window of the system interface.

Figure 15. *The platform motion window of the system interface.* [26]

After that, the print head is instructed to follow the print origin and high voltage tab is selected to initialize the high voltage system. It is done by tuning the system. After tuning the system, resonance spectrum is automatically measured and a peak is found which the frequency is of the voltage. The voltage frequency 71.6 KHz. is found in this case. When tuning is done the voltage is set using the voltage tab (red one). Normally for air plasma and nitrogen plasma voltage, it should be set at 5.00 kV. But, in this case the voltage is selected at 7.00 kV due to the thickness of PDMS and for higher efficient plasma generation. In the final step, the print preview is generated in the screen which shows the final image to print on PDMS. Needle alignments for different lines of the pattern are seen in the print preview. The motion speed is to 40.00 mm/s. This input is given to provide faster printing speed. It is done according to the print preview. Then, the print data is generated and the print station is ready to print the pattern.

To get effective plasma treatment the printing process is repeated 15- 20 times on the same image pattern. It is done to get bigger plasma exposure time to provide better plasma effect and more hydrophilic treatment on PDMS surface. Both air plasma and nitrogen plasma treatment is done by following the same process. For nitrogen gas plasma, the gas flow is controlled by a different user interface. Figure 16 shows the window of the user interface for gas flow controller. Plasma treatment on different image patterns is done in this thesis work. The comparison between the original image pattern and plasma treated pattern after Galinstan deposition will be added in the later part of this paper.

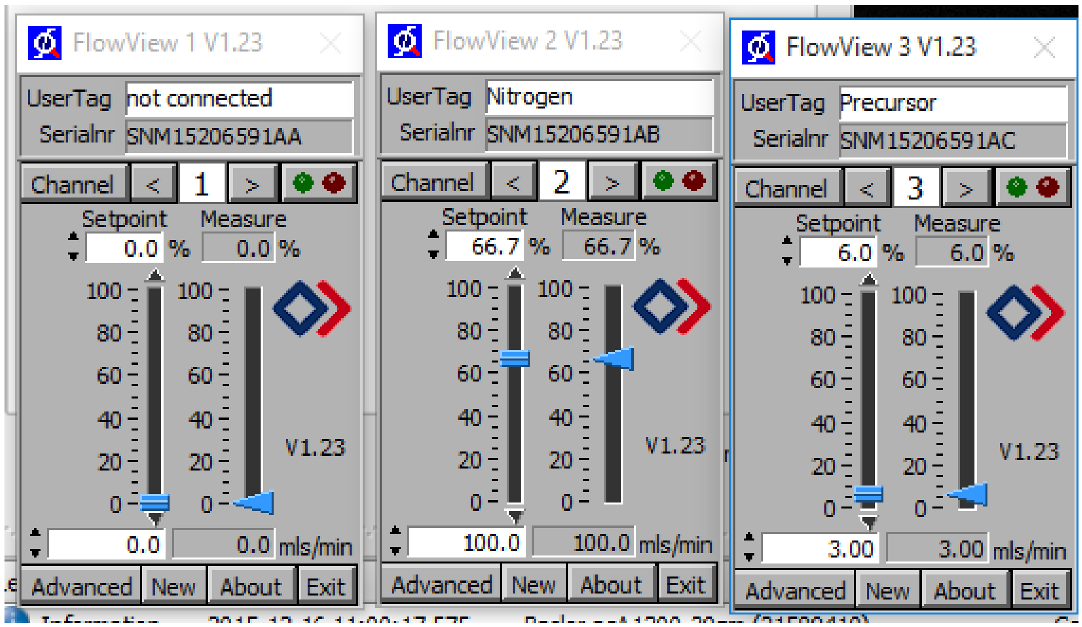


Figure 16. *Gas flow controlling parameter window.*

3.4 Contact angle measurement set up –

After the plasma treatment process, contact angle is measured to check the plasma effect on PDMS. There are three interfacial forces involved at the edge of a Galinstan drop. Two forces are in opposite directions and the third one is called contact angle which forms a particular angle to the substrate. [29] In this work, Contact angle is measured by a contact angle analyzer. Figure below shows the diagram of a contact angle analyzer. Plasma treated PDMS is placed on top of sample stage. A Syringe is loaded with Galinstan and placed on motorized syringe assembly which is controlled using steeper motor controller.

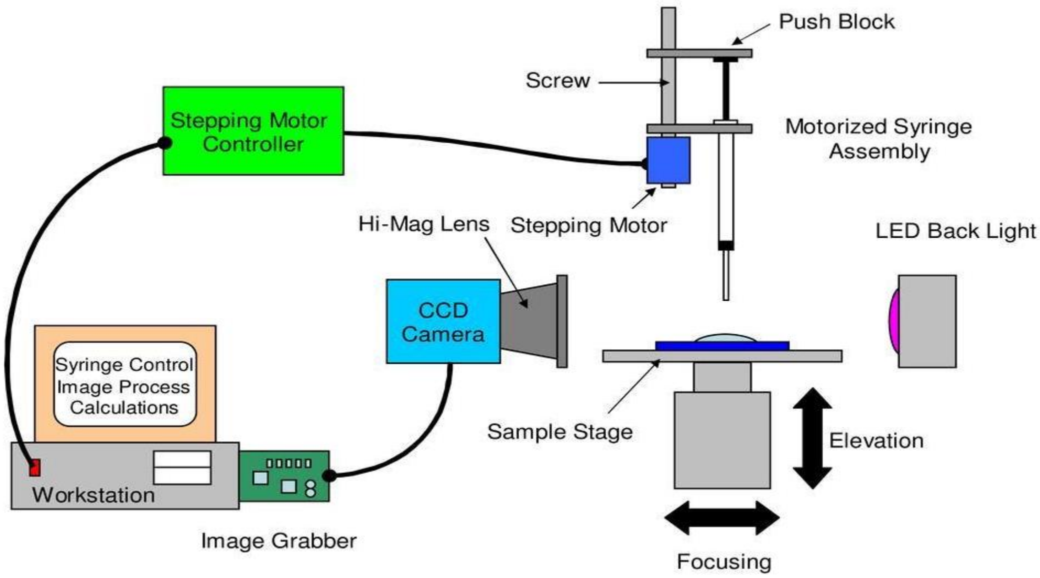


Figure 17. *Diagram of a contact angle analyzer.* [29]

The direction to Steeper motor is provided through the workstation. Then, CCD (charge coupled device) camera is adjusted with the height of motorized syringe assembly and sample stage. After that, A Galinstan droplet is placed on top of the substrate using motorized syringe assembly. CCD camera is focused carefully to droplet for a clear image which is very important in measuring contact angle. A Captured image of the droplet is then transferred to the workstation using image grabber for image processing and contact angle calculations. The figure below shows a sample of drop surface tension and surface energy analysis using the contact angle analyzer.

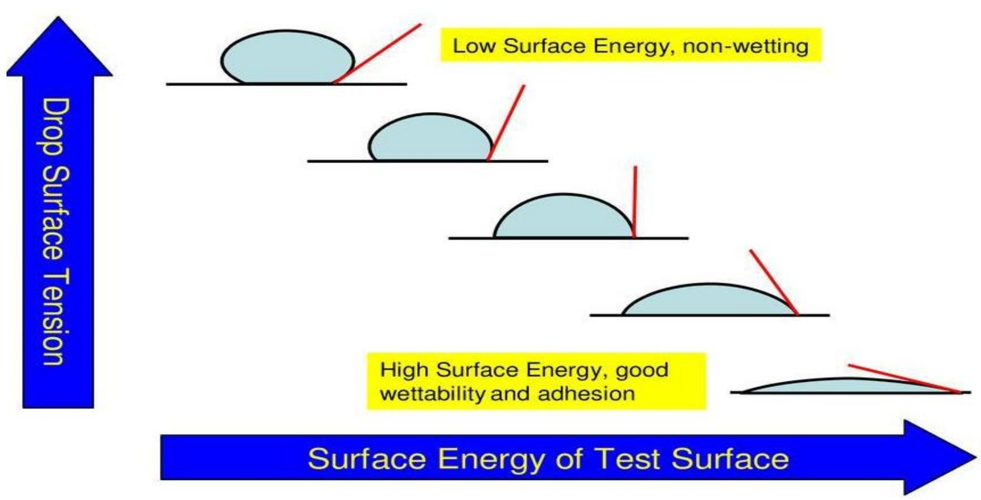


Figure 18. *A sample of drop surface tension and surface energy analysis using contact angle analyzer.* [29]

3.5 Galinstan deposition on Plasma treated PDMS –

After doing plasma treatment in the patterned area Galinstan is deposited on top of PDMS surface. It is done by blade coating manually on the surface. It is also called knife coating or doctor blading. It is one of the most popular fabrication methods for flexible substrate. For large scale printing, the blade is fixed on top of moving surface. [30] The substrate moves to the fixed blade direction as shown in figure 19. In this case the blade is used as a proper smoothing tool to remove extra coating layers. During blade coating ink is supplied from an adjustable position. [30] Generally it is placed in front of the fixed blade. The gap width is changed to provide variable thickness of wet layer. Actual thickness is approximately half of the gap width. It is also dependent on ink viscosity, coating speed, flow rate, surface energy of substrate, surface tension of liquid and surface temperatures etc.

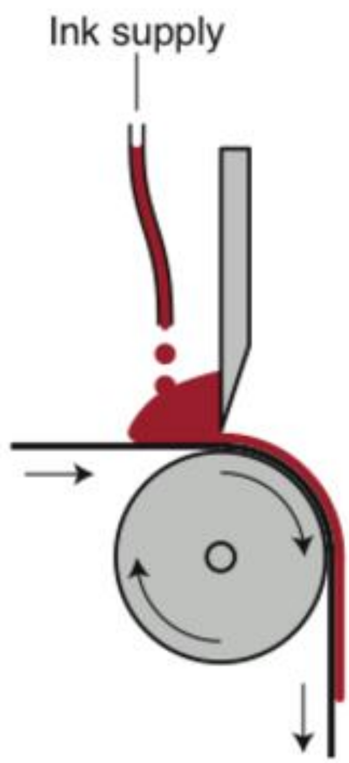
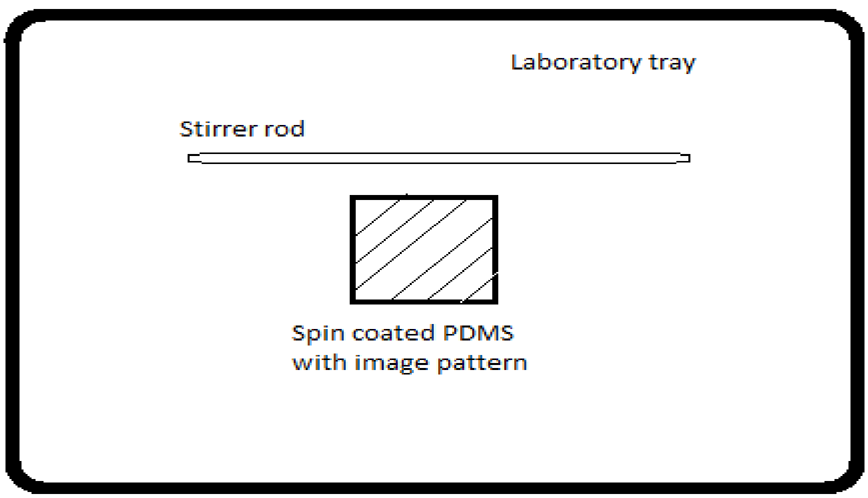
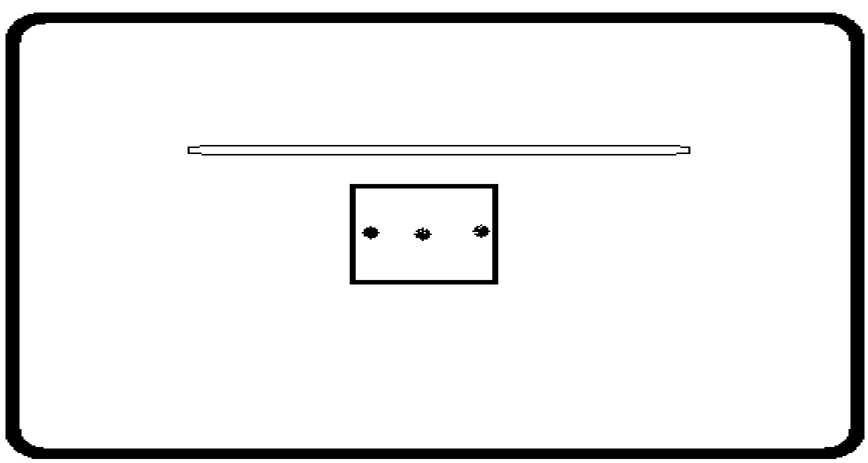


Figure 19. *Principle of blade coating.* [31]

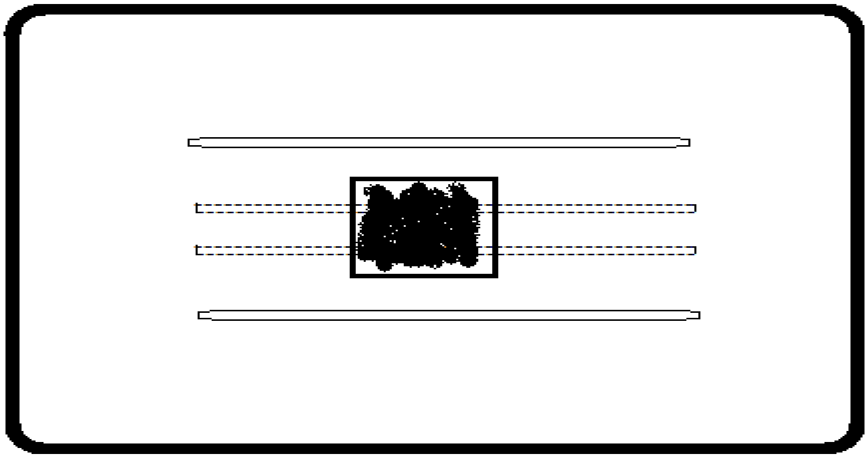
In this laboratory work, Blade coating is done manually over the surface of PDMS. Though, the main principle of the blade coating processing is followed in this process. To make blade coating effective, it is done just after (within few seconds) the plasma treatment. The use of plasma effects is maximized by this quick coating process. In this lab scale processing, very small drops of Galinstan are dropped on top plasma activated PDMS surface. Then, a stirrer rod is moved over the whole flat PDMS surface. Initial effect of plasma is seen instantly on the activated pattern area of PDMS surface. The visibility of Galinstan movement towards the activated part of PDMS is very clearly identified during this blade coating. The observation of surface energy change in patterned area is very precisely done after doing the blade coating. But, some other parameters are also observed which has great influence to change the plasma effect scenario. It will be discussed in the later part of this paper. Figure 20 shows the process flow of Galinstan deposition method on top of the plasma treated PDMS surface.



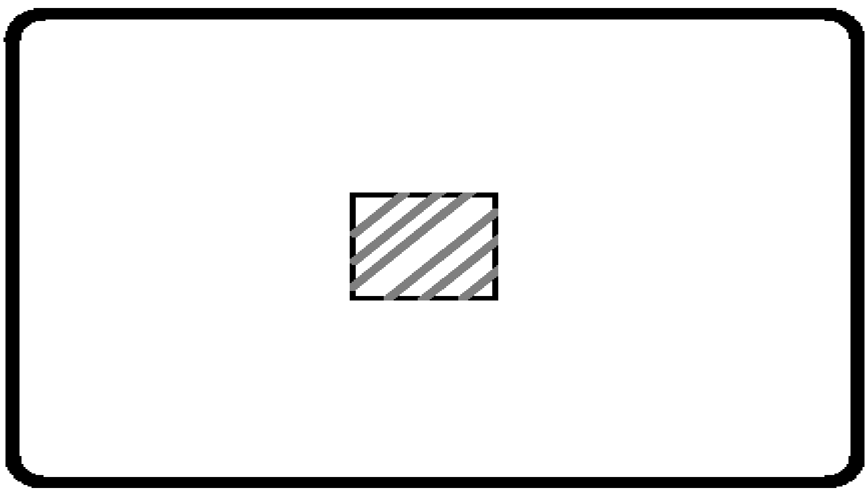
a)



b)



c)



d)

Figure 20. *Process flow of Galinstan deposition method on top of plasma treated PDMS surface. a) Original image pattern mounted on top of PDMS surface after plasma treatment. b) Galinstan deposition on top of PDMS surface. c) Manual blade coating using stirrer rod. d) The expected phase of image pattern after blade coating Galinstan on plasma treated PDMS.*

Chapter 4

Results and Discussions

4.1 Contact angle measurement from Galinstan deposition –

In a clean room environment, the liquid metal alloy is deposited in different levels of plasma treatment. There are a few remarkable outcomes are exhibited after analyzing the wetting behavior of Galinstan on top of PDMS. Unoriginal partial wetting is demonstrated during Galinstan deposition. The behavior of the alloy is found more similar to gel than liquid, which sticks everywhere. To investigate these particular characteristics and plasma activation result contact angle between the liquid alloy and PDMS surface is measured in this work. Figure 21 shows the Galinstan droplet deposition on PDMS (No plasma treatment) for contact angle measurement.

Case 1 –

Galinstan deposition on PDMS (No plasma treatment) -

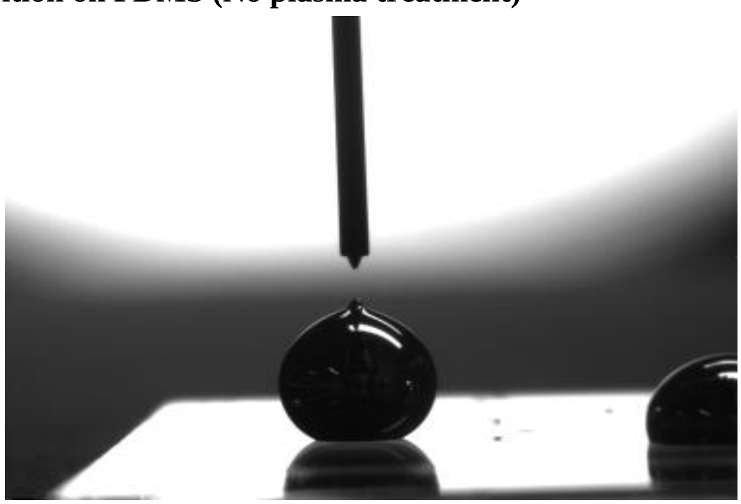


Figure 21. *Galinstan deposition on PDMS (No plasma treatment) for contact angle measurement.*

The contact angle is found here, **131.5 degree**.

To brighten the plasma effect on PDMS, contact angle is also measured when liquid alloy deposited on plasma treated PDMS. Figure 22 shows the Galinstan deposition on PDMS (with plasma treatment) for contact angle measurement.

Case 2 –

Galinstan deposition on PDMS (with plasma treatment)

Figure 22. *Galinstan deposition on PDMS (with plasma treatment) for contact angle measurement.*

The contact angle is found here, **100.5 degree.**

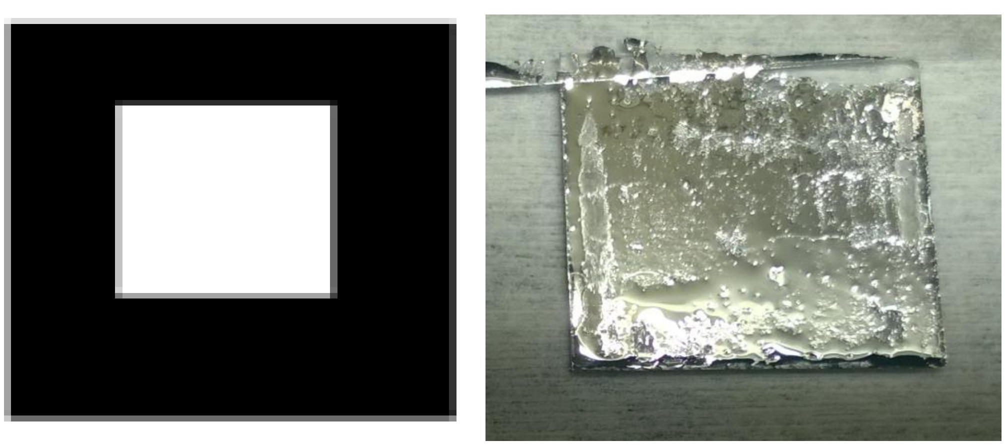
In this section, the significant effect of plasma treatment is clarified by measuring contact angle after Galinstan depositing in two different cases. It seems that, there is a clear difference – a decrease of 31.5 degree angle for plasma treated PDMS surface. Still, 100.5 degree is seemed to be heavily hydrophobic. Thus, it is only partially wetting the surface due to its very quick oxidation process. As it was said earlier, the quick oxidation process has a big impact on wetting behavior. It has been proven by this contact angle analysis. But, it is possible to overcome this limitation. The possible solution to this problem is also investigated in this work which will be discussed later.

4.2 Galinstan deposition on plasma treated PDMS (Sample 1) –

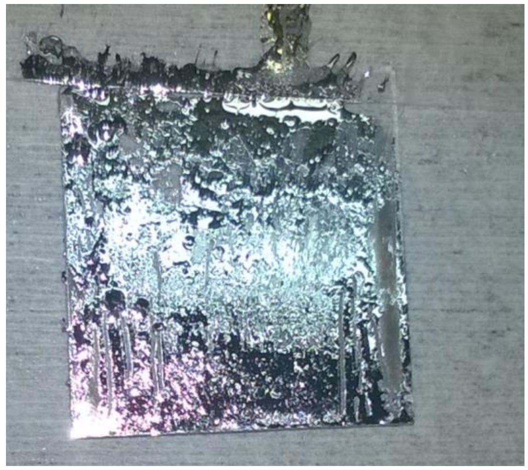
A new plasma printing method is experimented to explore the effect of Galinstan on plasma treated PDMS. Different printed liquid alloy patterns are compared with original patterns. The Galinstan deposited printed liquid alloy patterns are shown below. After plasma activation process, Galinstan is deposited very quickly on PDMS to use maximum plasma effect on Galinstan. But its oxidation process is considered to be one of the major concerns in this work. As, Galinstan oxidation is a rapid process, it is very difficult to prevent oxidation process.

As a result, some negative changes of liquid alloy behavior is noticed after the Galinstan deposition on plasma activated PDMS. Though, there is significant difference is found after altering the surface energy through plasma treatment. Still, the quick oxidation process has appeared as the main drawback of this process. The Galinstan characteristics after deposition are analyzed in this section. Here, Plasma treatment specifications and observations for different changes are added for Sample 1 and Sample 2. Other samples are explained in Appendix 1, 2 and 3. There, few changes in Galinstan characteristics after altering the plasma specifications are explained briefly with figures. The possible ways to improve the limitations will be explained further on.

4.2 Galinstan deposition on plasma treated PDMS (Sample 1)



a) b)



c)

Figure 23. *Galinstan deposition on plasma treated PDMS (Sample 1). a) Original pattern (20mm×20mm) b) Spin coated PDMS at 5.0 kV voltage plasma c) Spin coated PDMS at 7.0 kV voltage plasma.*

Plasma treatment specifications for sample 1 -

Voltage = 7.00 kV

Motions speed - 20 mm/s

Repeats – 5

Voltage frequency - 72.1 KHz

First, plasma is generated at 5.0 kV voltage and 5 repeats. But, in this case plasma generation is seemingly less than its expected level. The voltage level is then increased to 7.00 kV. In that voltage level, full bright plasma is generated on PDMS which is clearly noticed on screen through the print head camera. After blade coating Galinstan, two clear edges of the square pattern are visible on PDMS. The Galinstan movement through the plasma treated area is found at the very beginning of blade coating. But, later on it seems to be lost and flooded due to its quick oxidation process. Also, the pattern shape is appeared to be inaccurate for the very first effort. Though, the Galinstan is flooded, it still seemed to be very sticky on PDMS surface.

4.3 Galinstan deposition on plasma treated PDMS (Sample 2) –

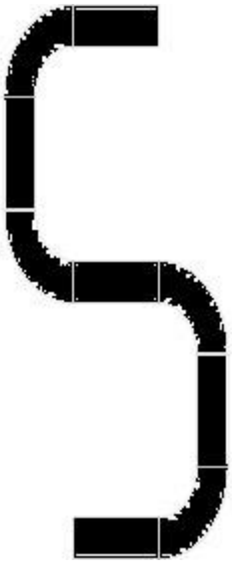


Figure 24. *Galinstan deposition on plasma treated PDMS (Sample 2). a) Original pattern (5mm×20mm) b) Spin coated PDMS at,7.50 kV voltage plasma.*

Plasma treatment specifications for sample 2 -

Voltage = 7.50 kV

Motions speed - 30 mm/s

Repeats – 15

Voltage frequency - 72.1 KHz

Observations –

- Brighter plasma generation on PDMS is seen in the screen through the camera as voltage increased up to 7.50 kV.
- A Very little portion of Galinstan is blade coated for this sample which resulted more accurate pattern shape than previous samples.
- While Galinstan is deposited on PDMS, the movement of ink showed more visibility due to a lesser amount of alloy deposition.

- Treatment cycle is increased and provided better result.
- Like the previous samples, It seemed to be very sticky on PDMS surface.

4.4 Spin coated Galinstan on PDMS –

It has already been examined during the work that, blade coating is not a totally uniformed method to deposit Galinstan on top of PDMS. During bade coating, it seemed to have few drawbacks in droplet distribution of alloy on PDMS. That's why Galnistan is spin coated to observe the proper droplet allocation on plasma treated PDMS. Figure 25 shows the spin coated Galinstan on plasma treated PDMS.

Specifications for plasma treatment -

Voltage = 8.00 kV

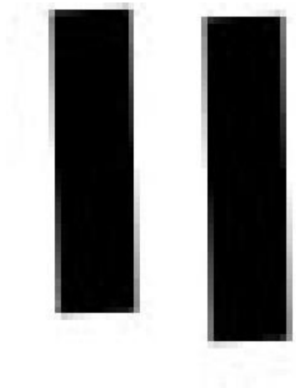
Motions speed - 30 mm/s

Repeats – 20

Voltage frequency - 72.1 KHz.

Observations –

- Bright plasma generation on PDMS is seen in the screen through the camera as voltage increased up to maximum 8.0 kV.
- Spin coating settings: Time - 1 min, Speed - 2500 rpm, acceleration – 250. It is kept same as PDMS spin coating.
- Galinstan is very much adhesive and most of the part of droplet is partly divided during spin coating.
- Unorganized distribution of Galinstan is shown after spin coating, due to its great adhesiveness to the PDMS surface.
- During the spin coating process small parts of droplet is separated into pieces and attached to spin coater wall.



a)

b)

Figure 25. *Spin coated Galinstan on plasma treated PDMS. a) Original pattern (10mm×22mm) b) After spin coating Galinstan.*

4.5 Discussions –

It is revealed for the experimental section that, the surface oxidation of the Gallium based alloy is a challenging problem. As it sticks to most of the surfaces very easily, it becomes very tough to implement in this work. As it is seen from the experiment, the contact area between the surface and alloy is maximized for normal PDMS. Contact angle is increased (case 1), due to its high contact area. It clarifies the hydrophobicity of normal PDMS surface. Although the plasma activated PDMS has contributed the contact angle reduction to 100.5 degree (case 2). Still, it is not good enough to execute the targeted intention of this work.

Even though, the Galinstan deposition is done very quickly after plasma treatment, the alloy is immediately oxidized in the surrounding environment and results thin layer of Gallium oxide. The behavior of the oxide is more like a solid layer on top of PDMS. It continues the similar state until it experiences any stress. In this state, the characteristics of the alloy are not much similar to liquid. Thus, it’s normal fluidic state is hampered by oxide layer behavior and sticks the alloy to almost every part of plasma treated PDMS.

To compare the difference with PDMS, Galinstan deposition is also studied on top of Teflon surface. According to the previous work, Galinstan droplet was tested to exhibit the wetting characteristics on Teflon coated glass slide. Where, glass slide was spin coated with 6% Teflon AF solution and cured at 165°C. [32] Using a pipette, Galinstan droplet was deposited to measure the contact angle. Figure 26 shows the Contact angle of Galinstan droplet on Teflon coated glass slide.

Figure 26. *Contact angle of Galinstan droplet on Teflon coated glass slide.* [32]

In this case, the angle for Galinstan droplet is 140.3 degree. It clearly shows the similarity with the wetting property of Galinstan droplet on normal PDMS surface. [32] The quick oxidation of Galinstan has shown an identical effect in contact angle measurement and it is seemed to be one of the most concerning issues in liquid alloy deposition. So, the recovery from quick oxidation process of Galinstan is also investigated in this thesis work. It will be added in the next chapter.

4.6 Possible oxidation removing approaches –

4.6.1 HCl vapor treatment –

There have been several studies are done in this work to recover the untoward gallium oxide (Ga_2o_3 and Ga_2o) layer characteristics for this liquid metal alloy. [33] A process based on HCl is one of the best solutions to overcome this particular limitation which was done by Kim, Daeyoung and his group. They showed that, surface modification can be done by using HCl for converting Ga_2o_3 to $GaCl_3$. [32] HCl can be utilized in different states for this process. Among them HCl vapor is one of the most reliable states. It results the improvement to non-wetting characteristics of Galinstan droplet. [32] Figure 27 shows the schematic diagram for HCl vapor treatment.

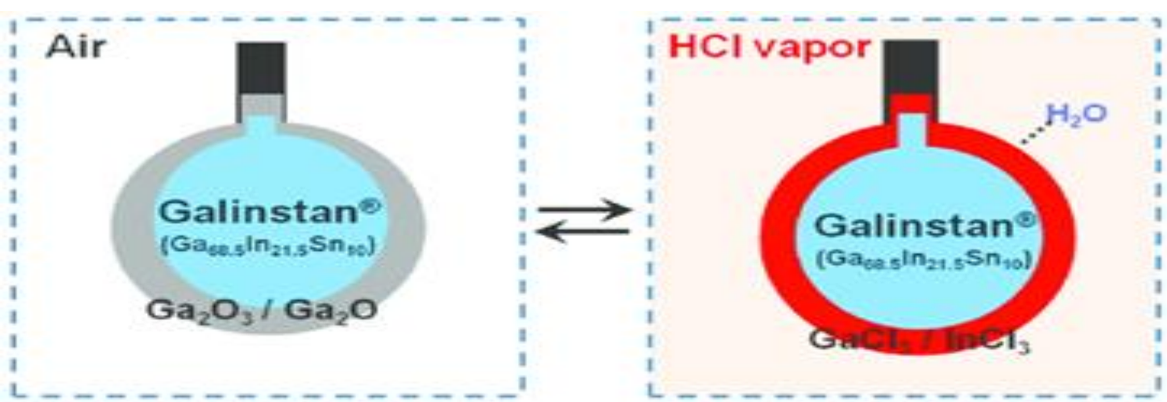


Figure 27. *Schematic diagram for HCl vapor treatment.* [32]

An oxidized Galinstan droplet is placed 2 mm away from HCl (37wt %) for 15 s. HCl vapor evaporation helps to react chemically with Galinstan oxide layer. [32] Figure 28 shows HCl vapor treatment of Galinstan droplet on different substrates.

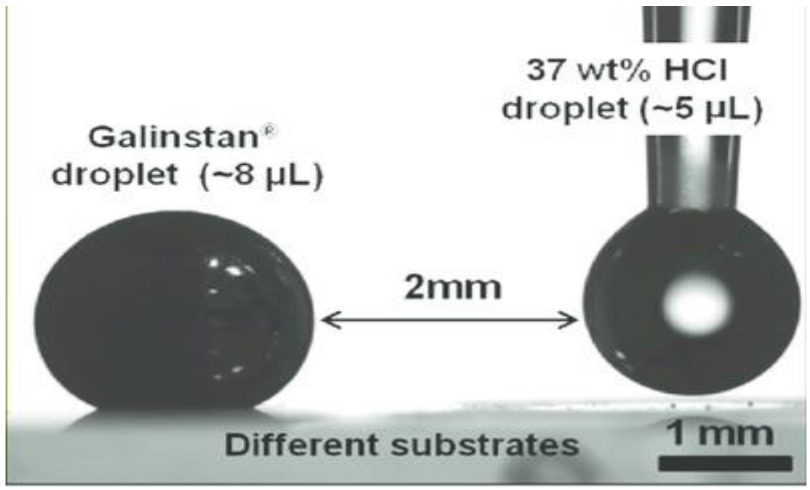


Figure 28. *HCl vapor treatment of Galinstan droplet on different substrates*. [32]

To compare the difference, three types of glass slides: a bare soda - lime glass slide, a Cytop-coated glass and Teflon coated glass slides are used in this process. [32] Using a pipette, Galinstan droplets are deposited on top of the substrates for contact angle measurement. Immediate change of contact angle is seen after this process. Figure 29 shows the Contact angle change of Galinstan droplets for three different substrates. Surface tension of the reduced oxide layer is also changed after HCl treatment. [32] Due to its viscoelastic state before treatment, Hysteresis change in surface tension change is seen during the measurement.

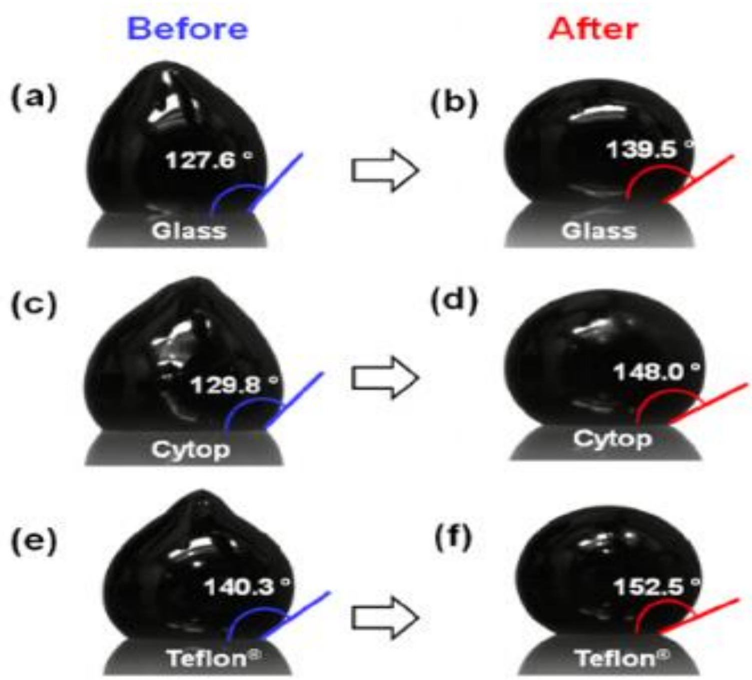


Figure 29. *Contact angle change of Galinstan droplets for three different substrates.* [32]

The oxide layer provides ability of the liquid metal alloy to stick quickly on any object or substrate. HCl vapor treatment plays a very effective part of this thesis work by removing the oxide layer and solving problem with wetting characteristics in an easy way. There is another study also found regarding the use of HCl to reduce the oxide layer. [32] Any of them can be included as a remarkable addition in the experimental set up of this thesis work.

4.6.2 HCl impregnated paper to remove viscoelastic oxide layer –

Hydrochloric acid impregnation method is a motive to improve lyophobic characteristic of a paper. It is an easy and very efficient method where HCl solution is used to remove the oxide layer of liquid metal alloy, which was also done by Kim, Daeyoung and his group. Hydropilicity of printing paper is treated with HCl, where the paper can be used as substrate. [34]

Printing paper which is broadly used in our daily life is an extremely hydrophilic substance due to its chemical structures. It has the ability to absorb almost all the liquid based inks. [34] The wetting characteristics of printing paper are analyzed after modifying with different substances. It is done to increase the lyophobicity of paper. Before HCl impregnation, inductively coupled plasma power mixed with fluorocarbon and Ar gas is supplied to printing paper. Like the previous HCl vapor treatment, 37 wt% HCl is applied to this combination. [35] In the clean room environment, around 8 micro liters Galinstan is deposited using a pipette on top of the surface. In the recent study, there were eight different papers were made from paper towel and printing paper to make a comparison between different treatment. Figure 30 shows the contact angle measurement of Galinstan droplet for various treatments.

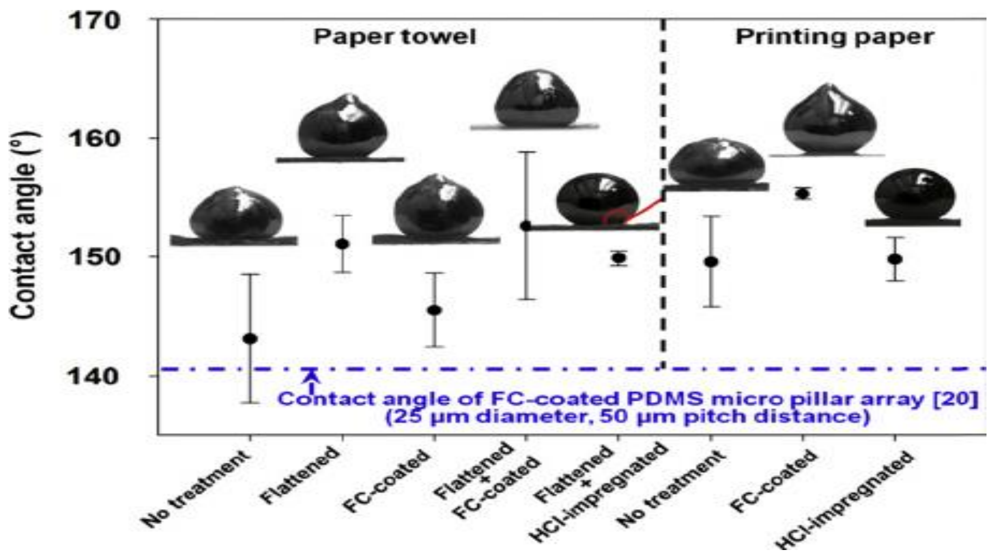


Figure 30. *Contact angle measurement of Galisntan droplet for various treatments.* [34]

The effect of HCl impregnation effect can be easily analyzed from the Galinstan droplet shapes on different surfaces. Only on the HCl treated paper, droplet is seems to be spherical. For non-treated papers, the contact angle was found to be very large which shows the, high lyophobic characteristics of paper against deposited Galinstan. Compared to other treatments, only the HCl impregnated papers has shown improvement of contact angle. It means that, it has improved more lyophobicity than any other treatments. Also, the removal of oxide layer was done through the direct reaction with HCl. Still, the Galinstan droplets were able to maintain their spherical shape even though it had to encounter with the viscoelastic behavior. To make further analysis on wetting and lyophobicity behavior, bouncing experiments were done for the oxidized Galinstan droplets. Figure 31 shows the time lapse image of Galinstan, dropping from 3 cm high for six different cases.

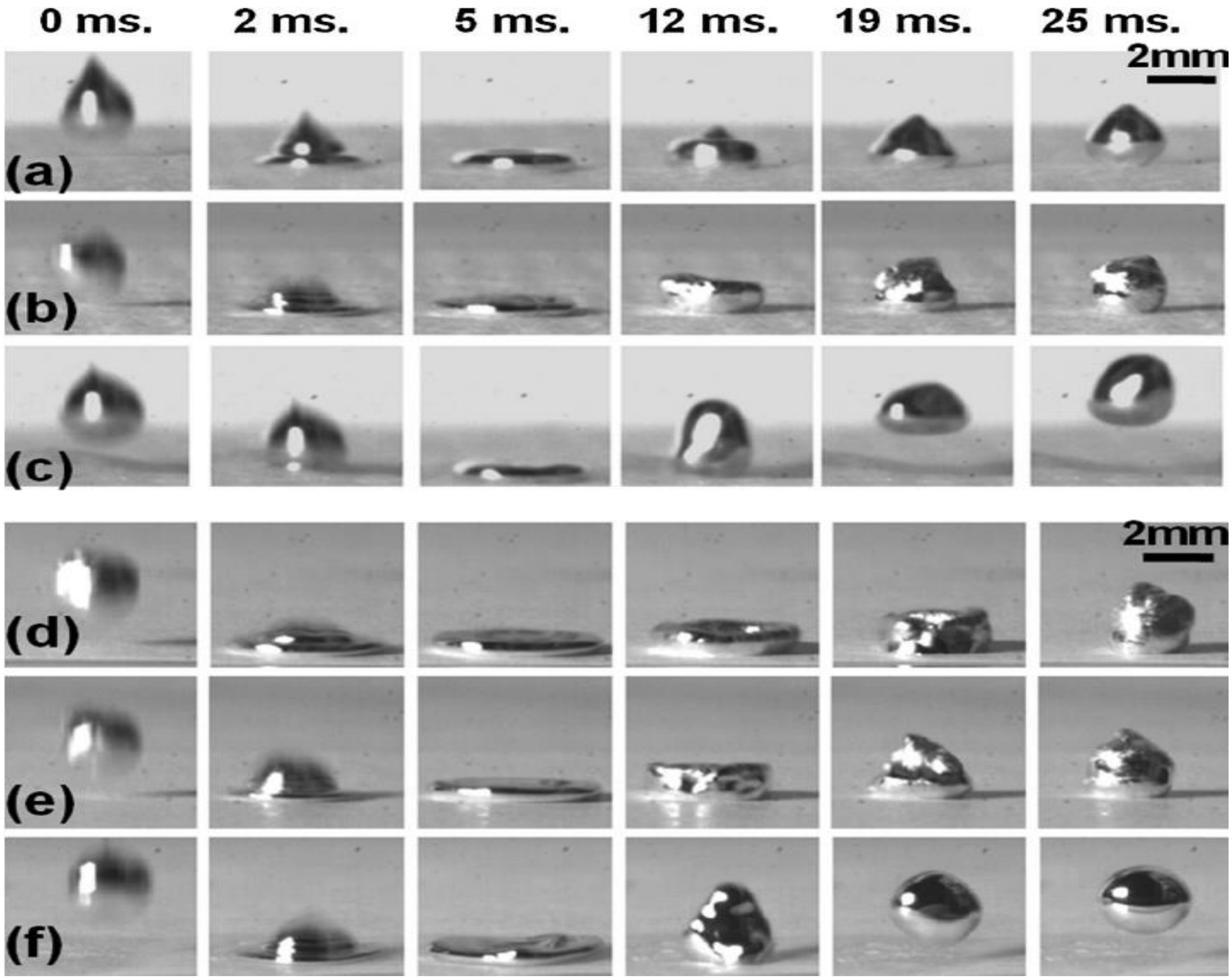


Figure 31. *The time lapse image of Galinstan, dropping from 3 cm high. a) the non-treated paper towel b) FC polymer coated paper towel c) HCl impregnated paper towel d) printing paper e) FC polymer coated printing paper f) HCl impregnated printing paper.* [34]

The liquid metal alloy was dropped from a certain distance to different surfaces for this step. Pictures of Fully oxidized Galinstan droplets were taken through a high speed camera with 1000 frames per second. [34] It can be seen from the bouncing experiment that, before hitting the surface all of the droplets were non-spherical due to its immediate oxidized layer. After hitting the surface the droplet was cracked except the HCl impregnated surface. Only because of HCl impregnation treatment, droplet made instant reaction with HCl and never cracked down during the hitting time. Also, the droplet was able bounce back to its spherical shape after hitting the surface only for HCl impregnated paper. From the figure it can be said that, the spherical form was fully recovered only for printing paper and this surface provided quicker recovery than paper towel surface (figure 32).

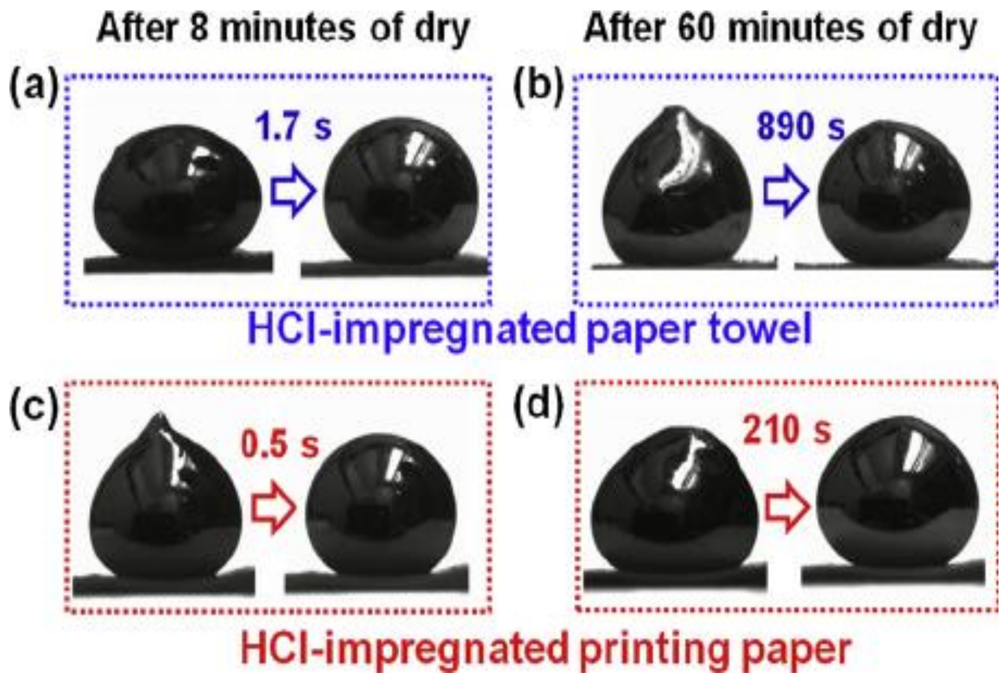


Figure 32. *Required time to change the shape of Galinstan droplet.* [34]

So, printing paper is considered as the better option for this work due to its faster chemical reaction and better oxide layer recovery. Thus, it is proved that, the non-wetting characteristics of liquid metal alloy can be exhibited from HCl impregnated paper and oxide layer can be removed after the reaction with HCl treated surface.

For this thesis work, removing oxide layer of Gallium based liquid metal alloy through HCl reaction, is a very effective way. But, maintaining such a sealed package with the original experimental set up of this thesis work is quite a tight and costly issue. Due to the state of current clean room set up and lack of time duration for this thesis work, it is not possible to include the whole package together in the laboratory.

4.6.3 Other methods –

Liquid metal droplet coated with ferromagnetic materials –

Liquid metal droplet can be manipulated using magnetic field induced ferromagnetic material coatings. [36] This idea was found from one of the work done by Kim, Daeyoung and Jeong-Bong Lee. The oxidized surface of Galinstan is coated with ferromagnetic materials to provide its non-wetting characteristics and it is controlled by applying magnetic field externally. Coating is done by using electroplated CoNiMnP layer or revolving liquid metal alloy droplet on Fe particle surface. [36]

For electroplating CoNiMnP, permanent magnet material neodymium iron boron (Nd-FeB) magnets are placed outside and it is kept parallel to each other. At the cathode Galinstan is placed at the bottom of the needle. [36] Figure 33 shows Schematic of the setup for electro-plating CoNiMnP.

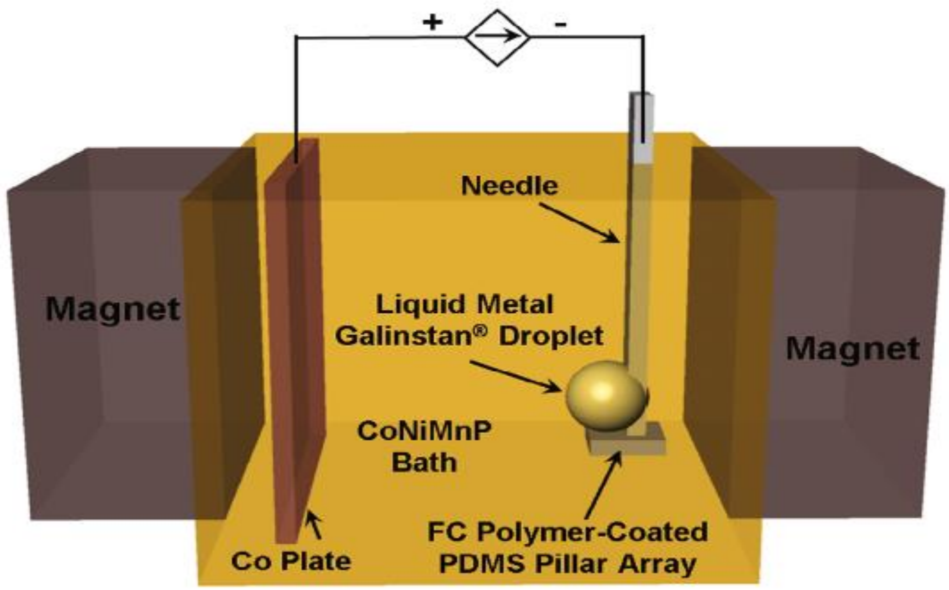


Figure 33. *Schematic of the setup for electro- plating CoNiMnP.* [36]

Galinstan is held using FC polymer coated PDMS pillar array. To provide continual supply of metal ions, Co plate is placed as anode. Electroplating is done by supplying 20 mA/cm^2 current density for 10 minutes. [36]

Another process to do the coating with ferromagnetic material is by revolving a droplet on top of Fe surface. [37] When it is done, droplet provides the non-wetting characteristics. Figure 34 shows the schematic of Galinstan rolling process over the Fe particle surface and Optical image of Fe particle coated liquid metal alloy. Fe particles are placed on top of the paper towel and Galinstan droplet is revolved over the surface. Due the movement of the surface the Galinstan is properly rolled within the substrate and the oxide layer of droplet is well attached to Fe material. [36] Thus, this process has the ability to provide thoroughly identical coating of Fe material.

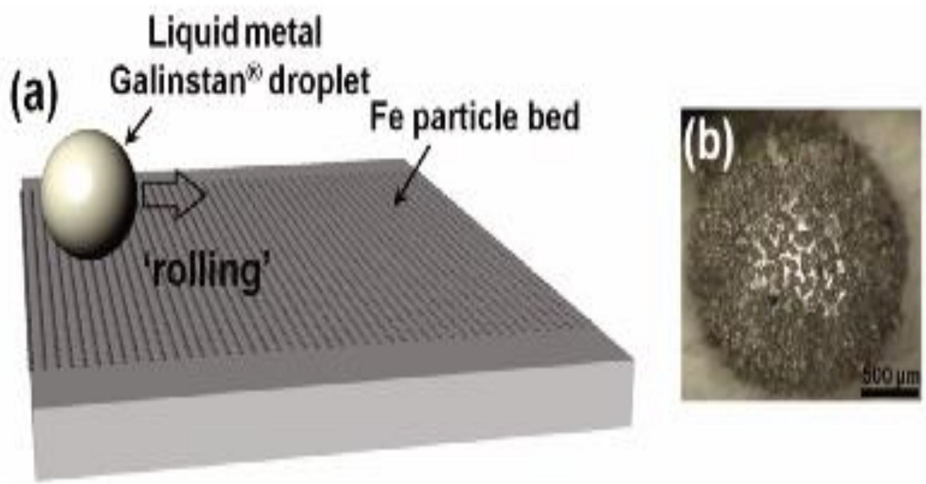


Figure 34. *a) Schematic of Galinstan rolling process over the Fe particle surface. b) Optical image of Fe particle coated liquid metal alloy.* [36]

Beside these methods there are some other processes tested in few recent research works to remove the oxidized layer and solving the wetting issues of Galinstan. [38] One of the methods was found from Michaud, Hadrien O., Joan Teixidor, and Stephanie P. Lacour. There, Gold thin film deposition on soft substrate was used as strain sensing element where the Gallium based liquid metal was placed on top of it to make interconnects. [19] Here, Chromium can also be used as the replacement of Gold. Cr/Au thin films are placed through by thermal evaporation through polyimide shadow mask. [19] Another research work was done by Kramer, Rebecca K., Carmel Majidi, and Robert J. Wood. There, masked deposition of Gallium Indium alloy was done using Tin foil. Tin foil was patterned on top of PDMS surface through photolithography. In this process, Tin foil was coated with Galinstan and it was done in a nitrogen filled environment to prevent liquid alloy from oxidizing. [18]

4.7 Encapsulation process –

The final step of the process would be the encapsulation of particular sample. For this the sample coated with Gallium based alloy should be kept in a nitrogen chamber for 24 hours to avoid any quick oxidation process and prevents the non-uniform wetting of the PDMS surface. [18] After removing the sample from Nitrogen chamber, the non-wetting part of Galinstan should be erased by thin film applicator. [18]It defines the height of the liquid alloy and helps to control the cross section of Galinstan deposited portions. The excess liquid metal alloy on PDMS surface can be removed by putting it into a de-ionized water bath. It removes the unwanted liquid alloy from the surface. [18]

In the next step, evaporation of remaining diluent would be done by placing it on a hot plate for several minutes. As the melting temperature of Galinstan is -19°C, Galinstan should be kept in a freezer, bellow it melting temperature to harden the Galinstan and maintain its form. [18] It is necessary to provide the intact form of liquid alloy in the further encapsulation process. [39] Then, the final layer of PDMS could be spin coated over the entire surface of the device to attach the liquid pattern into stretchable platform. [18] After that, the whole system will be ready to go for the final curing process. The time duration between the removal of sample from freezer and spin coating with PDMS surface should be carefully followed. Because, the temperature of the liquid alloy pattern should not get warm above the melting point to maintain the proper encapsulation process.

Finally, the liquid metal alloy deposited PDMS can be taken off from the glass slide substrate. It can be used for different applications through wiring the device with copper wire. It can be done externally after completing the encapsulation process in any particular positions. Then, the stretchable system will be ready for its mechanical testing and making inter connection between with the other flexible circuits. [18]

Chapter 5

Conclusions

As stretchable electronics, has gained very high popularity, nowadays several types of manufacturing methods have introduced in laboratory for different types of stretchable applications. [40] Using Gallium based liquid metal microfluidics has provided one of the most significant developments in printed and stretchable electronic devices. The higher conductivity and mechanical stability of this liquid metal alloy is the main reason behind its remarkable increase of interest in research laboratories. [41] More research work is needed to fabricate this microfluidic based electronic device in large scale.

The objective of this thesis work focused on a new fabrication method for Gallium based liquid alloy based stretchable electronics and its improvement. There are a few works already done using the same alloy. [42] But, there are too many steps involved in image patterning process which shows complexity in implementing those methods. The idea was to introduce a reliable and efficient method to improve several limitations of previous research works done on Galinstan. The Main focus of the work was to introduce a possible simple path to pattern particular images. To do this, surface energy modification of PDMS played a vital role here. Surface energy modification was done using plasma treatment process.

Plasma treatment of PDMS is the most significant step of this work. Plasma print station used here provided the important role to complete the whole method in fewer steps. Detailed description and principle was included in this paper for assistance. The variation of different levels of plasma power and its effect was shown through changing the plasma voltage. Numbers of plasma treatment repeats were increased to provide plasma stability.

The interconnection between the steps of plasma activation process was also provided for better understanding of the plasma print station. Plasma print head assembly and other different parts of the plasma print station were added here. Print station has gas flow for both oxygen and nitrogen plasma. Though no significant changes were seen, some of them were studied practically by varying the gas flow of the system. Particular images were patterned through plasma print station on top of PDMS. PDMS surface were plasma treated using maximum efficiency of the print station. There were more than 20 repeats of plasma treatment were done to have the maximum stability of plasma to provide smoother pattern after Galinstan deposition.

Galinstan deposition was done manually for this work. Droplets of liquid metal alloy were placed on top of plasma treated PDMS and the blade coating process was done using a stirrer rod. It is very important to do the blade coating as quick as possible. It helps to maintain better plasma stability of PDMS. All the samples were carried out very carefully from print station and Galinstan deposition was done in such a way that it didn't make any mess inside the laboratory. As it is a very sticky liquid, pre cautions were taken so that it didn’t get mixed up with other chemical materials inside the clean room environment. After blade coating every sample, PDMS were preserved carefully to see Galinstan characteristics on it.

Like some previous studies, here also Galinstan showed very much adhesiveness on the PDMS surface for most of the samples. [43] But, most of them were flooded and patterns seemed to be lost. In some cases similarity to the original pattern was found but it didn’t fulfill the expected level. The main reason for this unwanted result was investigated in this thesis work. It seemed, quick oxidation process of Gainstan has hampered its behavior on PDMS surface. The layer of deposited liquid alloy was easily oxidizing and the wetting ability was changed immediately. Though there was clear movement of Galinstan during deposition but later it behaved more like a Gel than a liquid. Then the oxidation process of Galinstan was studied briefly and it proved to be one of the big limitations of this work.

Contact angle measurement technique was also applied in this work to test the wetting ability of plasma treated PDMS. [44] Contact angle measuring steps for this particular liquid alloy was not that easy. Due to its properties, Galinstan detection seemed to be a bit tricky in controlling the droplets. For both treated and non-treated PDMS surface comparison was made for Galinstan droplets. For non-treated PDMS surface the contact angle found 131.5 degree and for PDMS surface treated with full efficient plasma treatment the angle was found 100.5 degree. There was a clear change of angle found in this case. But, it was not good enough to fulfill the expectation.

Galinstan oxidation seemed to be the one of the most challenging steps in this work. Several studies were investigated from different research works. The most of the solutions came from the chemical reactions with different states of HCl. Among them, HCl vapor was found to be one of the reliable sources where HCl converted Ga_2o_3 to $GaCl_3$ to remove the oxidized layer of PDMS. Under this approach, comparisons of contact angle for three different substrates were also shown in this paper. HCl impregnated paper is the type of solution that can be used to remove this oxidized layer. 37 wt% HCl was applied for both the cases to make the chemical reaction with Galinstan.

HCl impregnation method was briefly explained in this work. It is a very easy and efficient way where both paper towel and printing paper is used to remove the oxide layer of Galinstan. According to the work done by Kim, Daeyoung and his group, first the hydrophillicity of paper surface is reduced by using HCl solution on it. These HCl impregnated papers have the ability to behave with more lyophobic characteristics. Around 8 micro liters sized droplets of Galinstan were placed on to paper to modify the wetting behavior of liquid alloy. There are different comparisons between paper towel and printing paper are shown in this paper. Among these two paper surfaces printing paper was found better after analyzing the bouncing experiment. The time lapse images of Galinstan, dropping from 3 cm high were shown in this work to provide a better understanding. Instant reaction with HCl was found in these experiments. Among the two types of papers, printing paper provided faster chemical reaction and better oxide layer recovery.

As the removal of oxidized layer was one of the most concerning issues in this work, proper investigation was done to solve this problem. Some other methods were also introduced. Ferromagnetic materials can be also used in different ways to remove the oxidized layer. The Ferromagnetic material can be applied through electroplating and by rolling over the Galinstan droplet. Through this Ferromagnetic coating on liquid metal alloy, the wetting behavior can be changed by removing the oxidized layer. Beside the Ferromagnetic coating, the Gold thin film deposition on soft PDMS substrate is another solution to this limitation. Chromium and Tin foil can also be used in this case as the replacement of Gold. But, in these methods, the Galinstan deposition should be done inside the nitrogen chamber to avoid any kind of quick oxidation over Galinstan droplet.

These techniques involve significant steps in this work to remove the oxidized layer of Galinstan. But, the laboratory set up for oxidized layer removal process is quite tight and costly issue. Due to the state of current clean room set up and lack of time duration for this thesis work, it is not possible to include the whole package together in the laboratory.

Encapsulation process is the final step of this fabrication method. The possible encapsulation technique was also studied in this work. Among the fewer steps, evaporation is one of the most important parts of this process. It is done to remove the excess liquid alloy on PDMS surface. After that, the PDMS should be kept in a freezer below its melting temperature to harden the deposited Galinstan. Then, another layer of PDMS should be spin coated to attach the liquid alloy on stretchable platform. After the final curing process, the PDMS layer can be taken off to complete the encapsulation process. It is necessary to do the process inside nitrogen environment which was not possible in the current infrastructure of the clean room.

References –

[1] Jeong, Seung, Klas Hjort, and Zhigang Wu. "Tape Transfer Printing Of a Liquid Metal Alloy for Stretchable RF Electronics". *Sensors* 14.9 (2014): 16311-16321.

[2] "Flexible Printed Electronics: Past, Present, And Future | Industrial + Specialty Printing".*Industrial-printing.net*. N.p., 2016.

[3] "Printed, Organic & Flexible Electronics Forecasts, Players & Opportunities 2016-2026: Idtechex". *Idtechex.com*. N.p., 2015.

[4] "Material Challenge For Flexible Organic Devices". *Sciencedirect.com*. N.p., 2016.

[5] Jeong, Seung Hee, Klas Hjort, and Zhigang Wu. "Tape Transfer Atomization Patterning Of Liquid Alloys For Microfluidic Stretchable Wireless Power Transfer". *Sci. Rep.* 5 (2015): 8419.

[6] Li, Chun-Yi and Ying-Chih Liao. "Adhesive Stretchable Printed Conductive Thin Film Patterns On PDMS Surface With An Atmospheric Plasma Treatment". *ACS Appl. Mater. Interfaces* 8.18 (2016): 11868-11874.

[7] Kim, Jeonghyun et al. "Stretchable Electronics: Epidermal Electronics With Advanced Capabilities In Near-Field Communication (Small 8/2015)". *Small* 11.8 (2015): 905-905.

[8] Hussain, Aftab M. et al. "Wearable Electronics: Metal/Polymer Based Stretchable Antenna For Constant Frequency Far-Field Communication In Wearable Electronics (Adv. Funct. Mater. 42/2015)". *Adv. Funct. Mater.* 25.42 (2015): 6557-6557.

[9] Sun, Jiazhen et al. "Fabrication Of Bendable Circuits On A Polydimethylsiloxane (PDMS) Surface By Inkjet Printing Semi-Wrapped Structures". *Materials* 9.4 (2016): 253.

[10] "Stretchable Electronics That Quadruple In Length | Printed Electronics World". *Printed Electronics World*. N.p., 2016.

[11] Cheng, Shi and Zhigang Wu. "Microfluidic Electronics". *Lab on a Chip* 12.16 (2012): 2782.

[12] Khondoker, M A H and D Sameoto. "Fabrication Methods And Applications Of Microstructured Gallium Based Liquid Metal Alloys". *Smart Mater. Struct.* 25.9 (2016): 093001.

[13] Kuo, Po-Chin et al. "Mechanical Limitations Of Materials For Steel Foil Based Flexible Electronics". *MRS Proceedings* 1030 (2007): n. pag.

[14] Boley, J. William et al. "Direct Writing Of Gallium-Indium Alloy For Stretchable Electronics". *Adv. Funct. Mater.* 24.23 (2014): 3501-3507.

[15] "Galinstan | Chemistry Learner". *Chemistrylearner.com*. N.p., 2016.

[16] "Galinstan Metal Profile". *The Balance*. N.p., 2016.

[17] "The Galinstan fluid MSDS" (PDF). 2004

[18] Kramer, Rebecca K., Carmel Majidi, and Robert J. Wood. "Masked Deposition Of Gallium-Indium Alloys For Liquid-Embedded Elastomer Conductors". *Adv. Funct. Mater.* 23.42 (2013): 5292-5296.

[19] Michaud, Hadrien O., Joan Teixidor, and Stephanie P. Lacour. "Soft Flexion Sensors Integrating Strechable Metal Conductors On A Silicone Substrate For Smart Glove Applications". *2015 28th IEEE International Conference on Micro Electro Mechanical Systems (MEMS)* (2015): n. pag.

[20] Cheng, Shi and Zhigang Wu. "Microfluidic Stretchable RF Electronics". *Lab on a Chip* 10.23 (2010): 3227.

[21] "Microfluidic Electronics – SML". *Sml.me.cmu.edu*. N.p., 2016. Web. 30 Sept. 2016

[22] Zhu, Jiu Yang et al. "An Integrated Liquid Cooling System Based On Galinstan Liquid Metal Droplets". *ACS Appl. Mater. Interfaces* 8.3 (2016): 2173-2180.

[23] Morley, N. B. et al. "Gainsn Usage In The Research Laboratory". *Rev. Sci. Instrum.* 79.5 (2008): 056107.

[24] Liu, Tingyi, Prosenjit Sen, and Chang-Jin Kim. "Characterization Of Nontoxic Liquid-Metal Alloy Galinstan For Applications In Microdevices". *Journal of Microelectromechanical Systems* 21.2 (2012): 443-450.

[25] "SYLGARD® 184 5 G Clip-Pack | Sigma-Aldrich". *Sigmaaldrich.com*. N.p., 2016.

[26] "Manual μPlasmaPrint Station", (PDF). 2015

[27] "Mplasma Patterning And Inkjet Printing To Enhance Localized Wetting And Mixing Behaviour - Utpublications". *Doc.utwente.nl*. N.p., 2016.

[28] "SYLGARD 184 data sheet" (PDF), 2007.

[29] "Principles of Video Contact Angle Analysis, Medical". *www.wesrch.com*. N.p., 2011.

[30] Aidun, Cyrus K. and Nick G. Triantafillopoulos. "High-Speed Blade Coating". *Liquid Film Coating* (1997): 637-672.

[31] Madsen, Morten. "Blade Coating". *Plasticphotovoltaics.org*. N.p., 2016.

[32] Kim, Daeyoung et al. "Recovery Of Nonwetting Characteristics By Surface Modification Of Gallium-Based Liquid Metal Droplets Using Hydrochloric Acid Vapor". *ACS Appl. Mater. Interfaces* 5.1 (2013): 179-185.

[33] Li, Guangyong, Mitesh Parmar, and Dong-Weon Lee. "An Oxidized Liquid Metal-Based Microfluidic Platform For Tunable Electronic Device Applications". *Lab Chip* 15.3 (2015): 766-775.

[34] Kim, Daeyoung et al. "Hydrochloric Acid-Impregnated Paper For Gallium-Based Liquid Metal Microfluidics". *Sensors and Actuators B: Chemical* 207 (2015): 199-205.

[35] Li, Guangyong et al. "PDMS Based Coplanar Microfluidic Channels For The Surface Reduction Of Oxidized Galinstan". *Lab Chip* 14.1 (2014): 200-209.

[36] Kim, Daeyoung and Jeong-Bong Lee. "Magnetic-Field-Induced Liquid Metal Droplet Manipulation". *Journal of the Korean Physical Society* 66.2 (2015): 282-286.

[37] Kim, Daeyoung. "Microfluidic Platforms For Gallium-Based Liquid Metal Alloy".*Adsabs.harvard.edu*. N.p., 2014.

[38] Eaker, Collin B., M. Rashed Khan, and Michael D. Dickey. "A Method To Manipulate Surface Tension Of A Liquid Metal Via Surface Oxidation And Reduction". *Journal of Visualized Experiments*107 (2016): n. pag.

[39] Tabatabai, Arya et al. "Liquid-Phase Gallium–Indium Alloy Electronics With Microcontact Printing". *Langmuir* 29.20 (2013): 6194-6200.

[40] Bossuyt, Frederick, Thomas Vervust, and Jan Vanfleteren. "Stretchable Electronics Technology For Large Area Applications: Fabrication And Mechanical Characterization". *IEEE Transactions on Components, Packaging and Manufacturing Technology* 3.2 (2013): 229-235.

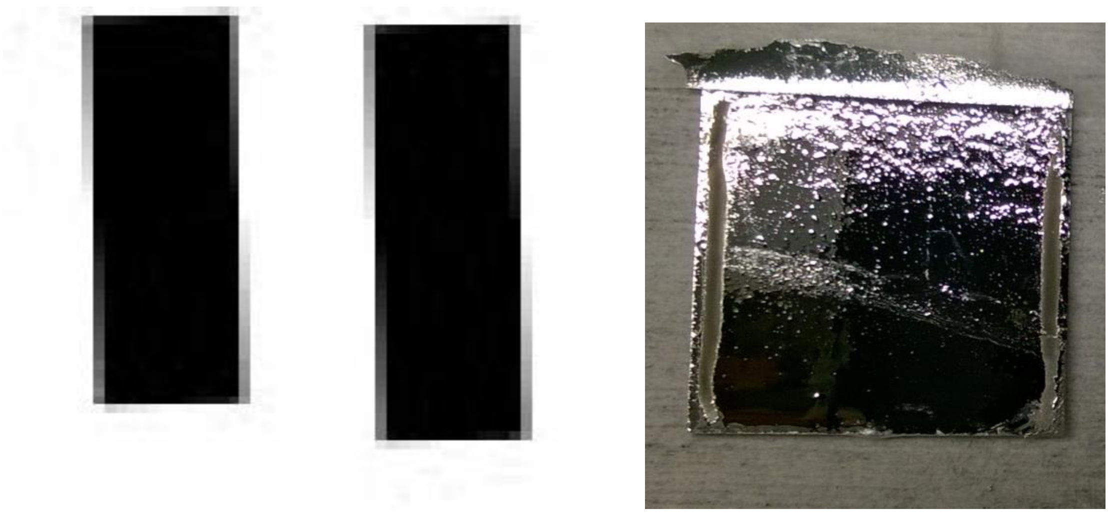
[41] "Galinstan - Physical Properties". *Liquisearch.com*. N.p., 2016.

[42] Kramer, Rebecca K. et al. "Effect Of Microtextured Surface Topography On The Wetting Behavior Of Eutectic Gallium–Indium Alloys". *Langmuir* 30.2 (2014): 533-539.

[43] Kim, Daeyoung et al. "A Super-Lyophobic 3-D PDMS Channel as A Novel Microfluidic Platform To Manipulate Oxidized Galinstan". *Journal of Microelectromechanical Systems* 22.6 (2013): 1267-1275.

[44] Bracco, Gianangelo and Bodil Holst. *Surface Science Techniques*. Chapter 1, Berlin: Springer, 2013. Print.

Appendix 1: Galinstan deposition on plasma treated PDMS (Sample 3)



a) b)

Figure A1. *Galinstan deposition on plasma treated PDMS (Sample 3). a) Original pattern (18mm×18mm) b) Spin coated PDMS at,7.00 kV voltage plasma.*

Plasma treatment specifications for sample 3 -

Voltage = 7.00 kV

Motions speed - 25 mm/s

Repeats – 7

Voltage frequency - 72.1 KHz.

Observations –

- Full bright plasma generation on PDMS is seen at 7.00 kV voltage in the screen through the camera.
- Two clear edges of the line pattern are visible on PDMS
- Plasma treatment circle is required to increase more than seven.
- Motion speed is increased to provide faster plasma treatment process.
- Pattern is lost and flooded though the ink movement was clearly visible when deposited on activated area.
- It is seemed to be very sticky on PDMS surface.

Appendix 2: Galinstan deposition on plasma treated PDMS (Sample 4)

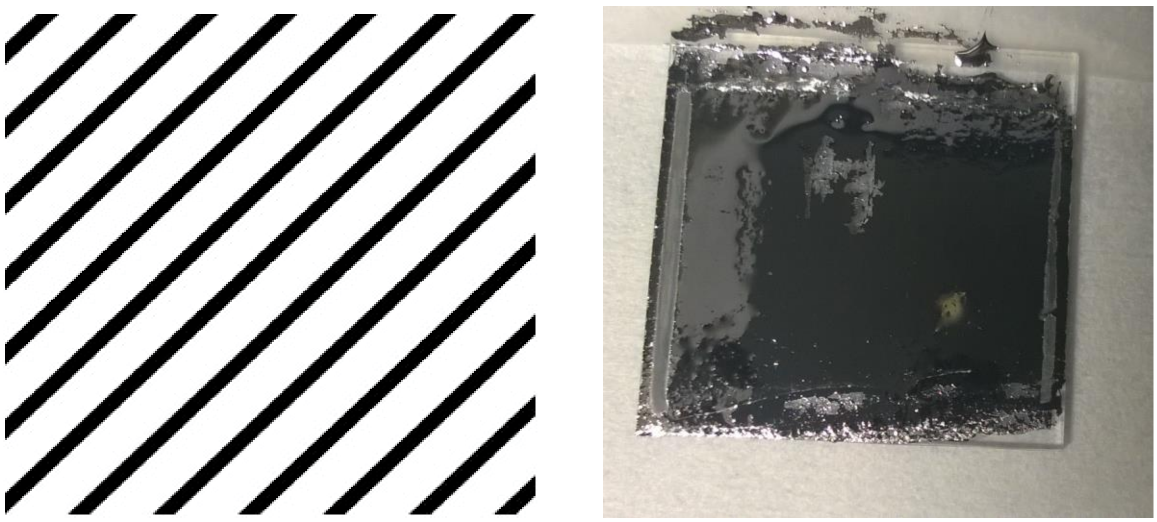


Figure A2. *Galinstan deposition on plasma treated PDMS (Sample 4). a) Original pattern (20mm×20mm) b) Spin coated PDMS at,7.50 kV voltage plasma.*

Plasma treatment specifications for sample 4 -

Voltage = 7.50 kV

Motions speed - 15 mm/s

Repeats – 15

Voltage frequency - 72.1 KHz

Observations –

- Full bright plasma generation on PDMS is seen at 7.00 kV voltages in the screen through the camera.
- Motion speed is decreased to 15 mm/s. higher motion speed is not supported by the print station for this particular pattern. So, It is required to adjust motion speed for different pattern types.
- Inappropriate Amount of Galinstan is deposited on this sample which made overflow of Galinstan in this case. So, it is seemed that the amount of liquid alloy is also an important factor for this experiment.
- Galinstan seemed to be very sticky on PDMS surface

Appendix 3: Galinstan deposition on plasma treated PDMS (Sample 5)

Figure A3.1. *Galinstan deposition on plasma treated PDMS (Sample 5). a) Original pattern (18mm×18mm) b) Spin coated PDMS at, 7.50 kV voltage plasma.*

Plasma treatment specifications for sample 5 -

Voltage = 8.0 kV,

Motions speed - 30 mm/s

Repeats – 20

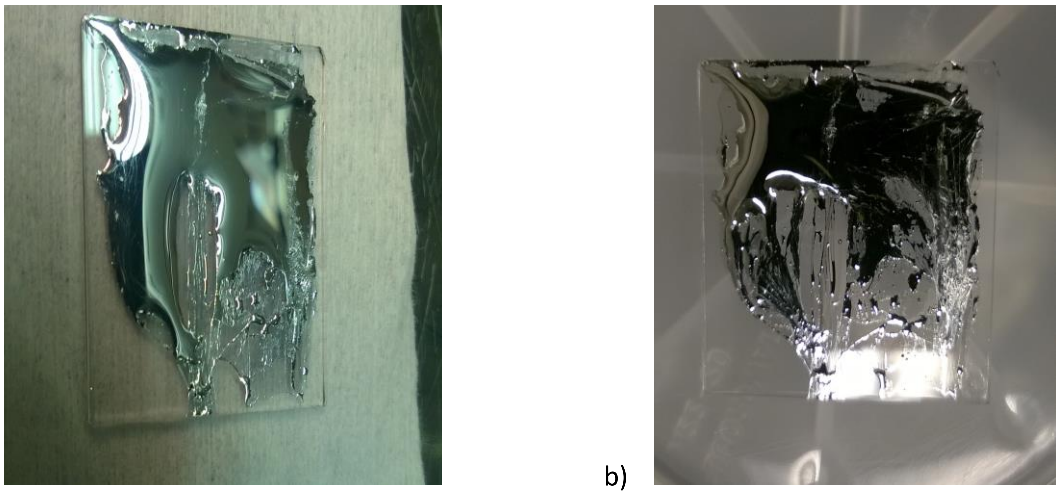
Voltage frequency - 72.1 KHz.

Observations –

- Brighter plasma generation on PDMS is seen in the screen through the camera as voltage increased up to maximum 8.0 kV.

- Plasma treatment cycle is also increased up to 20 provide higher plasma effect.
- Smaller droplet of Galinstan is used to deposit on top of PDMS.
- Pattern is not totally lost, but not a remarkably close to the original pattern.
- The liquid alloy is not overflown and seemed to be very adhesive on PDMS

In this sample better plasma is generated using maximum amount of voltage (8 kV) on PDMS surface. The treatment cycle is repeated up to 20 which is the maximum among all other samples. It is recommended not to increase the plasma treatment cycle to prevent the negative effect of plasma on print station. The process is examined with maximum amount of effort but the expected result is not found. To investigate the reasons, the process is investigated by analyzing few terms. It will be explained in the later part of this paper. To continue further analysis about Galinstan, sample 5 is kept in the clean room to observe changes of liquid alloy on PDMS. Figure 19 shows the Galinstan changes in two different time frames. There, no noticeable change is observed in couple of days after keeping in normal clean room environment.



a) b)

Figure A3.2. *Galinstan changes in two different time frames. a) day 1 b) day 3.*