A NOVEL FABRICATION METHOD FOR SURFACE INTEGRATION OF METAL STRUCTURES INTO POLYMERS (SIMSIP)

A Dissertation in
Industrial Engineering
by
Hector Carrion-Gonzalez

© 2010 Hector Carrion-Gonzalez

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Doctor of Philosophy

August 2010
The dissertation of Hector Carrion-Gonzalez was reviewed and approved* by the following:

Sanjay Joshi  
Professor of Industrial Engineering  
Dissertation Advisor  
Co-Chair of Committee

Stephen J. Fonash  
Bayard D. Kunkle Chair in Engineering Sciences  
Co-Chair of Committee

Richard A. Wysk  
Professor Emeritus of Industrial Engineering

Harriet Black Nembhard  
Associate Professor of Industrial Engineering and  
Bashore Career Professor

Amanul Haque  
Associate Professor of Mechanical Engineering

Paul Griffin  
Professor of Industrial Engineering  
Peter and Angela Dal Pezzo Head of Industrial and Manufacturing Engineering

*Signatures are on file in the Graduate School
Abstract

Recently developed flexible electronics applications require that the thin metal films embedded on elastomer substrates also be flexible. These electronic systems are radically different in terms of performance and functionality than conventional silicon-based devices. A key question is whether the metal deposited on flexible films can survive large strains without rupture. Cumbersome macro-fabrication methods have been developed for functional and bendable electronics (e.g., interconnects) encapsulated between layers of polymer films. However, future electronic applications may require electronic flexible devices to be in intimate contact with curved surfaces (e.g., retinal implants) and to be robust enough to withstand large and repeated mechanical deformations.

In this research, a novel technique for surface integration of metal structures into polymers (SIMSIP) was developed. Surface embedding, as opposed to placing metal on polymers, provides better adherence while leaving the surface accessible for contacts. This was accomplished by first fabricating the micro-scale metal patterns on a quartz or Teflon mother substrate, and then embedding them to a flexible polyimide thin film. The technique was successfully used to embed micro-metal structures of gold (Au), silver (Ag), and copper (Cu) into polyimide films without affecting the functional properties of the either the metals or the polymers. Experimental results confirm the successful surface-embedding of metal structures as narrow as 0.6 µm wide for different geometries commonly used in circuit design. Although similar approaches exist in literature, the proposed methodology provides a simpler and more
reliable way of producing flexible circuits/electronics that is also suitable for high volume manufacturing.

In order to demonstrate the flexibility of metal interconnects fabricated using the SIMSIP technique, multiple Au electrodes (5 μm and 2.5 μm wide) were tested using the X-Θ bending methodology. The X-Θ bending test captures data on the electrical resistivity of micro Au electrodes fabricated using the proposed SIMSIP technique by bending them at different angles between 0° and 180° up to 50 times. The data shows that the electrical resistivity of the Au electrodes remains constant (<1% variation) despite the interconnects being repeatedly subjected to extreme tensile and compressive forces during the X-Θ bending test. These results are significant from the perspective of flexible electronics and biotechnology applications since the fabricated thin films exhibit significant electrical stability, reliability and wear resistance.

These surface-embedded, flexible, and mechanically stable metal interconnects will enable the further development of new electronic products with applications in biotechnology (e.g., e-skin), space exploration (e.g., satellites), and microelectronics (e.g., flat panel displays). The SIMSIP technique is also a suitable process for the nanofabrication of flexible electronic devices in applications that require intimate contact with bendable curved surfaces (e.g., retinal implants).
Table of Contents

List of Figures .................................................................................................................. ix

List of Tables and Equations ........................................................................................... xiv

Acknowledgements ........................................................................................................... xv

Chapter 1. Introduction ........................................................................................................ 1
  1.1 Background .................................................................................................................. 1
  1.2 Motivation .................................................................................................................... 4
    1.2.1 Creating Metal Structures in Polymers .............................................................. 4
    1.2.2 Behavior of Flexible Electronics Under Bending Conditions ...................... 6
  1.3 Research Objectives .................................................................................................... 7
  1.4 Outline of the Dissertation ......................................................................................... 8

Chapter 2. Literature Review .............................................................................................. 10
  2.1 Flexible Electronics .................................................................................................... 10
  2.2 Types of Flexible Electronics .................................................................................... 15
  2.3 Strength Characteristics of Metallized Films .......................................................... 17
    2.3.1 Strength of Freestanding Thin Metals .............................................................. 17
    2.3.2 Strength of Metallic Films Bonded to Polymers ............................................. 18
  2.4 Overview of Metal-Polyimide Chemical Bonding ..................................................... 22
    2.4.1 Atomistic Modeling of Metal-Polyimide Interfacial Properties ..................... 23
2.4.2 Diffusion of Metals Onto Polyimide ................................................................. 24

Chapter 3. Initial Exploration ...................................................................................... 26

3.1 Replicating a Published Fabrication Method ......................................................... 26

3.2 Shadow Mask vs. Bi-layer Resist for Micro-Metal Features ................................. 30

3.3 Application of the TFOS and MPT Molecular Monolayers .................................. 32

3.4 Stack Layer for Transfer of Metal Patterns to PDMS .......................................... 34

3.5 Summary ............................................................................................................... 35

Chapter 4. Novel Fabrication Techniques .................................................................. 39

4.1 Fabrication Techniques ......................................................................................... 39

4.1.1 PDMS Metallization Fabrication Technique .................................................... 39

4.1.2 SIMSIP Fabrication using Quartz Mother Substrate ....................................... 45

4.1.3 SIMSIP Fabrication Using Teflon Mother Substrate ....................................... 48

4.1.4 Fabrication of Metal Patterns on Top of Polyimide Film (Control) ............... 49

4.1.5 SIMSIP Nano Fabrication Technique ............................................................... 51

Chapter 5. Testing Method for Bending Radii in Flexible Films ................................. 53

5.1 The X-Ø System ................................................................................................... 53

5.2 The Design of the Thin Film Bending Machine .................................................... 55

5.2.1 The Right Clamp Arm \((d_i, a_i)\) ...................................................................... 56

5.2.2 The Left Clamp Arm \((a_i)\) ........................................................................... 60
7.3 Future Research Directions ................................................................. 102

7.3.1 Thin-film Transistors (TFTs) .......................................................... 103

7.3.2 RFID Antennas ............................................................................... 103

7.3.3 Semiconductor Sensors (SCS) .......................................................... 104

7.4 Conclusions ......................................................................................... 105

References .................................................................................................. 107
List of Figures

Figure 2-1 A photograph of the RFID wetness sensor (Yang, 2008) ........................................... 13

Figure 2-2 Electronics on flexible materials, (a) Flexible metal foil with polysilicon TFT circuits (Troccoli, et al., 2006), (b) Picture of the calcium test apparatus used for the flexible barrier sample (Chen, et al., 2007), (c) Optical micrograph of the flexible SWCNT TFT (Takenobu, et al., 2009) .......................................................................................................................... 14

Figure 2-3 Metal film on top of polymer film ................................................................. 15

Figure 2-4 Metal film fully-embedded between two polymer films............................. 16

Figure 2-5 Surface-embedded Au in polymer................................................................ 17

Figure 2-6 Freestanding metal film................................................................................ 18

Figure 2-7 Schematic diagram of PMDA-ODA polyimide cluster model used by Ramos (2002) ............................................................................................................................................. 24

Figure 3-1 Schematic representation of two fabrication methods used to embed metallic patterns in PDMS (Lee, et al., 2005) .............................................................................................................................. 28

Figure 3-2 Optical microscope pictures of the initial experiment for PDMS metallization, (a) TFOS and MPT agglomeration on Au thin film, (b) Broken 5 µm Au patterns on PDMS ..... 29

Figure 3-3 Gold patterns on hard substrate, (a) Gold pattern with shadow mask, (b) Gold pattern after bi-layer resist was removed from substrate ......................................................... 31

Figure 3-4 Gold (Au) electrodes embedded in Parylene D, (a) Electrode pad, (b) Four 5 µm wide electrodes......................................................................................................................... 33

Figure 3-5 Gold (Au) electrodes embedded in PDMS bonded to a lab slide glass, (a) 5 µm wide electrodes, (b) Electro pad .......................................................................................................... 35
Figure 4-1 Illustration of PDMS metallization fabrication steps: (a) Si substrate with a 
SiO₂ layer, (b) TFOS layer on SiO₂, (c) stack layer on top on TFOS layer, (d) spin-on bi-layer 
resist, (e) UV exposure and developing, (f) deposition of Au and lift-off of bi-layer resist, (g) 
MPT layer on Au, (h) PDMS and slide glass on substrate, (i) separation of mother substrate from 
stack later/PDMS, (j) wet etching of Ni, (k) Au structure on PDMS (no steps between Au and 
PDMS structure) ................................................................. 44

Figure 4-2 SIMSIP Fabrication Technique ................................................................. 47

Figure 4-3 Control Fabrication Technique............................................................... 50

Figure 4-4 SIMSIP Submicron Fabrication Technique ............................................ 52

Figure 5-1 The bending systems used to test flexible substrates, (a) Schematic of the X-Θ 
bending system, (b) Schematic of the X-Y-Θ bending system ........................................ 54

Figure 5-2 Image of the metallized films tested with the X-Θ system, (a) Schematic 
drawing of the metal-polyimide film, (b) Picture of a tested sample ..................................... 55

Figure 5-3 Illustration of the bending for a 10 mm long polymer film (a) Length of thin 
polyimide film (L₀) in the flat position, (b) Distance between the device clamps when sample of 
length L₀ is bent to 180° ................................................................. 56

Figure 5-4 Design of a fixture guide used for the ‘right clamp arm’ of the X-Θ system... 57

Figure 5-5 Design schematic views of the triangle guide fixture and the right clamp 
guide bar .................................................................................................................. 58

Figure 5-6 A conceptual dry run for the operation of the right clamp arm................. 59

Figure 5-7 Illustration of the left clamp rotation, (a) The use of the length of a circular 
area equation to calculate the length of the left guide bar (2.3 mm), (b) The estimated parameter 
values X, α for the left clamp arm ............................................................................. 60

Figure 5-8 Design schematic views of the string guide fixture and the left clamp guide 
bar .......................................................................................................................... 62
Figure 5-9 A conceptual dry run for the operation of the left clamp arm..........................63

Figure 5-10 The bending machine used to bend thin polyimide film, (a) A top view of the bending machine, (b) The clamp separation is 10.4 mm at $\Theta = 0^\circ$, (c) The clamp separation is 6.4 mm at $\Theta = 180^\circ$, (d) A side view of the measurement system used to track the contraction displacement of the bending machine ...............................................................................................................................65

Figure 5-11 Schematic drawing of the elements targeted for measurement in the validation run ...............................................................................................................................................................66

Figure 5-12 A graphical representation of bending angles ($\Theta$) 45° and 135°....................67

Figure 5-13 Film in tension or compression testing, (a) Au-interconnect is in tension stress, (b) Au-interconnect is in compression stress...............................................................................................................................70

Figure 6-1 Illustration of the Step-And-Grow electrodes, (a) Schematic of the electrode layout, (b) Optical microscope image of 200 nm PANI nanowires..................................................................................................................72

Figure 6-2 AFM images of 5 µm electrodes on substrates, (a) A 5 µm electrode embedded in a SiO$_2$ substrate, (b) A 5 µm electrode embedded in PDMS.................................................................................................73

Figure 6-3 A polyimide film embedded with gold features being separated from the quartz substrate ..................................................................................................................................................................74

Figure 6-4 Optical images of surface integration of metal structures into polyimide (SIMSIP), (a) Optical images of the geometrical features in the photomask, (b) SIMSIP Au patterns in polyimide film, (c) SIMSIP Ag patterns in polyimide film, (d) SIMSIP Cu patterns in polyimide film.................................................................................................................................75

Figure 6-5 FESEM images of the metal pattern geometries in SIMSIP samples, (a) and (c): Circle and square metal patterns geometries from 16 µm to 2µm wide, (b) and (d): Magnified images of the 2 µm wide metal pattern features .............................................................................................................................................76

Figure 6-6 SIMSIP AFM images, (a) Au wire (100 nm), (b) Ag wire (100 nm), (c) Au wire (30 nm), (d) Cu wire (30 nm) fabricated on a quartz-DSP substrate..................................................................................77
Figure 6-7 Scotch tape test (Control sample on the left side and SIMSIP sample on the right side) ........................................................................................................................................78

Figure 6-8 SIMSIP process with Teflon sheets, (a) optical image of the Au geometrical pattern design in the polyimide film, (b-d) AFM and FESEM studies show a complete transfer of Au metal patterns with 2 µm wide features (100 nm thick) ........................................................................80

Figure 6-9 Electrical conductivity of SIMSIP Au-interconnects ..............................................82

Figure 6-10 AFM Images of Au-interconnects (5 µm wide), (a) Control Au-interconnect on polyimide film, (b) SIMSIP Au-interconnect embedded in the surface of a polyimide film...83

Figure 6-11 Resistance measurements for SIMSIP 10 µm samples using the X-Θ system, (a) SIMSIP Au-interconnects 10 µm wide under bending tension test, (b) SIMSIP Au-interconnects 10 µm wide under bending compression test ..................................................85

Figure 6-12 Resistance measurements for SIMSIP 5 µm samples using the X-Θ system, (a) SIMSIP Au-interconnects 5 µm wide under bending tension test, (b) SIMSIP Au-interconnects 5 µm wide under bending compression test ..................................................86

Figure 6-13 Cycling loading bending of flexible 2.5 µm Au-interconnects, (a) Resistance ratio of Au-interconnects 2.5 µm wide during tension cycling loading, (b) Resistance ratio of Au-interconnects 2.5 µm wide during compression cycling loading........................................88

Figure 6-14 Cycling loading bending of flexible 5 µm Au-interconnects, (a) Resistance ratio of Au-interconnects 5 µm wide during tension cycling loading, (b) Resistance ratio ofAu-interconnects 5 µm wide during compression cycling loading .............................................90

Figure 6-15 FESEM images of Au-interconnects after compression cycling loading, (a) Control 2.5 µm wide Au-interconnect, (b) SIMSIP 2.5 µm wide Au-interconnect .......................91

Figure 6-16 SIMSIP Nano validation images, (a) optical image of the Au geometrical pattern design in the polyimide film, (b-d) AFM and FESEM studies show a complete transfer of Au metal patterns with 2 µm features wide (100 nm thick)...................................................93

Figure 6-17 Electrical conductivity of SIMSIP Submicron Au-interconnects .........................94
Figure 7-1 Conceptual diagram of the SIMSIP fabrication method used in a continuous very-low-cost manufacturing process of organic electronic devices.
List of Tables and Equations

Table 5-1 Estimated values for the bending process of the left clamp arm .................. 66

Table 5-2 Results from the 12 validation runs on the assembled X-Θ bending machine . 68

Table 5-3 Statistical values for the bending system angles ($\alpha_1$, $\alpha_2$, $\Theta$) errors .............. 69

Table 6-1 Resistivity measurements of Au-interconnects ................................................. 81

Equation 6-1 Electrical resistance formula ........................................................................ 89

Table 6-2 Comparison of different fabrication techniques used for flexible electronics ... 96
Acknowledgements

I am deeply indebted to Dr. Sanjay Joshi and Dr. Stephen J. Fonash for their advice, direction, and support. I certainly could not have completed this dissertation without their constant guidance and encouragement. Together, they have demonstrated a thirst for knowledge, commitment to excellence, and compassion for others, all of which have helped me to be a better graduate student and human being. I am thankful to Dr. Richard A. Wysk, Dr. Harriet Black Nembhard, and Dr. Amanul Haque for their generosity in sharing their knowledge, experience, and time while serving on my committee.

I am thankful for the nanofab team at Penn State: Guy Lavalle, Mike Rogosky, Shane Miller, Andrzej Mieckowski, and Tad Daniel. Their help, guidance and suggestions were invaluable. A special note of thanks to Dr. Shawn A. Keebaugh from CNEU for teaching me the “special technique procedures” performed on the nanofab equipment and stations.

I wish to express my sincere thanks to all my wonderful friends at Penn State for their support. Special thanks go to my best friends at Penn State: Pranav Garg, Rohan Shirwaiker, Rachel Abrahams, Zhi Yang and Chumpol Yuangyai. I also want to thank Mr. Daniel Supko and Mr. Randy Wells, technicians in the PSU FAME lab.

I have to thank my parents, who have always been there to give me everything I needed to succeed in life. Finally, and most importantly, I want to thank my daughter Carin and Lui for her love and support over all these years. They are constant source of love, joy, support and motivation.
Chapter 1.

Introduction

1.1 Background

During the past decade, focus on the design, fabrication and application of large-scale flexible electronics has risen sharply. With the advent of mechanically flexible electronics, mass production of many products hitherto constrained by the rigidity of inflexible substrates can now become a reality. Such products include deployable active antennas, large area displays, and flexible sensor arrays and electronic artificial skin (e-skin) for prosthetic applications. However, with currently available technologies, the inability to consistently and easily produce high quality, flexible, active electronic elements and interconnects has been a persistent problem and a significant inhibitor to mass production (Someya, et al., 2005).

Flexible electronic surfaces are conformable skin-like structures with large surface areas, high mechanical flexibility, stretchability, and multifunctional capabilities. These electronic systems are radically different in terms of performance and functionality than conventional silicon-based devices (Lacour, et al., 2005). Such structures are built on flexible substrates, which can be made to conform to any surface shape, once or many times. Applications include antenna arrays, nondestructive health monitoring “skins”, electrotexiles, flexible displays, smart airplane wings, and smart prosthesis (Chen, et al., 2007; Feili, et al., 2006; Kim, et al., 2009; Lumelsky, et al., 2001; Forrest, 2004, Gray, et al., 2004). The field of biomedical engineering is particularly benefitted by these types of technological advances, as biocompatible stretchable
electronics can enable the development of electrically and mechanically matched interfaces between machines and living tissues (Lacour, et al., 2005). In addition, future prosthetic applications may require electronic flexible devices to be in intimate contact with curved surfaces (e.g., retinal implants) (Peterman, et al., 2003), and to be robust enough to withstand large and repeated mechanical deformations (e.g., joint prostheses or electronic skin) (Wagner, et al., 2004; Someya, et al., 2005; Engel, et al., 2005). In many of these applications it is necessary that the flexible substrates, with their electronic circuits, be in intimate contact with curved surfaces and be able to withstand repeated mechanical bending deformation (Peterman, et al., 2003; Wagner, et al., 2004; Someya, et al., 2005; Engel, et al., 2005; Chen and Ding, 2007; Leung, et al., 2006). Central to continued advances in high-performance flexible electronics is the development of flexible electronic surfaces that are capable of both bending and stretching while retaining their functionality while in use. Equally important are the flexible and durable polymer substrates that have attracted significant interest as a pathway to low cost and large area electronics. Conventional micro-nano fabrication processes such as vacuum deposition and photolithographic patterning have been well developed for use with polymeric substrates (Zschieschang, et al., 2003; Redinger, et al., 2004). A key question is whether the metal electrodes and interconnects basic to the circuits on these polymer materials can maintain their polymer substrate integration, mechanical integrity, and electrical resistance in these application situations.

Among the polymers suitable for microelectronics applications, polyimides (PI) have received increased attention in flexible electronics due to their good mechanical strength, higher
glass transition temperature, low dielectric constant, electrochemical stability, and flexibility (Soane, 1989; Kraft, et al., 2000; Briand, et al., 2006; Ryosuke & Akira, 2007; Tsuyoshi, et al., 2007). For all these reasons, polyimides have been widely used in microelectronics as dielectric spacing layers, protective coatings, and substrates for thin metal films, replacing traditional inorganic insulators such SiO$_2$ in many applications.

Although there are multiple fabrication techniques for thin flexible electronics, a research gap exists for fully bendable and electrically stable electronic devices made of a single flexible polymer layer. The research presented in this dissertation, describes a new fabrication method for forming surface integrated metal patterns within thin and flexible polymer films. The process is extremely simple and allows full lithography capabilities to be employed, permitting complex metal patterning. The process is also fully compatible with the practice of positioning metal structures and active devices on the neutral plane, if desired. Optionally, the surfaces can be chemically treated prior to application to further increase bonding to the polymer. This technique allows for the creation of a planar functional surface without any step heights between the metal patterns and the polyimide surface. We demonstrate our process, which we term surface integration of metal structures into polymers (SIMSIP), by embedding different metals such as Au, Ag, and Cu into polyimide while using 2 different mother substrates, and different metal geometries and dimensions ranging from 600 nm to 16 µm.
1.2 Motivation

1.2.1 Creating Metal Structures in Polymers

Metallic films bonded to polymeric substrates have been studied and extensively in circuit manufacturing (Suo and Li, 2007; Kuo, et al., 1994; Lu, et al., 2007; Shinozaki, et al., 1998). Compared with electronic devices on rigid substrates such as Si, metal features in flexible polymer substrates can be used to produce robust, lighter weight, and economical electronic devices that are capable of absorbing mechanical stresses. There are three main methods for metallizing flexible polymer films. The most commonly used fabrication method deposits the metal elements on top of the polymer film (Ono, et al., 1985; Xiang, et al., 2005; Suo and Li, 2006). Another approach fully-embeds the metal elements between two layers of polymer films (Befahy, et al., 2007; Kim, et al., 2008). The third and the most recently studied approach embeds the metal into the surface of the polymer film (Lee, et al., 2005; Lim, et al., 2006).

Although the top of the film approach is currently more popular, there are some inherent drawbacks associated with it. For example, a metal film grown directly on a polymer film can be easily damaged or debonded during the device’s operation (Chiu, et al., 1994; Alaca, et al., 2002; Lacour, et al., 2003; Schmid, et al., 2003; Li, et al., 2005; Suo and Li, 2007). This characteristic affects the reliability of flexible electronic devices when their flexible substrates are bent. The metal films debond and break with parallel cracks that run through them at the strain locations.
In order to mitigate this problem, fabrication techniques have been reported for fully-embedding metal structures between PDMS films (Befahy, et al., 2007; Kim, et al., 2008). Approaches developed for fully embedding metal structure into polymers tend to provide good bendable characteristics, support micro and nano scale elements, and provide good resistance to wear and tear. However, devices fabricated using such approaches are subject to interconnection problems and uneven surfaces.

Recently developed fabrication methods for surface embedding metal features in polymers have shown the potential to overcome many of the drawbacks associated with the prior two approaches. In these methods, metal patterns are fabricated on a solid substrate and then embedded into the surface of PDMS film instead of direct metal patterning onto the polymer (Lee, et al., 2005; Lim, et al., 2006). These new methods allow the metal elements to have better adherence to the polymer because 3 of the 4 metal surfaces of a rectangular cross-section can be used to anchor it. This provides more surface area for chemical bonding between the metal and the polymer film. These techniques were first used to fabricate a curved convex PDMS photomask. These fabrication techniques are expected to produce flat functional surfaces without step heights between the metal and polymer films, although this has not been tested. The flat metallized polymer surfaces can then be used for the integration of other electronic devices (e.g., transistors, sensors) in order to perform specific functions. Also, this technique eliminates the sometimes cumbersome process of polishing surfaces in the fabrication of electronics (Adam, et al., 2010). Currently these techniques have been tested only using gold
These fabrication techniques tend to stretch and buckle the Au films that are transferred onto flexible PDMS films.

In this work, a novel fabrication technique for surface embedding metal patterns (e.g., interconnects) into polymers without any buckling, step heights or mechanical hindrances is presented. This approach can aid the development of ongoing applications in flexible circuits (e-skin), flexible antennas (RFIDs), and flexible displays.

1.2.2 Behavior of Flexible Electronics Under Bending Conditions

Mechanical failure, such as the rupture and debonding of metal interconnects, poses a significant challenge. Low and stable contact resistance is a universal requirement for all electrical interconnects when cycled through stretching and relaxation. A key question is whether the metals on flexible polymers can survive large bending strains without rupture. This topic has attracted much research attention in recent years (Lacour, et al., 2005).

Limits in present day electronics technology prevent the manufacture of flexible and wear-resistant electronics such as e-skin, but the needs for it are increasing. Flexible electronics represent a new paradigm in sensing and control. Flexible and mechanically-stable SIMSIP electronic devices will enable researchers to develop new inexpensive consumer electronics products, including displays and printers, as well as new ways to store and share information in products similar to electronic paper.

Although several mechanical deformation geometries of conforming substrates are possible (e.g., hemispherical, helical, twisted), the simplest configuration that a rollable device
must be able to withstand is bending around a cylinder of a given radius. Conceptually, the simplest approach to the characterization of failure due to bending in a cylindrical geometry is to use a large number of identical samples, in conjunction with a set of mandrels of varying diameters, bending each sample around a mandrel at a similar rate, while applying a similar pressure (Grego et al., 2005; Lewis et al., 2005). However, the mandrel testing approach has drawbacks associated with it which makes it inadequate for comprehensively testing flexible electronics. For example, the results from the test are limited to a single radius of curvature being tested and testing for continuous cyclic loading also becomes infeasible (Cai et al., 2009; Wang et al., 2006). This approach necessitates many more tests and many more samples to statistically analyze failure as a function of radius. A better approach is the X-Y-θ system proposed by Grego et al. (2005) and the system proposed by Sun et al. (2005). Their approach was to bend the flexible films by using a mechanical apparatus that could simultaneously increase the angle at the edges of the film and reduce the distance between these edges. This them to test these films for a complete range of bending angles (0° to 180°) in a cyclic manner. However, a new bending technique which eliminates the need for movement in the Y-axis (Grego et al., 2005) and constant adjustments of needle electrical probes during a the bend cycle (Sun et al., 2005) is desired.

1.3 Research Objectives

The primary goal of this research is to generate knowledge by developing a novel fabrication technique for surface integration of metal structures into polymers (SIMSIP) for use in flexible electronics. The resulting samples will be evaluated under bending and cycling
loading conditions for electrical characterization. The specific objectives of this work are as follows:

1) Surface integration of metal structures into flexible polymers. Development of a novel fabrication technique that can support micron sized (≥ 2 µm) structures of different metals (e.g. Au, Ag, Cu) in flexible polymers (e.g. polyimide) without producing steps heights between the metal features and the polymer film.

2) Definition of critical process parameters. Define process parameter values for critical steps in the fabrication technique used for metallization of polyimide.

3) Electrical characterization of SIMSIP interconnects. Test and analyze electrical characteristics of SIMSIP interconnects under bending and cyclic loading conditions.

4) Exploration of process scalability. Study the feasibility of integrating nano-scale features in flexible polymers using SIMSIP.

1.4 Outline of the Dissertation

This dissertation is organized as follows. Chapter 2 presents a literature review related to the specific problems addressed in this research. In Chapter 3, fabrication techniques for surface integration of metal structures into polymers (SIMSIP) are discussed. Chapter 4 presents the X-Θ bending system for electrical characterization of samples fabricated using SIMSIP. A discussion of the preliminary results for surface-embedding thin Au metal structures in PDMS using previously proposed techniques (Lee, et al., 2005; Lim, et al., 2006) are presented in Chapter 5, followed by the experimental results from this research in Chapter 6. This
dissertation concludes in Chapter 7 with a discussion of the contributions, limitations and research extensions related to this research.
Chapter 2.

Literature Review

In this chapter, an introduction to flexible electronics and a discussion on their desirable characteristics and applications is presented. Then, the types of design architectures for flexible electronics are explained. The last section provides an introduction to the mechanical strength of metallized films.

2.1 Flexible Electronics

In recent years, the ability of polymers to function as semiconductors, diodes, and transistors in polymer integrated circuits has aroused the attention of both industry and academia (Xu, et al., 2002; Hattori, et al., 2008; Baklar, et al., 2010). Flexible electronics are attracting significant attention because of the potential advantage of being able to form three-dimensional (3D) circuits by using multilayer techniques (Mei, et al., 2005; Liu, et al., 2009). Flexible electronics are unique because they offer mechanical strength and flexibility, high density electrical interconnects, DC power distribution, and electro-magnetic compatibility (EMC) solutions within one integrated package (Cauwe, et al., 2006; Doyle, et al., 2007). Additionally, flexible interconnects enable the development of highly compact electronic packages (e.g., portable video cameras, automotive electronic systems, and medical equipment) with little “empty” volume, by allowing for the use of discrete electronic modules connected by flexible strips that can conform to the irregular contours of a unit (Stampanoni and Schmidt, 2000; Bock, et al., 2003). This integrated nature is advantageous because it offers a complete
electrical and mechanical solution, often for less cost than alternate solutions. Unfortunately, the method of forming metal wires on such flexible electronics has not yet been fully explored, since the compatibility of the traditional lithography process with organic compounds is limited (Sidler, et al., 2008; Barbu, et al., 2009).

While the demands for higher performance, lightweight, portable systems has spurred the development of flexible electronic packaging, these same needs have driven the flat-panel display (FPD) industry to pursue the development of active control circuitry on flexible substrates, with the promise of thinner and lighter thin-film transistor (TFT) backplanes. Current glass-based liquid crystal display (LCD) backplanes are patterned at critical dimensions of 3–5 µm, and TFT backplanes-on-flex would call for similar requirements (Gengel, 1994). In addition to the advantages of thinner and lighter LCD displays that will result from flexible TFT backplanes, rollable displays will be possible when flexible backplanes are used to drive organic light-emitting diode (OLED)-based displays (Ma, et al., 2008). With even higher levels of integration, TFTs, OLEDs, and all supporting electronics may be fabricated on a single flexible substrate material — a monolithic electronic system (Kattamis, et al., 2006). Further extensions of this monolithic fabrication technology will eventually usher in the era of macro-electronics.

In other words, micro/nano systems (e.g., integrated circuits, microelectronic mechanical systems (MEMS), microoptical electronic mechanical system (MOEMS) devices, fiber optic communications links, and microfluidics) are going to be integrated and fabricated on a single monolithic flexible substrate material. Another recent research direction seeks to develop methods and materials that enable the fabrication of high performance circuits on
unconventional substrates with unusual form factors (Forrest, 2004), such as flexible plastic substrates for paper-like displays and optical scanners (Chen, et al., 2003), spherically curved supports for focal plane arrays (Hsu, et al., 2004), and configurable skins for integrated robotic sensors (Lim, et al., 2005).

A module-type elastic transistor circuit was enabled by elastic interconnects on an elastomeric substrate (Lacour, et al., 2004). The circuit connections were made by embedding 100 µm diameter Au wires in silver paste on top of the Au-interconnects from each module. The study did not explain the variation in electrical resistance when the system was tested in tension. The following year, the first flexible organic complementary integrated circuit in which p-channel and n-channel transistors were built on a flexible polyethylene naphthalate substrate was created (Klauk, et al., 2005). The dynamic performance of the circuits was limited by the relatively poor mobility of the organic n-channel semiconductor. Recently, a printable, flexible CNT-TFT device was fabricated on a “standard” transparent film (Vaillancourt, et al., 2008). However, the smallest feature size was 4 µm and the characterization was done on an unstressed device.

Advancements in medicine are increasingly accomplished through the innovative application of flexible electronics. Among them is the development of a novel flexible MEMS based pressure sensor for a manometric-catheter (Teng, 2008). The manometric-catheter is used to measure the pressure profile along the esophagus during swallowing disorder diagnosis. It illustrates an idea for the design and fabrication of polymeric pressure sensors using a polyimide material. Another recent biomedical application was the creation of a flexible surface
wetness sensor using a radio-frequency identification (RFID) device that is small, inexpensive, disposable, soft, wireless, and passive (Yang, 2008). A wetness sensor can immediately alert nurses or caretakers to replace a patient’s wet diaper. The RFID components were fabricated and assembled in a flexible polymer film (Fig. 2-1).

![A photograph of the RFID wetness sensor (Yang, 2008)](image)

According to Sematech’s International Technology Roadmap for Semiconductors (Gupta, 2004), it is expected that flexible substrates may consist of up to three or four layers, with line features down to 10 µm within a few years. In recent years, various systems have been explored in order to close the gap between manufacturing capabilities and technology demands for flexible electronic circuits. One of these tools is roll-to-roll high-resolution projection imaging over a large exposure area on a flexible organic polymer substrate (Jain, 2005). It achieved a maximum diffraction-limited resolution of 10 µm and an alignment precision of ± 2.5 µm. Other flexible materials have also been explored to achieve greater dimensional stability for the implementation of circuit designs with micron feature electronics. For example: (1) The design of TFT circuits on flexible stainless steel foils (Troccoli, et al., 2006) has been demonstrated (Fig. 2-2 (a)); (2) a multilayer barrier structure composed of silicon nitride, silicon oxide, and encapsulated parylene on a polycarbonate substrate (Chen, et al.,
2007) has been investigated for flexible electronic applications (Fig. 2-2 (b)); (3) the fabrication of single-walled carbon nanotube (SWCNT) TFTs on plastic substrates using the ink-jet printing method (Takenobu, et al., 2009) has been developed (Fig. 2-2 (c)). However, these studies never discussed the device performance after mechanical distortions.

Figure 2-2 Electronics on flexible materials, (a) Flexible metal foil with polysilicon TFT circuits (Troccoli, et al., 2006), (b) Picture of the calcium test apparatus used for the flexible barrier sample (Chen, et al., 2007), (c) Optical micrograph of the flexible SWCNT TFT (Takenobu, et al., 2009)
2.2 Types of Flexible Electronics

Flexible electronics are made with a variety of materials and fabrication techniques suitable for different applications and can be single or multilayer. Considerations such as cost, flexibility, and desired electrical characteristics will determine which materials are used to fabricate flexible electronics. Primarily, there are three types of design architectures for flexible electronics: (a) top of film, (b) fully embedded, and (c) surface embedded.

Top of film electronics (Fig. 2-3) consist of functional devices and circuitry on top of a flexible substrate and are the simplest type of flexible electronics. They are also the most widely used and economical types of flexible electronics, and can often be produced in large volumes using conventional micro/nano fabrication techniques (Ono, et al., 1985; Xiang, et al., 2005; Suo and Li, 2006; Cao, et al., 2008; Baca, et al., 2008 Ahn, et al., 2009). However, the functionality of these electronics can be easily affected when subject to tensile and bending stresses (Chiu, et al., 1994; Alaca, et al., 2002; Yu and Spaepen, 2004; Bohm, 2004).

![Figure 2-3 Metal film on top of polymer film](image)

Another type of flexible electronics is the fully embedded (Fig. 2-4). In this design, the electronic devices are embedded in between two flexible films. Fabrication methods for fully
embedded electronics are similar to the ones available for top of film electronics, but are mostly constrained to batch process flow (Befahy, et al., 2007; Kim, et al., 2008). The encapsulation of the electronics allows the operation of complex integrated devices under strain and stress conditions (Someya, et al., 2004; Lacour, et al., 2005; Befahy, et al., 2007; Gonzalez, et al., 2008). Some of these electronics have been able to withstand cyclic loading (Lacour, et al., 2006). However, at present, there are several shortcomings associated with this architecture such as poor interconnections, processing cost, and creation of thicker films that are unable to wrap around distorted surfaces.

![Diagram of Embedded Metal](image)

**Figure 2-4 Metal film fully-embedded between two polymer films**

In 2005, Lee, et al (2005) introduced a new design architecture to fabricate flexible electronics. Figure 2-5 shows the surface-embedding of the metal structures into a polymer film. The technique of surface-embedding metal films provides more surface area contact between the metal and the polymer, allowing for increased chemical bonding to take place. The most important characteristic of this design is that it produces a flat surface without step heights, and the electronics are closer to the neutral plane of the flexible film. Such a planar surface is advantageous since it provides a flat surface for subsequent device attachment and eliminates...
the need for the sometimes cumbersome process of polishing surfaces on a flexible substrate (Adam, et al., 2010). However, there are some drawbacks associated with the currently available surface embedding techniques (Lee et al., 2005; Lim et al., 2006). Although these techniques can successfully embed metals into polymers (e.g., PDMS), the polymer substrates are not functionally flexible since they are supported on glass. As a result, there have been no studies related to the mechanical strength and electrical characteristics of the surface embedded metallized films at different bending radii.

![Figure 2-5 Surface-embedded Au in polymer](image)

**2.3 Strength Characteristics of Metallized Films**

**2.3.1 Strength of Freestanding Thin Metals**

Plastic deformation in metals is a classic subject of metallurgy and materials science (Frost, 1982). A common basic understanding of metallic film (≤ 100 nm thick) plasticity has neither experimentally nor theoretically been obtained. Experimentally, it is difficult to perform suitable mechanical tests to determine the stress-strain behavior of metallic thin films (Kraft & Volkert, 2001). Compared to bulk metals, freestanding thin metal films usually have small rupture strains (Huang and Spaepen, 2000; Espinosa, et al., 2003; Lee, et al., 2003). The tensile
deformation of a freestanding metal film is unstable: a perturbation in its thickness promotes
the film to thin down locally, and a single neck causes the film to rupture (Fig. 2-6).

Figure 2-6 Freestanding metal film

According to the law of volume conservation, upon rupture, the local thinning causes a
local elongation on the order of the film thickness ($d$). Given the small thickness-to-length ratio
of film ($\leq 100$ nm thick), this local elongation contributes little to the overall rupture strain.
Therefore, the fracture of the freestanding thin metal films is not due to brittleness, but rather
localized deformation. More recent studies have shown that freestanding thin metal film
usually ruptures at about the same small strain percentage (~1%) (Xiang, et al., 2002; Lee, et al.,
2003; Espinosa, et al., 2003). The characterization of the elastic behavior of thin metal films
allows for a better understanding of flexibility in thin metallized polymer films.

2.3.2 Strength of Metallic Films Bonded to Polymers

Metallic films bonded to polymeric substrates (top of film) have been used extensively in
circuit manufacturing and their mechanical behavior has been studied by a number of groups
(Kuo, et al., 1994; Shinozaki, et al., 1998; Lu et al., 2007; Suo and Li, 2007). Freestanding metal
films (debonded from a substrate) deform with a smaller strain than thin films ($\leq 100$nm thick)
attached to a polymer substrate (Li, et al., 2005). Yu & Spaepen (2004) provides a bibliography of earlier literature on the subject.

Several groups have reported rupture behavior of metal films deposited onto polymer substrates (Chiu, et al., 1994; Alaca, et al., 2002). In all cases, it was observed that when metalized polymer film is subject to a modest axial tensile strain (e.g., 20%), strain localization and debonding of the metal film on the polymer will co-evolve (Li, et al., 2005). When the metalized polymer films are subject to larger strains (e.g., 50%), it was found that cracks through the metal films are formed (Jones, et al., 2004). To try to overcome this localized strain and debonding problem, several groups have used pre-stressed or pre-strained polymer substrates. For example, Lacour et al. (2003) demonstrated that a gold film deposited onto an elastomeric substrate with built-in compressive stress maintains electrical conductivity up to 22% tensile strain. Another approach has been to build spring-like behavior into the metal interconnect structures using scalloped profile metal stripes (buckled) (Suo and Li, 2007). Gold films were attached on a prestretched silicone film of polydimethyl siloxane (PDMS). It was shown that the metal film remained electrically conductive but its electrical resistance increased by 24.7% at 100% strain (Jones, et al., 2004).

Significant work has been reported at the University of Illinois at Urbana-Champaign in developing fabrication techniques for flexible electronics (Menard, et al., 2004; Mack, et al., 2006; Cao, et al., 2008; Baca, et al., 2008 Ahn, et al., 2009). Sun, et al. (2005) showed that transistors with Au source gates on top of a polyethylene terephthalate (PET) under bending caused the tensile strain at the device to vary between 0% and 1.2% with a change in the performance up to
20%. In general, disparity is observed in the rupture strains of the metal films deposited on polymer substrates (Chiu, et al., 1994; Alaca, et al., 2002; Yu and Spaepen, 2004; Bohm, 2004). This is believed to be caused, at least in part, by the disparity in the quality of bonding. It is believed that a metal film that is well bonded to a polymer substrate should be able to sustain plastic deformation by tens of percent (Xiang, et al., 2005).

Other studies regarding polymer materials for flexible films have shown that when a substrate is too compliant, its constraint is insufficient to prevent strain localization in the film. The experimental results of Li and Suo (2006) demonstrated that a substrate of Young’s modulus in the megapascal range (e.g., an elastomer) conforms to the localized deformation of the film and the rupture strain of the film is comparable to that of a freestanding film. However, a substrate of Young’s modulus in the gigapascal range (e.g., polyimide) retarded the strain localization in the metal film. In recent years, PI films have been used in a variety of interconnect and packaging applications, including passivation layers and stress buffers on integrated circuits and interlayer dielectrics in high-density interconnects on multichip modules in the electronics industry (Soane, 1989; Kraft, et al., 2000; Briand, et al., 2006; Ryosuke & Akira, 2007; Tsuyoshi, et al., 2007). PI films can serve as a model material for flexible substrates which are important for various applications in the area of flexible electronic devices.

Many electronic materials can provide good flexibility when prepared in thin-film form near neutral mechanical planes (fully embedded) in substrate laminates (Loo, et al., 2002). In these cases, the strains experienced by the active materials during bending can remain well below the typical levels required to induce fracture (~1%). Full stretchability, a much more
challenging characteristic, is required for devices that can flex, stretch, or reach extreme levels of bending during operation, including devices that have to be wrapped around supports with complex curvilinear shapes. In such systems, strains in the circuit can exceed the fracture limits of nearly all known electronic materials. This problem can be circumvented, to some extent, with circuits that use stretchable conducting wires to interconnect electronic components (such as transistors) supported by rigid isolated islands (Lacour, et al., 2004).

The designs of flexible micro/nanoelectronic devices have centered on minimizing and/or uniformly applying stress forces on them in order to eliminate stress location defects on the electrical components and materials. It is known that minimal elongation (strain <1%) of the metallic film is ensured by placing the metal layer in the neutral axis or center plane of the flexible structures (Crawford, 2005).

When metal films are deposited or encapsulated between elastomeric substrates (polymer films) on a center plane, they are no longer constrained to just planar or developable surfaces (Grego, et al., 2005). Rather, they can expand reversibly (Befahy, et al., 2007), conform to objects of complex shape (Someya, et al., 2004) or move together with the human body (Axisa, et al., 2007). Stretchable metallization can be prepared using either thin (≤ 100 nm thick) films (Lacour, et al., 2005) or thick (>1 µm thick) films (Gonzalez, et al., 2008) embedded between the elastomer films. For example, 25 nm to 100 nm thick evaporated Au stripes embedded between two silicone films can stretch reversibly both uniaxially (Lacour, et al., 2003) and radially (Lacour, et al., 2005) without electrical failure. Furthermore, Lacour, et al. (2006) demonstrated that Au-interconnects (50 nm thick) encapsulated in elastomeric substrates are
robust to extensive cyclic loading, up to 250,000 cycles to 20% strain and present stable electrical conduction over cycling. However, there are two major issues for the fabrication of electrical devices between layers of polymer films. First, these electrical devices are grown directly on one polymer substrate (film) and most polymers deform at temperatures of only 100-200°C, placing severe limitations on the quality of the micro/nano devices that can be made directly on them. Second, the micro/nano devices laminated between polymer films require “etch holes” for electrical terminals, which causes cracks to be formed in the nearby electrodes when stress forces exceed those supported by metal films on a single polymer film (Kim, et al., 2008).

2.4 Overview of Metal-Polyimide Chemical Bonding

Among the polymers suitable for microelectronics applications, PIs have received increased attention due to their thermal and chemical stability, low dielectric constant, high electrical resistivity and relative ease of processing into coatings and films (Soane, 1989). For all these reasons, PIs have been widely used in microelectronics as dielectric spacing layers, protective coatings, and substrates for thin metal films, replacing traditional inorganic insulators such as SiO₂ in many applications.

In these and other applications, good adhesion between individual metal atoms and a PI substrate is required. The mechanism responsible for the adhesion is often not well understood, though chemical bonding at the interface is believed to play an important role in adhesion. The interfacial bonding and subsequent adhesion are directly influenced by the way in which the interface is formed. Therefore, variations in the preparation of polymers or metal substrates can lead to PI/metal interfaces with different adhesive strengths. Adhesion when a PI is deposited
on a metal is therefore, a different problem than adhesion when a metal is deposited on a cured PI. The former situation tends to give stronger adhesion than the latter, but there can be problems of metal dissolution, particularly when the metal is Cu. The interaction between the metals and the PI has been studied in great detail using x-ray photoelectron spectroscopy (XPS) and other surface analysis techniques, but there is not complete agreement on the form of the interaction. However, it is clear that strong interaction and electron transfer occurs when the metal is deposited from vapor onto the PI. When the polyamic acid is deposited on the metal and cured, reaction occurs between the acid and the metal (Brown, 2000). A better understanding of the chemical interactions at PI/metal interfaces and their consequences for adhesion has the potential to yield significant progress in the field of adhesion between metals and polymers.

2.4.1 Atomistic Modeling of Metal-Polyimide Interfacial Properties

As in other areas, atomistic modeling has played an important role in understanding the nature of bond formation between metals and PI. Ramos (2002) modeled the interaction of Cr, Cu, and Ni atoms with a specific groups of pyromellitic dianhydride-oxydianiline (PMDA-ODA) PI fragments (Fig. 2-7) with hydrogens saturating the dangling bonds. PMDA-ODA is normally deposited from solution as polyamic acid and cured in-situ to the imide form. The results suggest that metal atoms react preferentially with five- and six-fold rings (sites II and III, respectively). The chemical interaction between metal atoms and the PI fragment leads to charge transfer, causing one-orbital energy shifts until the Fermi levels of both materials are in coincidence. The changes in the atomic charges of the PI atoms due to interaction with
transition metal atoms were predicted. It is believed that the different adhesion behaviors, observed experimentally, might be related to the number of bonds rather than their strength. The same effect was predicted for metals with only s and p electrons, such as aluminum (Ramos, 1993).

Figure 2-7 Schematic diagram of PMDA-ODA polyimide cluster model used by Ramos (2002)

2.4.2 Diffusion of Metals Onto Polyimide

Cu and Ti layers (~10 nm thick) deposited on a PI film (75 µm thick of Kapton material) were studied under annealing treatment (Marin, 1995). In this study, it was shown by Rutherford backscattering spectrometry and cross-sectional transmission electron microscopy that when the annealing temperature goes beyond the PI glass transition temperature ($T_g \approx 360^\circ C$), the Cu clusters formed by unwetting are immediately immersed inside the polymer which has become viscous. This behavior also occurs when thin film metal layers are deposited at elevated temperatures. For samples treated at temperatures above $T_g$, it was observed that the Cu thin metal layer migrated up to 500 nm in depth with the formation of new carbonaceous materials by the loss of the more volatile elements (H, N, O). In contrast, for Cu-PI samples
annealed at temperatures below $T_g$, the unwetting of the Cu layer formed clusters on the PI surface by a surface diffusion process.

In the Ti-PI study, the layer under annealing showed strong stability. This system did not experience modification after thermal annealing for temperatures both below and above the glass transition temperature. The non-unwetting and the non-diffusion of the oxidized Ti layer may be explained by the strong increase in adhesion strength at the interface due to the reaction of Ti with the carbonyl oxygens in the PI (Freilich, 1987). Therefore, it is certain that the diffusion barrier formed at the interface is strengthened by the oxidized character of the Ti layer.
Chapter 3.

Initial Exploration

Initially, a hands-on experimental study was conducted to find a procedure that could embed metal patterns in an elastomeric polymer substrate (PDMS) without inducing structural damage. A summary of this exploration is presented in the following discussion.

3.1 Replicating a Published Fabrication Method

An “optimized” process to embed metallic microstructures in an elastomeric polymer substrate had already been published (Lee, et al., 2005). This process of embedding metallic microstructures in an elastomeric polymer substrate (PDMS) is outlined schematically in Figure 3-1. Two separate experimental conditions are described as Method I and Method II. The difference between the methods is primarily related to the process used to pattern metal structures on a mother substrate before embedding them into PDMS. The deposition of the 3-mercaptopropyltrimethoxysilane (MPT) adhesion layer and the Tridecafluoro-1,1,2,2,-Tetra-Hydrooctyl silane (TFOS) release layer occurs in a different order for each method. The MPT is referred to as the adhesion layer, as it improves adhesion between PDMS and the gold (Au) features, while TFOS is referred to as the release layer, as it prevents bonding between PDMS and the mother substrate (i.e., silicon dioxide (SiO₂)) during the transfer of the Au features from the substrate into PDMS. The application procedure for these two layers and how they function will be discussed in more detail in Section 3.3. Once the metallic structures and molecular self-assembly (SAM) layers are patterned, the PDMS-embedding procedure that follows is identical.
The metallic thin film structure patterning process in Method I uses a wet etching protocol while the one in Method II is based on a lift-off lithography process. For the former, the photoresist pattern is developed on top of a thin film which has been deposited on a mother substrate (typically quartz, glass or Si/SiO₂) that has been previously treated with a fluorosilane release agent (steps 1-1 through 1-3). Wet etching and resist stripping yield metallic structures that are weakly adherent on the mother substrate (steps 1-4 through 1-5), which are then prepared for the polymer embedding process through treatment with a silane coupling agent (steps 1-5 through a). In method II, photoresist is developed on the mother substrate (step 2-1), the thin film materials are deposited (step 2-2), and the patterned structures are obtained by lift-off (step 2-3). The sample is then treated sequentially with silane coupling agents which assemble in order on both the metal surface (step 2-4) and the oxide surfaces of the carrier to generate architectures suitable for embedding in PDMS (step a). The structures prepared by either of the process variants are then embedded in a thin, glass backed PDMS film (step b), and after curing, the bonded structures are delaminated from the carrier (step c).
The methods mentioned above were considered as viable and simple solutions for the step height problem encountered in the Step-And-Grow process (Nam, et al., 2007). It also promised a flat surface for growing conductive polymers, such as polyaniline (PANI) nanowires on a flexible polymer material.

However, after months of experimentation, neither of these two methods worked effectively to transfer the metal features into the PDMS. Over 99% of the trials were unsuccessful and those that were successful had mixed results with some buckling and breakage of the metal features. The authors of the above mentioned work were contacted but never clarified or provided sufficient information that would help us solve the reliability and reproducibility problems encountered in both methods.
Six critical findings pertaining to the developed process were identified during experimentation.

- Au pattern features were broken from mother substrate during lift-off processes.
- TFOS and MPT molecular monolayers were affected or removed in each of the two methods. Figure 3-2(a) shows a chemical reaction on the Au surface when one monolayer is deposited on top of the other monolayer.
- There were some uneven mechanical stresses during the separation process between the mother substrate and PDMS. A picture of broken and buckled Au electrodes after the separation step can be seen in Figure 3-2(b).
- A thicker Au film allowed for a more successful transfer of the metal into the PDMS. However, the Au electrodes continued to be broken and buckled.
- A layer of Ti between the Au thin film layers did strengthen the electrode structure. This reduced the broken and buckled defects.
- The PDMS material experienced some shrinkage when cured above room temperature.

Figure 3-2 Optical microscope pictures of the initial experiment for PDMS metallization, (a) TFOS and MPT agglomeration on Au thin film, (b) Broken 5 µm Au patterns on PDMS
3.2 Shadow Mask vs. Bi-layer Resist for Micro-Metal Features

One of the main challenges faced when working with the process was to pattern the Au features onto the TFOS coated hard substrate (Si or SiO$_2$). Typically, the substrate is coated with the TFOS release layer, and the features are fabricated on top of the TFOS layer. This is critical to ensure proper transfer of the features to PDMS later in the process.

The most convenient method of fabricating Au features on top of TFOS coated mother substrates is via evaporation through a shadow mask. A shadow mask is a perforated thin metal plate that can be used to deposit a thin metal layer onto a mother substrate through the metal pattern openings. It is a tool commonly used to deposit thin films of metals with micro-features in micro/nano-fabrication facilities. This method eliminates the need to use the lithographic and lift-off processes. However, there is a process limitation with respect to the feature sizes that can be etched into the metal plates. New advances in laser drilling technology have opened the door to making smaller-sized features on metal shadow masks. A new shadow mask with 100 µm wide features was fabricated using the Lenox Laser and used in this study. A metal deposition process showed the uneven cutting from the laser drill in the shadow mask (Fig. 3-3(a)). It is clear that there is room for new academic research with regards to the fabrication of shadow masks with small continuous feature sizes (<100 µm). It was decided to eliminate the shadow mask as an option, as the aim of this research was to obtain small-sized (~5 µm, or even higher resolution) metal patterns.
The most common method of defining micron-sized metal features on substrates is via a photolithography - metal deposition - lift-off process. Using a single-layer photoresist for the lift-off process usually causes the feature to shift, break, and delaminate from the substrate. Therefore, a multilayer resist stack is used. A multilayer resist stack offers the following three advantages over a single-layer photoresist process during lift-off: it creates a suitable resist pattern profile for easy lift-off; the first layer helps to planarize the substrate surface topography, allowing the other resist layers to spread uniformly; and it helps to achieve higher resolution lithography. An ideal resist pattern profile to facilitate easy lift-off for thin metal film is one with a narrow opening at the top and a broad opening at the bottom, the so called undercut profile. Metals are thermally evaporated and deposited onto the resist surface as well as onto the mother substrate through the resist pattern openings. The thin metal film covering the resist surface has to disconnect from the metal film landing at the mother substrate surface, so that the metal pattern on the substrate will stay when the resist layer is dissolved. A bi-layer resist stack can easily form such an undercut profile.
In this current research, a bi-layer resist stack consisting of a bottom lift-off-resist (LOR 5A) and a top photosensitive resist (SPR-3012) is used for all lithography. Using the LOR as the bottom layer in a bi-layer resist stack produces a precisely controlled undercut profile. Once the SPR-3012 (top layer photoresist) is exposed and developed, LOR 5A is dissolved separately. The developed top thin layer then serves as a mask, and pattern transfer to the bottom resist layer is done using a wet etching technique.

The bi-layer method gave the expected results (Fig. 3-3(b)) with some changes in the standard lift-off procedure. First, the substrate was dipped in acetone to remove the SPR-3012 resist but not the LOR 5A. Then, the exposed LOR 5A was dissolved in NANO® Remover PG. The substrate was cleaned up in isopropyl alcohol (IPA) for 15 min and blow-dried with N₂ gas. It is important not to rinse the substrate in deionized water because it will delaminate the Au features from the substrate. The bi-layer technique helped to improve the resolution of the process, but did not resolve all the problems with transfer to PDMS.

3.3 Application of the TFOS and MPT Molecular Monolayers

The TFOS layer is a commonly used release layer on top of the SiO₂ substrate. It changes the surface of the mother substrate from hydrophilic to hydrophobic. This prevents the adhesion of the PDMS (hydrophobic material) to the SiO₂ mother substrate. On the other hand, the MPT layer binds the Au to PDMS. If both layers are deposited after the lift-off process, some type of agglomeration and chemical reaction is observed, as shown in Figure 3-2(a). Several experiments with different concentrations of the chemicals showed the same type of chemical
reaction across the substrate. This created an uncontrolled method for both, embedding the Au into the PDMS and for separating the PDMS from the mother substrate.

It was decided to apply each layer in such a manner that limits their interaction. The TFOS layer was deposited after the substrate cleaning process (before lithography). A protective photoresist layer (lithography step) and Au (metal deposition step) were then deposited on top of the TFOS. After metal deposition, the entire mother substrate was covered with Au. At this point, a layer of MPT was applied to the Au surface. This approach helped to selectively apply the monolayers to specific surfaces and not on top of each other. During lift-off, the photoresist layer was removed from the TFOS surface and the MPT remained on the patterned Au features.

A better transfer of Au features was observed in the PDMS, but they were still not defect free structures. However, when the transfer was investigated for another polymer Parylene D, instead of PDMS, a complete transfer of Au features was observed without any defects as shown in Figure 3-4. Further research is needed to fully understand the physical forces or chemical reactions that occur between the Au features, MPT and Parylene D.

![Figure 3-4 Gold (Au) electrodes embedded in Parylene D, (a) Electrode pad, (b) Four 5 µm wide electrodes](image-url)
3.4 Stack Layer for Transfer of Metal Patterns to PDMS

PDMS is flexible; therefore, it is difficult to detach it from a mother substrate without damaging the Au patterns. Cracks and buckling may occur when the PDMS is bent. Even if a slide glass is used as a hard support for the metalized polymer (PDMS), it does not eliminate the bending of the PDMS during the separation process.

The use of a metal stack layer of Au/Ti/Au (150 nm/50 nm/5 nm) was demonstrated as a method to transfer metal features into PDMS (Lim, et al., 2006). This metal stack layer was deposited on the entire silicon (Si) mother substrate without using a TFOS release layer. The metal features were defined on top of this stack layer. After the features were defined, a MPT adhesion layer was applied to the Au features, and PDMS was cured on top. After PDMS curing, the sample was immersed in water, and the Au/Ti/Au stack layer easily delaminated from the substrate. The Au/Ti/Au stack layer was then removed one layer at a time by selective wet etching to leave behind only the metal pattern embedded in the PDMS. Since the metal pattern was Au, the same as the second Au layer of the stack, a controlled timed etch was required to remove the second Au layer without over etching the metal patterns. The success of the fabrication technique depends on the handling of the stack layer through the fabrication process.

Great care is required to protect the metal stack layer from mechanical damage in the process. Any damaged metal stack layer can delaminate from the mother substrate when dipped in the developer after photo-exposure or a photoresist lift-off solution. One hundred percent of the samples that were prepared experienced some damage to the metal stack layer.
during fabrication. However, the partial layers that survived the lithography and lift-off processes transferred defect free Au patterns into the PDMS. Figure 3-5 shows pictures of partial Au electrode patterns that were transferred to the PDMS substrate. As a result, this method proved to be unreliable for fabrication, but it showed the benefits of creating a stack layer film for easy detachment of PDMS with unstressed Au patterns.

![Figure 3-5 Gold (Au) electrodes embedded in PDMS bonded to a lab slide glass, (a) 5 μm wide electrodes, (b) Electro pad](image)

3.5 Summary

A wealth of knowledge was obtained from the successes and failures of the above experiments. The following is a list of some of the concepts that were learned, that provided potential leads to be investigated for the enhancement or development of a new fabrication processes.

1. The defective metal patterns post-lift-off were related to the use of a single resist layer. The Au thin film covering the resist surface did not disconnect from the metal film deposited at the substrate surface; therefore, the metal pattern shifted and delaminated
from the substrate surface. A bi-layer resist helped to give a successful lift-off process as long as the samples were not rinsed with deionized water.

2. In terms of molecular self-assembly monolayers (SAM), the concept of selectivity for a chemical reaction is very important. Selectivity represents the ratio of reaction rates in chemistry. The chemical terminals of a SAM monolayer might react very strongly and organize in a predictable manner against a specific material. However, if conditions are appropriate, then the same process will allow a slow reaction rate with other materials in the same medium. This is the case for the TFOS and MPT layers. The TFOS is deposited to functionalize the SiO$_2$ surface as a release layer and MPT on the Au as an adhesion layer. A sequential deposition via evaporation of both SAM layers affects the functional properties of the surfaces with some kind of a secondary chemical reaction. Therefore, a new process should be developed to functionalize the SiO$_2$ surface and Au surfaces but it must protect these surfaces against undesirable chemical reactions.

3. It was found that there is moderate adhesion between the PDMS and the TFOS layer. This adhesion caused some bending on the PDMS (with the metal film) during separation. An unpredictable amount of buckling and cracks were found in the metal patterns on PDMS. One part of the problem is that PDMS shrunk when cured at temperatures above ambient. The other problem is with the unidirectional wave-like surface separation between PDMS and TFOS. Ideally, we would like to separate the entire metallized PDMS film at once. Another alternative is to use a sacrificial layer between the mother substrate and the metallized PDMS that can be dissolved in a chemical solution as a passive release technique. A continuous film of Au can be
separated easily from a Si substrate and wet etched from PDMS, but it is very costly and breaks easily when dipped in development and lift-off solutions. Parylene D is an inexpensive polymer that does not attach to a TFOS monolayer and is strong enough to endure the micron patterning processes. However, the same chemicals that dissolve parylene will chemically react with PDMS.

4. Any fabrication technique that uses an Au thin layer pattern must be conducted in a continuous and sequential manner in a limited timeframe. The Au patterns tend to spread (diffusion occurs in Si substrates) on top of mother substrates when they are left unattended for prolonged period of time.

5. In the stack layer experiments, the top sacrificial Au film was substituted with a Ni film. Experiments showed that sacrificial Ni layer can be wet etched on top of the metallized PDMS without affecting the Au patterns. However, if the Ni wet etchant solution stays in contact with Au features for a period of a few hours, then it will etch the Au pattern. Again, the concept of selectivity played a role in this fabrication step. Best results were obtained with a 30 nm Ni film thickness and a 30 min etch time.

6. It was found that MPT-coated Au adheres more strongly to PDMS containing 1% (by weight) or more of SiO₂ powder. However, the powder increases the surface roughness and curing time of the PDMS. If this mixture of SiO₂/PDMS is spun on a substrate, then an observable agglomeration of particles was distributed all over the substrate, which negated uniform distribution of the particles in the PDMS.
A set of positive results came from our last experiments with the Au/Ti/Ni stack layer. These results were obtained from pieces of unbroken stack layer on the mother substrate. The stack layer was damaged in all tested samples. It seems that a less expensive and stronger stack layer that can withstand the development and lift-off fabrication steps is required. This new stack layer should have a dual purpose: 1) to effectively separate from the mother substrate when PDMS is cured, and 2) to be a sacrificial layer during wet etching.
Chapter 4.

Novel Fabrication Techniques

A novel micro/nano fabrication technique for surface integration of metal structures into polymers (SIMSIP) was developed. The SIMSIP technique was primarily developed using surface-polished quartz wafers as mother substrates but can be extended to Teflon substrates as well.

4.1 Fabrication Techniques

4.1.1 PDMS Metallization Fabrication Technique

The fabrication of micron-scale metal features on PDMS substrates used in this work is explained in the following procedure. First, a silicon wafer coated with a silicon dioxide (SiO$_2$) layer (120 nm thick) was cleaned with Nanostrip® (OM Group Ultra Pure Chemicals Ltd.) solution for 20 min and rinsed with deionized water, blow-dried with N$_2$ gas, and dried at 120 °C for 20 min (Fig. 4-1 (a)).

The surface condition of the substrate is very important since the surface energy affects the separation of films from the substrate. The lower the energy of the substrate surface/film interface, the easier the separation. As the surface of a polymer is more hydrophobic (low surface energy) than SiO$_2$, the hydrophilic SiO$_2$ layer that is at the surface of the substrate needs to be converted to hydrophobic by depositing an organic layer via a molecular self-assembly (SAM) technique. For this process, a molecule which has a linker at one end and a hydrophobic
functional group at the other end was used. As the linker side bound with the SiO$_2$ surface, the hydrophobic side was outward facing, thereby changing the surface condition of the mother substrate from hydrophilic to hydrophobic. The chemical solution of Tridecafluoro-1,1,2,2,-\-Tetra-Hydrooctyl Silane (SIT8174, Gelest) (TFOS), which has a tri-chlorosilane at one end and fluorocarbons at the other, was used for this process. The mother substrate was exposed to TFOS vapors under vacuum (~50 torr) for 20 min (Fig. 4-1 (b)). As the dehydrated substrate was exposed to the molecule, the tri-chlorosilane reacted chemically with a hydroxyl bond on the surface of the substrate, and a thin organic layer was formed by the reaction. The organic film formation was verified using contact angle measurement. The contact angle changed from about 30 °C to 100 °C after the layer was formed.

Next, a film of Parylene D (Specialty Coating Systems), a PPX (Polyparaxyylene) plastic material, was deposited via thermal evaporation (Model PDS 2010 LABCOTER) on a bare SiO$_2$ substrate with a TFOS monolayer. The Parylene D thin film encapsulated the substrate, but did not adhere to the hydrophobic surface of the substrate. This micron-thin film was the first layer of the sacrificial stack layer to be deposited on the substrate. Parylene D was chosen over the other two products in the series (Parylene N and Parylene C) because the material maintains its physical strength (tensile strength 11,000 psi) at higher temperatures (< 220 °C). It had the mechanical strength to endure the lithography, metal deposition, and lift off processes. Then, the substrate was loaded in thin film metal deposition equipment (Semicore e-gun/Thermal Evaporator) and a 70 nm titanium (Ti) layer followed by a 30 nm nickel (Ni) layer was e-gun
deposited at a rate of 0.1 nm/s. The Ti layer was added to strengthen the stack layer and the Ni layer was used as a sacrificial layer (Fig. 4-1 (c)).

Once the stack layer was assembled, a lift-off resist (LOR 5A, MicroChem Corporation) was spun on at a speed of 500 rpm, which was accelerated to 4000 rpm over 10 s and maintained at this speed for 40 s. The substrate was then baked at 180 °C for 7 min on a contact hot plate, resulting in a LOR film thickness of ~150 nm. After a 30 s cool down period, a positive photoresist (Megaposit SPR-3012, Shipley) was spun onto the substrate. This process involved a dual layer (LOR 5A / SPR-3012) resist structure which was deposited after the development process to help prevent fencing of the metal structure. SPR-3012 was spun onto the substrate at 4000 rpm for 40 s. The substrate was then soft-baked on a contact hot plate at 110 °C for 90 s providing a ~1.2 µm thick resist layer (Fig. 4-1 (d)). The wafer was then exposed for 5 s on a Karl Suss MA-6 contact aligner through a contact pattern mask containing an array of 5 µm electrode features. The mercury lamp ultraviolet source was unfiltered and exhibited an output power of 12 mW/cm² at the substrate surface. A post-exposure bake was subsequently performed at 110 °C for 90 s.

The features were developed for 1 min and 10 s in developer (MF-CD-26, Shipley) and then rinsed with deionized water, and blow-dried with N₂ gas. An oxygen plasma (PlasmaTherm 720 RIE Etcher) was then used to descum (O₂:150 sccm, 50 mTorr, 50 W, 30 s) the resist and make a clean surface for contact between the Ni surface layer and the gold (Au) patterned electrode features to be deposited in the e-gun evaporator (Fig. 4-1 (e)). The sample was then loaded in an evaporator and an Au/Ti/Ni (30 nm/ 50 nm/ 20 nm) stack was e-gun
deposited (deposition rate ~0.1 nm/s). This metal deposition was made to provide an electrode (30 nm of Au), a high-strength layer (50 nm of Ti), and an adhesion layer (20 nm of Au) (Fig. 4-1 (f)). After metal deposition, lift-off was carried out by immersing the substrate in a strip/remover resist solution (NANO® Remover PG, Microlithography Chemical Corp) at ambient temperature for ~1 hr, which revealed the metal pattern on the substrate. The substrate was cleaned up in isopropyl alcohol (IPA) for 15 min and blow-dried with N₂ gas (Fig. 4-1 (g)).

Before metal transfer, the formation of a strong adhesive bond between the metal surface and the PDMS is of prime importance to the success of the embedding process. The 3-mercaptopropyltrimethoxysilane (SIM6476, Gelest) (MPT) was a logical choice to serve as a bonding agent because of its heterofunctional nature. The thiol terminal group can interact with a Au surface, allowing for selective assembly, while the silane terminal alkoxy groups remain available to interact with the silicon of the PDMS (Si-O-Si linkages). The patterned substrate was then exposed to MPT under vacuum for 30 min. This process organized the MPT on the Au surface to form a SAM. The purpose of this step was to get a strong bond between the metal pattern and the PDMS (Fig. 4-1 (h)).

The PDMS (Dow Corning Sylgard Elastomer 184 Kit) pre-polymer mixture (1:10 by volume) was poured on this patterned substrate and then cured at room temperature to prevent distortion or buckling of the metal layer caused by temperature differences. Because PDMS is flexible, it is not easy to detach it from the substrate without damaging the pattern. Cracks can be generated and extended when the PDMS is bent. Hence, the PDMS was spun onto the substrate at 3000 rpm for 40 s. This resulted in a ~30 µm thick layer on the substrate. A glass
slide (3 mm thick) was placed on the PDMS to prevent the PDMS from bending. The PDMS was cured at ambient temperature for 5-7 days (Fig. 4-1 (i)).

An X-Acto knife (Elmer’s Products, Inc) was used to cut the stack layer (Parylene D, 70 nm of Ti, and 30 nm of Ni) from the edges of the substrate (Fig. 4-1 (j)). After detaching the PDMS from the substrate, the stack layer (attached to the PDMS) was removed by selective etching with Ni etchant type I (Transene Company, Inc.) at 40 °C for ~45 min to complete the device fabrication ((Fig. 4-1 (k) and 4-1 (l)).

The results of PDMS metallization experiments are presented in Chapter 6 (see Section 6.1).
Figure 4-1 Illustration of PDMS metallization fabrication steps: (a) Si substrate with a SiO$_2$ layer, (b) TFOS layer on SiO$_2$, (c) stack layer on top on TFOS layer, (d) spin-on bi-layer resist, (e) UV exposure and developing, (f) deposition of Au and lift-off of bi-layer resist, (g) MPT layer on Au, (h) PDMS and slide glass on substrate, (i) separation of mother substrate from stack later/PDMS, (j) wet etching of Ni, (k) Au structure on PDMS (no steps between Au and PDMS structure)
4.1.2 SIMSIP Fabrication using Quartz Mother Substrate

The primary steps in the fabrication technique are illustrated by the schematic in Figure 4-2.

The quartz substrate was cleaned with Nanostrip solution for 20 min and subsequently rinsed with deionized water, blow-dried with N₂ gas, and dried on a hot plate at 120 °C for 20 min. The substrate was cooled for 5 min on an aluminum plate (Fig. 4-2 (a)). A Shipley 1827 positive photoresist was spin coated onto the substrate at 400 rpm for 40 s. As per the technical data for the photoresist, the quartz wafer was soft-baked at 110 °C for 90 s and cooled down on top of an aluminum plate for 30 s (Fig. 4-2 (b)). The substrate with the photoresist was then exposed to ultraviolet (UV) light for 12 s on the photolithography contact aligner through a contact pattern mask. In this demonstration the mask contained an array of geometrical features from 2 µm to 16 µm in width. The mother substrate was subjected to a post-exposure bake treatment with the same parameters used for the soft-bake treatment and then developed for 2 min in the developer chemical solution, rinsed with deionized water, and blow-dried with N₂ gas (Fig. 4-2 (c)). Oxygen plasma from a reactor ion etcher was used to descum (O₂:150 sccm, 50 mTorr, 50 W, 30 s) the photoresist to provide a clean surface for contact between the mother substrate and the metal (i.e., Au, Ag, or Cu) to be deposited. Several metal film thicknesses (i.e., 30 nm, 50 nm, and 100 nm) were deposited using the e-beam physical vapor deposition (EB-PVD) process (deposition rate ≤ 0.1 nm/s). After metal deposition, lift-off was conducted by immersing the substrate in a resist strip/remover solution in two consecutive 30 min baths at 80 °C. The patterned metal on the mother substrate was revealed in this step, after which the
sample was cleaned in IPA for 15 min and blow-dried with N₂ gas. It is important to not rinse the substrate with deionized water at the end of this step because deionized water will cause the unattached thin metal structures to delaminate from the substrate in less than a second (Fig. 4-2 (d)). After lift-off, polyimide was spin coated onto the substrate at 1500 rpm for 40 s. The mother substrate, with the metal features embedded in a polyimide film, was then soft-baked at 115 °C for 7 min (Fig. 4-2 (e)). In order to obtain a uniformly flat film, the sample was clamped between two silicon wafers and loaded into an oven at 150 °C. The oven temperature was gradually ramped to 280 °C for 4 hr (Rosmus, 2009). This step helps to drive off solvents and initiate the imidization reactions that create the final polyimide film (~11.6 µm thick). Subsequently, the assembly was allowed to cool for 15 min at room temperature (Fig. 4-2 (f)) after which the mother substrate was unloaded from the assembly. At this point, the thin film of polyimide with embedded metal structures was loosely bonded to the quartz mother substrate, allowing for an almost stress-free separation process (Fig. 4-2 (g)). The ultra-smooth polished quartz wafers utilized in this study gave rise to a weak adhesive interface layer between the fully-cured polyimide (PI) 2610 film and the mother substrate (Shioda, 2002). This polished (surface roughness < 2 nm) crystal surface permitted a smooth and continuous separation of the metallized PI thin film.

The results of SIMSIP fabrication using quartz mother substrates are presented in Chapter 6 (see Section 6.2.1).
Figure 4-2 SIMSIP Fabrication Technique
4.1.3 SIMSIP Fabrication Using Teflon Mother Substrate

One of the main objectives of the SIMSIP process is to fabricate stable, functional, and flexible electronic circuits using a simple and potentially economical manufacturing technique. A conceptual vision is to be able to apply the new fabrication method to a continuous, single line manufacturing process. The use of Teflon as substrate instead of quartz offers the potential to implement the SIMSIP process in large area, low-cost production environments. Teflon, containing PTFE (polytetrafluoroethylene) fluoropolymer (repeating chains of \(-\text{CF}_2\text{-CF}_2\)-), has a very low surface energy which gives it non-stick properties. These non-stick properties make it possible to reliably separate the metal-polyimide thin film from the mother substrate. As such, we found that the Teflon surface does not require any treatment in order to separate the cured metal-polyimide flexible films. The Teflon used was in sheet form (3 mm thick), and was received from the supplier with an unpolished surface finish. AFM results, to be discussed later, showed that the rough features of the mother substrates subsequently transferred into the embedded metal films made on them.

A change in the substrate from quartz to Teflon only affects the hot plate soft-baking temperatures and times in the SIMSIP unit processing steps described in the previous subsection, primarily due to the poor heat transfer characteristics of the Teflon. Through experimentation, the soft-baking characteristics for the Shipley 1827 photoresist were adjusted to 150 °C for 3 min for a 3 mm thick Teflon substrate. At this set point on the hot plate, it was found that it took 90 s for the temperature at the Teflon/1827 surface to reach 110 °C after which the photoresist-substrate interface was kept at 110 °C for the remaining 90 s and then the
substrate was cooled down for 5 min on an aluminum plate. To soft-bake the PI film, the hot plate was set at 150 °C and the substrate was heated at this temperature for 12 min. The hard-baking characteristics of the Shipley 1827 after UV exposure and the lift-off process remained unchanged when Teflon was used as the mother substrate. The results of SIMSIP fabrication using Teflon mother substrates are presented in Chapter 6 (see Section 6.2.2).

4.1.4 Fabrication of Metal Patterns on Top of Polyimide Film (Control)

A set of samples were needed with metal patterns (Au-interconnects) on top of a PI film. In this work, these sets of samples are called the control samples for the bending test experiments. This fabrication technique is commonly used for metallized or electronic devices grown on top of polymer materials (e.g., semiconductor sensors).

The procedure begins by spin-casting a sacrificial layer of PMMA (2000 rpm, 180 °C for 10 min) followed by a thin film layer of PI (1500 rpm, 115 °C for 7 min) on a quartz mother substrate that serves as a temporary carrier. The final curing of the PI film is carried out in an oven which is gradually ramped to 280 °C for 4 hr. The Au electrode interconnect pattern is placed on the PI substrate (film) with the same conventional lithography, metal deposition, and lift-off processes followed by nanofabrication labs (Ono, et al., 1985). In order to release the metallized-PI film from the quartz substrate, a razor is used to cut the outer edges of the PI film from the quartz. Immersion in acetone dissolves the PMMA as the solvent flows through the outer edges to release the metallized PI film. Finally, rinse with deionized water and blow-dry with N₂ gas. Results from samples fabricated using this method are presented in Chapter 6 (Section 6.3).
Figure 4-3 Control Fabrication Technique
4.1.5 SIMSIP Nano Fabrication Technique

A derivative of the SIMSIP fabrication technique was developed for surface-embedding nano (< 1 µm) metal patterns into PI film. It is the same SIMSIP fabrication process with a change in the lithography process. The photo-contact lithography process is replaced by an e-beam lithography process. This work follows the same e-beam recipe that was used to grow nano elements on a silicon substrate (Garg, et al., 2008). The e-beam writer is capable of producing submicron size patterns in the e-beam resist (PMMA). After this lithography process, the PMMA is patterned on the silicon substrate and ready for metal deposition. However, it is recommended that a deposit of metal film equal or smaller than 35 nm is used, because the PMMA film thickness is typically around 120 nm. The SIMSIP nano follows the same process steps for lift-off and metal transfer to a PI film. Figure 4-4 shows a schematic drawing of the SIMSIP nano process.

The results of SIMSIP Nano fabrication using are presented in Chapter 6 (see Section 6.4).
Figure 4-4 SIMSIP Submicron Fabrication Technique
Chapter 5.

Testing Method for Bending Radii in Flexible Films

The simplest configuration that a flexible electronic device must be able to withstand is bending around a cylinder of a given radius \( r \). The X-\( \Theta \) system was developed as a concept of an apparatus capable of bending flexible thin film polymers by overcoming the limitations of a non-uniform bending radius and the constantly changing sample length of the collapsing radius set-up (Grego, et al., 2005). This type of test allows for the measurement of electrical resistance in-situ at different bending radii and analysis of its dependence upon the bending radius. The mechanics of the X-\( \Theta \) system for testing surface-embedded thin metallized polymer films will be described in this chapter.

5.1 The X-\( \Theta \) System

In the X-\( \Theta \) system, the sample is clamped in a flat position between two parallel plates whose separation distance and angle is controlled by one linear \(( d_i )\) and two rotary \(( \alpha_i )\) degrees of freedom (Fig. 5-1 (a)). These degrees of freedom control the spatial coordinates of the sample ends as a function of radius compared with an automated set-up such as the X-Y-\( \Theta \) system (Fig. 5-1 (b)) proposed by Grego et al. (2005) and the system proposed by Sun et al. (2005). The angle \( \Theta \) is defined as the angle between the tangent to the two dimensional (cross-sectional) orientations of the sample film’s right end and its left end.
As illustrated in Figure 5-1 (a), the procedure used for the testing is initiated first by fixing the sample between the two clamps, so as to allow a sample segment $L_i$ to be free between the clamps, and then systematically and simultaneously changing both clamp angles $\alpha_i$ identically to thereby bend the sample into tension (interconnects on the outer surface) or compression (interconnects on the inner surface). It should be noted that the left clamp has one degree of freedom (rotation) while the right clamp has two degrees of freedom (rotation and linear motion). The length $L_o$ of the free segment is chosen so that $L_o = \pi r_f$, where $r_f$ is the smallest (final) bending radius achieved with parallel clamps (i.e., when $\alpha_f = 90^\circ$). Since the ends of the tested sample move along the same plane, the length of the sample remains constant throughout the bending (i.e., the length of the sample will always be equal to $L_i + d_i$). The study assumes perfectly elastic behavior for the thin polyimide film; it is assumed that the bending moment is uniform across the length of the sample and the sample is bent uniformly at the corresponding radius.
In order to avoid contact between the clamps, the bending is limited to the angle values between 0° and 180° (Fig 5-1 (a)). Therefore, \( r_f \) is equal to 3.2 mm when the thin polyimide films of 10 mm length (Fig 5-2) are bent to 180°. Also, the clamps should stop linear motion towards each other at a distance of 6.4 mm \( (L_d = 2 \times r_f) \). Since the sample starts in a flat configuration (0°), there is no upper limit to the test range radius.

There are three main constraints in the design of the proposed X-Θ testing system. First, the final linear contraction motion \( (d_f) \) between the device clamps should not exceed 3.6 mm \( (d_f = L_o + L_d) \). Second, the device clamps must change their angles of orientation simultaneously \( (\alpha_i) \) from 0° to 90° during the linear contraction displacement of 3.6 mm along the X-axis. Finally, the ends of the thin polyimide films should move along the X-axis during the testing operation at different bending angles \( (\Theta_i = 2 \times \alpha_i) \).

### 5.2 The Design of the Thin Film Bending Machine

A bending test apparatus was assembled to reproducibly and systematically bend flexible polymer films as illustrated in Figure 5-3. The apparatus has a set of mechanical guide
features to provide linear and rotary movement accuracy and reproducibility. These guides changed the angle at the edges of the tested sample flexible film by \( \alpha \approx 22.5^\circ \) per \( \approx 1\text{mm} \). Therefore, the tested sample film was bent approximately to \( 45^\circ, 90^\circ, 135^\circ, \) and \( 180^\circ \) (\( 2\alpha \) values) as the right clamp moved linearly in increments of 1 mm. The bending apparatus was designed to step through each of these angles with a \( \pm 4^\circ \) margin of error. The details of the design for each of the machine clamp arms will be discussed in the next subsections.

![Illustration of the bending for a 10 mm long polymer film](image)

**Figure 5-3** Illustration of the bending for a 10 mm long polymer film (a) Length of thin polyimide film (\( L_0 \)) in the flat position, (b) Distance between the device clamps when sample of length \( L_0 \) is bent to \( 180^\circ \)

### 5.2.1 The Right Clamp Arm \((d_i, \alpha_i)\)

The right clamp arm used to hold the film is designed to move along a linear axis from right to left \((d_i)\) and simultaneously rotate from \( 0^\circ \) to \( 90^\circ \) \((\alpha_i)\). The base block of the right clamp arm is manually pushed towards the left clamp arm in 1 mm increments, and it can move a maximum of \( \approx 3.6 \text{ mm} \). At the same time, the clamp arm will rotate clockwise in increments of \( 1^\circ \) per 0.04 mm of linear motion. A guide fixture (Fig. 5-4) was designed to control the rotation of the right clamp arm from \( 0^\circ \) (0 mm) to \( 90^\circ \) (3.6 mm). The design called for the machining of a fixture block in the form of a right isosceles triangle measuring 3.6 mm on each side. This
triangular fixture guide was attached to the stationary left block of the bending machine and a 3.6 mm guide bar was added to the right clamp arm.

Figure 5-4 shows the motion of the right guide bar on the triangular guide fixture. The starting set-up point of motion is located at the base of the triangular guide fixture ($X_o = 0, \alpha_o = 0^\circ$). The guide bar moves upwards along the triangular slope at a $45^\circ$ angle until the lateral motion reaches ~3.6 mm. At this point, the right clamp arm completes the clockwise rotation to a $90^\circ$ angle ($\alpha_f$) and the guide bar is at the top of the triangular fixture.

![Figure 5-4 Design of a fixture guide used for the 'right clamp arm' of the X-O system](image)

A conceptual schematic of the triangular guide fixture and the right clamp guide bar is shown in Figure 5-5. The top view shows an L-shaped guide bar attached to the right clamp arm. Also, it can be seen that the point of rotation of the right clamp arm is between the guide bar and the clamp sample nest. The sample nest is where the right end of the thin polyimide film is placed. In the front view picture, a reference plane along the X-axis is located between the bottom side of the guide bar and the top surface of the sample nest. The linear motion ($d_l$)
of the polyimide film ends (left end of the right sample nest) should move along this plane.

Also, the right clamp arm uses the X-axis as a reference for the clockwise rotation angle ($\alpha_i$).

Finally, the right side view shows that the bottom side of the guide bar runs over the triangular guide fixture. This allows the right clamp fixture to rotate from $0^\circ$ to $90^\circ$ without any obstacles in the pathway.

Figure 5-5 Design schematic views of the triangle guide fixture and the right clamp guide bar
Once the triangular guide fixture and right clamp guide bar were designed for the bending machine, a conceptual dry run was done on paper (Fig. 5-6). It is important to understand the expected $X$, $\alpha$, and $d$ values as the right clamp arm moves a distance of ~3.6 mm from right to left. Figure 5-6 shows the movement of the right clamp arm as the guide bar climbs the slope of the triangular guide fixture. These values change from 0 to the expected desirable values of $X = 3.6$ mm, and $\alpha = 90^\circ$. This allows verification that the design fully complied with the three basic design constraints for the bending machine.

![Diagram of the operation of the right clamp arm](image)

Figure 5-6 A conceptual dry run for the operation of the right clamp arm
5.2.2 The Left Clamp Arm ($\alpha_l$)

In principle, we could use the same type of triangular guide fixture to rotate the left clamp arm. However, the installation of this system constrains the space available to properly load the thin polyimide film samples and the connection of wire terminals to the sample electrodes. As a result, a different type of a guide fixture is required to achieve a $90^\circ$ rotation on the left clamp arm. The idea is to rotate the left clamp arm by $90^\circ$ as the right clamp arm moves 3.6 mm. Therefore, the perimeter length of this $90^\circ$ rotation should be equal to 3.6 mm.

The circular arc equation ($l = \theta \times [\pi/180^\circ] \times r$) was used to estimate the length of the guide bar designed on the left clamp arm. This length is equal to 2.3 mm when $\theta = 90^\circ$ and $l = 3.6$ mm (Fig. 5-7 (a)). In Figure 5-7 (b), the desirable values of $X$ and $\alpha$ during the left clamp arm rotation can be seen. The right edge of the left clamp arm should not have lateral motion in order for $X_o$ and $X_f$ to have a value of 0. However, the clamp must be able to rotate freely from $0^\circ$ to $90^\circ$ within a circular perimeter length of 3.6 mm.

![Figure 5-7 Illustration of the left clamp rotation, (a) The use of the length of a circular area equation to calculate the length of the left guide bar (2.3 mm), (b) The estimated parameter values $X$, $\alpha$ for the left clamp arm](image)

A rotation angle of $90^\circ$ can be achieved on the left clamp arm by attaching a wire string to the left clamp guide bar and pulling it 3.6 mm (Fig 5-8). However, there are three design...
requirements for achieving a desirable rotation of the left clamp arm. First, the angle (θ) between the wire string and the left clamp arm should be less than or equal to 90°. Second, the wire string length (h) should be greater than the guide bar length (2.3 mm). Third, the wire string should be pulled in the direction of desirable rotation for the left clamp guide bar.

The schematic drawings of the guide fixture, wire string, and left clamp arm are shown in Figure 5-8. The rotation (αl) of the left clamp arm is along the X-axis which is the same axis used for the rotation of the right clamp arm. However, the left clamp arm rotation is counterclockwise with respect to the X-axis geometrical plane of reference. The guide fixture is attached to the right mobile block of the right clamp arm. This wire string is attached between the guide bar and guide fixture. Also, this wire string has a perpendicular orientation to the X-axis. The left clamp sample nest is used to hold the left edge of the thin polyimide sample to be tested in the bending machine. Once the design guidelines were established for the left clamp arm, then a conceptual dry run was done on paper.
The critical design requirements are linked to the motion of the wire string. Some wire string materials will have elasticity when tensile force is applied. The left clamp design assumes that the elasticity is negligible because of the very small resistance required for the left clamp arm to rotate freely. The main concern is the space between the guide bar and the guide fixture. If the design requirements are followed, then the guide fixture should not obstruct the rotation.
path of the left clamp arm. Both guide parts are moving simultaneously as the right frame block
is moving from right to left. Figure 5-9 shows the expected \( X, \alpha, \) and \( d \) values as the left clamp
arm rotates a distance of \( \approx 3.6 \text{ mm} \). Only the rotation variable \( \alpha \) changes its value, from \( 0^\circ \) to
\( 90^\circ \). The design makes it possible to achieve one degree of freedom for the rotational movement
of the left clamp arm. Also, the \( \alpha \) angle increases its rotation angle proportionately and
simultaneously with the right clamp angle when the machine clamps move closer together
through a distance of \( 3.6 \text{ mm} \) \((d_i)\).

![Diagram showing the path of the left clamp arm with labels for \( X_0, \alpha, \) and \( d \) with values and constraints.]

Figure 5-9 A conceptual dry run for the operation of the left clamp arm
5.2.3 The Bending Machine Setup

The X-Ө bending machine was assembled using all of the design requirements generated in the conceptual development stage. This system had to bend the film samples to angles ($\theta_i$) of 45°, 90°, 135°, and 180° with respect to the X-axis plane. Also, the clamps of the bending machine had to have a contraction movement that provided a separation distance (a) of 9.1 mm (45°), 8.2 mm (90°), 7.3 mm (135°), and 6.4 mm (180°). However, the objective was for the bending angle machine to provide approximate angles and distances when bending thin polyimide films. As a result, a ± 4° margin error on the obtained machine bending angles (θ) was considered an acceptable performance for this manual system.

Once the objective of the study was established, then a system to take measurements had to be developed. This measurement system had to be as economical as possible, both in terms of cost and time spent on data collection. However, the accuracy of the measurements had to meet or exceed the dimensional tolerance of the elements to be measured in the system. The dimensional tolerance for linear distances was ±0.1 mm in our study. All of the design concepts were installed in a BESSEY 4” Drill Press Vise. The BESSEY 4” Drill Press Vise provides a steady hard frame for the thin flexible polyimide film bending machine. A 6” Kobalt electronic caliper with a measurement accuracy of ±0.02 mm met the required dimensional tolerances. This bending test apparatus assembled to reproducibly and systematically carry out the steps described above is illustrated in Figure 5-10.
5.2.4 Validation Run

Figure 5-11 shows a conceptual schematic of linear distances to be measured between the machine clamps during the bending process. The lengths of the triangle are obtained by measuring the length of the machine clamp (b) and the distance between the edges of the clamps (a, c). These measurements can be used to estimate the angle $\gamma$ from the law of cosines set of equations. Then angle $\alpha_1$ is calculated from its complementary angle $\gamma$ along the X-axis ($\alpha_1 = 180^\circ - \gamma$). The same is followed to obtain angle $\alpha_2$ from the right clamp arm.
The estimated values of each of the variables considered during the validation run are shown in Table 5-1. These results are the targeted values for the bending of thin polyimide film (10 mm long) in the X-Θ system. All of the calculated operational values will be compared against these estimated values. The angle $\alpha_2$ values are the same as those for angle $\alpha_1$. This procedure allows the calculation of the error values for all bending angles, which should not exceed a value of $8.0^\circ$.

<table>
<thead>
<tr>
<th>$b$</th>
<th>$\alpha_1$</th>
<th>$\gamma$</th>
<th>$a$</th>
<th>$c = (a^2 + b^2 - 2ab \cos \gamma)^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2 mm</td>
<td>$22.5^\circ$</td>
<td>157.5$^\circ$</td>
<td>9.1 mm</td>
<td>15.99 mm</td>
</tr>
<tr>
<td>7.2 mm</td>
<td>$45^\circ$</td>
<td>135$^\circ$</td>
<td>8.2 mm</td>
<td>14.23 mm</td>
</tr>
<tr>
<td>7.2 mm</td>
<td>$67.5^\circ$</td>
<td>112.5$^\circ$</td>
<td>7.3 mm</td>
<td>12.06 mm</td>
</tr>
<tr>
<td>7.2 mm</td>
<td>$90^\circ$</td>
<td>$90^\circ$</td>
<td>6.4 mm</td>
<td>9.63 mm</td>
</tr>
</tbody>
</table>

After a preliminary overview of the estimated values for the X-Θ system, it was decided to measure the bending angles ($\Theta$) of $45^\circ$ ($\alpha_1 = \alpha_2 = 22.5^\circ$) and $135^\circ$ ($\alpha_1 = \alpha_2 = 67.5^\circ$). These two angles allowed the measurement of both acute and obtuse angles within the spectrum of bending angles ($\Theta$) in an X-Θ system. Therefore, they could be considered meaningful representations of the types of bending angles obtained by the X-Θ bending machine. A graphical representation of these two bending angles is shown in Figure 5-12. The bending
angle (\(\theta\)) of 45° should be obtained by moving the base frame block of the right clamp arm a
distance of ~1 mm. An angle of 135° should be obtained with ~3 mm of contraction
displacement. A series of test measurements at different bending angles were done prior to the
validation run. The purpose was to verify that no significant differences existed between
process bending angles and estimated bending angles.

![Figure 5-12 A graphical representation of bending angles (\(\Theta\)) 45° and 135°](image)

The validation run was done with one operator and three thin polyimide film samples
(~11.6 µm thick). Each sample had two repetitive measurements at a specific bending angle (\(\theta =
45°\) and \(\theta = 135°\)). This study required a total of 12 validation runs in random order. Minitab
software provided the random order of the validation runs (RunOrder in Table 5-2). After each
validation run, the bending machine was completely reset. The reset operation consisted of
rotating the machine clamp arms back to a bending angle of 0° and unloading the tested thin
polyimide film sample. Linear distance measurements between the clamps (variables \(a\) and \(c\) in
Fig. 5-11) were obtained at each validation run. Both clamp nests had a length of 7.2 mm
(variable \( b \) in Fig. 5-11). The tested sample films did not break or degrade during the validation process. The equations from the law of cosine equations were used to calculate the angles \( \alpha_1 \) and \( \alpha_2 \) (Table 5-2). The bending angle error comes from the difference between the estimated \( \theta \) and calculated \( \theta \).

**Table 5-2 Results from the 12 validation runs on the assembled X-\( \theta \) bending machine**

<table>
<thead>
<tr>
<th>StdOrder</th>
<th>RunOrder</th>
<th>Film Sample</th>
<th>( \theta ) (degrees)</th>
<th>( a ) (mm)</th>
<th>( c ) of the left clamp (mm)</th>
<th>( \alpha_1 ) (degrees)</th>
<th>( c ) of the left clamp (mm)</th>
<th>( \alpha_2 ) (degrees)</th>
<th>Calculated ( \theta ) (degrees)</th>
<th>Error (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>45</td>
<td>9.4</td>
<td>16.4</td>
<td>19.2</td>
<td>16.3</td>
<td>23.0</td>
<td>42.2</td>
<td>2.8</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>3</td>
<td>45</td>
<td>9.0</td>
<td>15.9</td>
<td>22.2</td>
<td>15.9</td>
<td>22.2</td>
<td>44.5</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>45</td>
<td>8.9</td>
<td>15.8</td>
<td>20.6</td>
<td>15.7</td>
<td>24.3</td>
<td>45.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>1</td>
<td>135</td>
<td>7.5</td>
<td>12.3</td>
<td>66.4</td>
<td>12.3</td>
<td>66.4</td>
<td>132.8</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>2</td>
<td>45</td>
<td>9.4</td>
<td>16.4</td>
<td>19.2</td>
<td>16.3</td>
<td>23.0</td>
<td>42.2</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>1</td>
<td>135</td>
<td>7.7</td>
<td>12.6</td>
<td>64.7</td>
<td>12.4</td>
<td>67.6</td>
<td>132.3</td>
<td>2.7</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>2</td>
<td>135</td>
<td>7.3</td>
<td>12.1</td>
<td>66.9</td>
<td>12.0</td>
<td>68.3</td>
<td>135.2</td>
<td>0.2</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
<td>3</td>
<td>135</td>
<td>7.3</td>
<td>12.1</td>
<td>66.7</td>
<td>12.0</td>
<td>68.1</td>
<td>134.8</td>
<td>0.2</td>
</tr>
<tr>
<td>11</td>
<td>9</td>
<td>3</td>
<td>45</td>
<td>9.2</td>
<td>16.1</td>
<td>22.1</td>
<td>15.9</td>
<td>22.2</td>
<td>44.3</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>3</td>
<td>135</td>
<td>7.4</td>
<td>12.3</td>
<td>65.6</td>
<td>12.1</td>
<td>68.4</td>
<td>134.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>2</td>
<td>135</td>
<td>7.7</td>
<td>12.6</td>
<td>64.7</td>
<td>12.4</td>
<td>67.6</td>
<td>132.3</td>
<td>2.7</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>2</td>
<td>45</td>
<td>9.0</td>
<td>15.9</td>
<td>22.2</td>
<td>16.2</td>
<td>21.5</td>
<td>43.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Finally, the study calculated the mean and standard deviation of the errors (Table 5-3) in the rotation of the clamp arms ($\alpha_1, \alpha_2$) and the bending angle ($\theta$). Analysis of the errors revealed that the variation of all the system angles ($\alpha_1, \alpha_2, \theta$) was less than $\pm 3^\circ$. Also, the design for the right clamp arm worked better than the one for the left clamp arm, although the variation of $\alpha_1$ error (left clamp arm) did not exceed the target value of $\pm 4^\circ$ or cause the $\theta$ error to exceed $\pm 4^\circ$. In conclusion, the assembled X-$\Theta$ bending machine could be used to bend thin polyimide films at different bending angles with angle variations of less than $\pm 3^\circ$.

Table 5-3 Statistical values for the bending system angles ($\alpha_1, \alpha_2, \theta$) errors

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_1$ Error</th>
<th>$\alpha_2$ Error</th>
<th>$\theta$ Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.62</td>
<td>0.66</td>
<td>1.42</td>
</tr>
<tr>
<td>Variance</td>
<td>1.41</td>
<td>0.25</td>
<td>1.3</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>1.19</td>
<td>0.5</td>
<td>1.14</td>
</tr>
</tbody>
</table>

5.3 Compression and Tension Testing

The bending apparatus just described was used to test the electrical conductivity behavior of metallized structures (e.g., interconnects embedded in the SIMSIP polymer film samples). Each metallized polymer film sample was tested in both tension and compression bending mode. All metallized polymer film samples tested for tension were loaded face-up in the bending machine (Fig. 5-13 (a)). For compression testing, the sample films were loaded with the metal structures facing down (Fig. 5-13 (b)). Once the metallized polymer film sample was placed in the bending apparatus, its electrical resistance was tested under compression or tension stress at $\theta = 0^\circ, 45^\circ, 90^\circ, 135^\circ$, and $180^\circ$ bending angles. The electrical behavior is
monitored by double-sweeping a given interconnect’s current-voltage (I-V) characteristics at -0.5 Volts to 0.5 Volts using an Agilent 4156C Precision Semiconductor Parameter Analyzer. The electrical conductivity characteristics of metal structures are always linear, allowing a sample resistance \( R_{\text{meas}} \) to be obtained.

![Diagram](image)

Figure 5-13 Film in tension or compression testing, (a) Au-interconnect is in tension stress, (b) Au-interconnect is in compression stress

5.4 Resistance Values During In-situ Electrical Measurements

The metallized polymer film samples can be tested in-situ in the X-\( \Theta \) system by a two-point electrical-resistance measurement. Conformable and rollable flexible polymer substrates with metal structures must be able to withstand being bent to various radii \( r \) without degradation of mechanical, and more importantly, electrical properties. The bending test apparatus, described in Sections 5.1 and 5.2, not only provided the required variable radius capability, but also overcame the limitations of the non-uniform bending radius and the constantly changing sample length of the alternative collapsing radius set-up described by Grego et al. (2005). The testing approach allowed us to measure electrical resistance in situ at different bending radii and thereby allowed \( R_{\text{meas}} \) to be analyzed as a function of the bending radius \( (\theta) \). The results of electrical characterization during compression and tension testing are presented in Chapter 6 (see Section 6.3).
Chapter 6.

Results

The preliminary research findings, SIMSIP fabrication technique and X-Θ bending system were introduced in Chapters 3 through 5. This chapter presents the results based on the proposed novel fabrication techniques for surface-embedding thin metal in polymers. Section 6.1 shows the initial experimental results for the metallization of PDMS, Section 6.2 explains the SIMSIP fabrication results of embedded metal (Au, Ag, Cu) in thin polyimide films, and Section 6.3 discusses the resistance results from the X-Θ bending test of SIMSIP flexible Au-interconnects.

6.1 PDMS Metallization Results

A PDMS metallization fabrication technique was used to create the following metallic electrode structure for use in the Step-And-Grow process. A set of four 5 µm wide electrodes were positioned with 10 µm spacing between them (Fig. 6-1 (a)). This electrode configuration was used to grow 200nm PANI nanowires (Fig. 6-1 (b)).
This novel fabrication technique gave reliable and a repeatable results for embedding metal patterns in PDMS. Figure 6-2(a) shows an AFM picture of an gold (Au) electrode in SiO$_2$. The electrodes were fabricated using a photolithography – etching – metal deposition – lift-off process. The etching step after photolithography is meant to create recessed features in the SiO$_2$ substrate, which are then completely filled during the metal deposition step. By carefully monitoring the SiO$_2$ etching and metal deposition steps, electrodes which are completely embedded in SiO$_2$ can be fabricated. As can be seen in Figure 6-2 (a), there are some limitations in the current fabrication processes, which result in electrodes of different micro/nano step heights from the SiO$_2$ surface.

Figure 6-2 (b) shows that the proposed novel fabrication technique for transfer of metal features into PDMS produces a defect-free Au electrode without trenches or steps on the PDMS substrate. There is a difference in height of only 3 nm to 5 nm between the valleys and peaks on the PDMS substrate. This process was repeated four consecutive times with the same results. The use of embedded metals in PDMS structures minimizes the possibility of solution leaking when a material (such as PDMS) with nano or microfluidic channels is placed on top. Lab-on-
Chip devices can be fabricated completely in PDMS. Using metallized PDMS will be beneficial for new micro/nano fabrication methods due to the simplicity of the fabrication methods, the prospects for reversible device assembly, its reusability, and its extremely low cost.

![AFM images of 5 µm electrodes on substrates](image)

**Figure 6-2** AFM images of 5 µm electrodes on substrates, (a) A 5 µm electrode embedded in a SiO$_2$ substrate, (b) A 5 µm electrode embedded in PDMS

### 6.2 SIMSIP Fabrication Results

To demonstrate that the new technique for surface-embedding metal patterns into flexible polyimide substrate has applications for future integrated flexible devices such as TFTs, it is essential to determine the minimum metal feature size and type of feature geometries that can be supported with the new technique. Samples were fabricated on both quartz and Teflon mother substrates using the proposed method to evaluate the feature characteristics.

#### 6.2.1 Fabrication on quartz substrate

During fabrication, different geometries (circles, squares, lines) of metal features with various feature widths and thicknesses were embedded in polyimide films. The metallized films were later subjected to optical, AFM and FESEM microscopy analyses to validate the fabrication method. Figure 6-3 shows a polyimide film embedded with Au features being
separated from the quartz mother substrate. Such polyimide films were fabricated using three different metals (Au, Ag and Cu) and three different feature thicknesses (30nm, 50nm and 100nm). Figure 6-4 (b-d) shows optical images of differently patterned metal structures embedded in polyimide films. The metal patterns in Figure 6-4 (b) are Au, Fig. 6-4 (c) are Ag, and Figure 6-4 (d) are Cu. For each of the three different patterns, there are four different feature widths – 2 µm, 4 µm, 8 µm, and 16 µm. While the larger feature widths can be clearly seen from the optical images, the optical magnification is not sufficient to properly show the 2 µm width features.

Figure 6-3 A polyimide film embedded with gold features being separated from the quartz substrate
The metal-polyimide surface was coated with a thin layer of Au (5 nm) and observed under an FESEM to study the feature widths. The images from the FESEM for two different surface geometries are shown in Figure 6-5 (a) and (c). The enlarged images of 2 µm wide
features from the same geometries are shown in Fig. 6-5 (b) and (d). The metal features in these flexible polyimide films are visibly clean and free of any defects. The limit on the width of metal features that can be obtained from the SIMSIP fabrication technique is only constrained by the capabilities of the optical photolithography tool.

![Figure 6-5 FESEM images of the metal pattern geometries in SIMSIP samples, (a) and (c): Circle and square metal patterns geometries from 16 µm to 2µm wide, (b) and (d): Magnified images of the 2 µm wide metal pattern features](image)

AFM studies were also performed to examine the free surfaces of SIMSIP flexible films.

The study found that surface planarization of polyimide films with embedded metallizations was affected when films of different metal structure thicknesses were utilized. Films with 100 nm thick metal structures showed a planar functional surface between the metal patterns and
the polyimide surface (Fig. 6-6 (a-d)). These results demonstrate capabilities of the proposed fabrication method to produce planar functional surfaces for metal features (≥100 nm thick) in a polyimide film.

![Figure 6-6 SIMSIP AFM images, (a) Au wire (100 nm), (b) Ag wire (100 nm), (c) Au wire (30 nm), (d) Cu wire (30 nm) fabricated on a quartz-DSP substrate](image)

To gauge the adherence of the embedded metal patterns to the polyimide, a Scotch tape test (Lim et al., 2006) was performed. Clear adhesive tape was applied over the surface and smothered to remove any air bubbles. The tape was then peeled off the polyimide surface at a constant speed. Two types of samples were tested this way – one with Au electrodes on top of the polyimide film and the other with the Au electrodes embedded into the polyimide film (Ono et al., 1985). For the electrode on top of the film sample, a section of the electrode was partially lifted-off the polyimide film and was found attached to the Scotch tape (Fig. 6-7).
However, the Au electrode embedded into the surface of the polyimide remained adhered to the polyimide film after removal of the Scotch tape. We note that this result was obtained without any chemical surface treatments to the metal film prior to polyimide application. In previous studies, bonding layers were built using self-assembling molecules such as thiol-terminated entities prior to the polymer (PDMS) addition (Lee et al., 2005).

![Figure 6-7 Scotch tape test (Control sample on the left side and SIMSIP sample on the right side)](image)

### 6.2.2 Fabrication on Teflon substrates

One of the main objectives of the SIMSIP process is to fabricate stable, functional, and flexible electronic circuits using a simple and economic manufacturing technique. A conceptual vision is to be able to apply the new fabrication method to a continuous single line manufacturing process. The use of Teflon as a mother substrate instead of quartz offers an opportunity to implement the SIMSIP process for large-area low-cost production.

Several experimental runs were done using the SIMSIP process with Teflon sheets (3 mm in thickness). The Teflon sheets were received from the supplier with an unpolished surface finish. A visual inspection with an optical microscope revealed grooves and scratches on
the unaltered Teflon surface obtained from the supplier. We considered this to be acceptable since the goal was to determine if flexible Teflon sheets could serve as the mother substrate in the SIMSIP process. With proper soft-baking, as discussed above, a complete transfer of metal patterns into the polyimide flexible film was obtained using Teflon sheet mother substrates. As it can be seen in Figure 6-8 (a), the metal features embedded in the polyimide reflect the scratches that are present in the surface of the Teflon. AFM and FESEM studies (Fig. 6-8 (b-c)) show a complete transfer of Au metal patterns with 2 µm wide features (100nm thick). These experimental results confirm the feasibility of using Teflon in a SIMSIP process for fabricating large surface areas.
6.3 **X-Θ Bending Test of SIMSIP Interconnects**

There were two fabrication techniques used for the metallization of polymer films in this study. One set of Au-interconnect samples were fabricated with the SIMSIP technique for Teflon mother substrates and in a second set of samples, the Au-interconnects were grown on top of a polyimide film. The second set was called the ‘control’ samples of the experiment because this fabrication technique is commonly used in nanofabrication labs (Ono, et al., 1985). The objective
of the bending test was to measure the electrical resistivity of the flexible Au-interconnects at different bending angles.

### 6.3.1 Electrical Conductivity and Topography of Au-Interconnects

The SIMSIP fabrication technique was used to attach Au-interconnects to a thin polyimide film (Au-interconnects/polyimide). Each Au-interconnect had a structural dimension of 10 mm long and 10 µm, 5 µm, or 2.5 µm wide (≤ 100 nm thick). The SIMSIP samples were tested with an I-V measurement tool by applying a bias from -0.5 Volts to 0.5 Volts (Fig. 6-9). In Table 6-1, it can be seen that the resistivity of the Au-interconnects are very similar to the theoretical value of 2.44 x 10^{-8} at 20°C (Cutnell & W.J., 1998). These electrical resistivity values provide confidence that the Au-interconnect features had the expected structural dimensions. In other words, the deposition, patterning, and transfer of Au material had been successfully accomplished by the fabrication methods described in Chapter 4.

<table>
<thead>
<tr>
<th>Interconnect Width Size</th>
<th>Control Sample Resistivity (Ω-m)</th>
<th>SIMSIP Sample Resistivity (Ω-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 µm</td>
<td>2.22 x 10^{-8}</td>
<td>2.77 x 10^{-8}</td>
</tr>
<tr>
<td>5 µm</td>
<td>2.36 x 10^{-8}</td>
<td>2.89 x 10^{-8}</td>
</tr>
<tr>
<td>2.5 µm</td>
<td>2.47 x 10^{-8}</td>
<td>2.96 x 10^{-8}</td>
</tr>
</tbody>
</table>
AFM analysis of the control and SIMSIP samples showed different Au-interconnect topographies on the polyimide film. The AFM images (Fig. 6-10) contrasted the control sample interconnects on the polyimide film versus the surface-embedded interconnects in the SIMSIP samples. The profilometer measurements established that the polyimide film used on the SIMSIP and control samples had a thickness of approximately 11.6 µm. The results of the electrical conductivity and physical characteristics allowed us to conclude that the fabricated samples were fully functional for testing.
6.3.2 Tension and Compression Testing of Flexible Au-Interconnects

In Section 5-4, the set-up of samples to be tested for tension and compression in the X-Θ bending machine was discussed. The mechanical performance of the Au-interconnect/polyimide samples was tested using the X-Θ mechanical apparatus. This test consisted of gathering the electrical resistivity characteristics of Au-interconnects under bending conditions. The I-V measurements used a two-point electrical-resistance test (double sweep) with a bias between -0.5 Volts and 0.5 Volts at every bending angle step.

In the mechanical testing phase, both types of Au-interconnect/polyimide samples were bent from flat to a minimum radius of \( r = 3.2 \text{mm} \). The electrical I-V data and the resistances were obtained in steps of \( 2\alpha = 45^\circ \) during the bending tests. The bending speed, which is defined as the change of the bending radius per unit time was approximately 0.25 mm/sec. It was observe that increasing or decreasing the bending speed did not change measured electrical resistance, although we did not explore thoroughly. Figure 6-11 presents data showing the
resistance $R_{\text{meas}}$ as a function of $2\alpha$ for SIMSIP samples. The graphs show the $R_{\text{meas}}$ responses when 10 µm wide SIMSIP Au-interconnects were tested under tension and compression. A positive slope was observed for this resistance with increasing tension. A negative slope resulted when another set of SIMSIP Au-interconnects (10 µm wide) were tested under compression. The range in the observed values of $R_{\text{meas}}$ was between 1.6 Ω to 2.3 Ω in both testing configurations. These data show that different bending angles have negligible effects on the electrical resistances of the SIMSIP Au-interconnects. The data also imply that the SIMSIP Au-interconnects do not experience any structural damage (debonding or cracking) when they were bent from $0^\circ$ to $180^\circ$. 

![Graph showing resistance as a function of bending angle](image)
Figure 6-11 Resistance measurements for SIMSIP 10 µm samples using the X-O system, (a) SIMSIP Au-interconnects 10 µm wide under bending tension test, (b) SIMSIP Au-interconnects 10 µm wide under bending compression test

A second set of data for 5 µm wide SIMSIP Au-interconnects are presented in Figure 6-12. This figure shows a similar electrical resistance behaviors exhibited by the 10 µm wide samples under bending conditions were observed for the 5 µm wide SIMSIP Au-interconnect/polyimide samples. The data show that the change in $R_{\text{meas}}$ due to bending angle was smaller for the 5 µm samples than for the 10 µm samples, in both tension and compression tests. The variations in $R_{\text{meas}}$ for the 5 µm samples due to bending angle were larger in compression than in tension, which was also observed in the 10 µm samples. Similarly consistent electrical resistance results had been observed previously, when thin metal interconnects embedded between two thin polymer films were positioned on the neutral plane (Han et al., 2008; Moon et al., 2010). However, to our knowledge, interconnects directly deposited on top of a single polymer film have never successfully withstood such vigorous testing while maintaining high levels of electrical resistance.
Figure 6-12 Resistance measurements for SIMSIP 5 $\mu$m samples using the X-$\Theta$ system, (a) SIMSIP Au-interconnects 5 $\mu$m wide under bending tension test, (b) SIMSIP Au-interconnects 5 $\mu$m wide under bending compression test

In order to validate these results, a set of SIMSIP and control samples need to be tested with cycling loading test. This should answer questions on the effect of mechanical stresses on Au-interconnects in flexible films when using the X-$\Theta$ system.
6.3.3 Cycling Loading of Flexible Au-Interconnects

Fatigue failure, defined as the failure of a structure by repeated loading, was examined for these SIMSIP structures using cyclic loading. To expose samples to fatigue conditions, both SIMSIP and control Au-interconnect/polyimide structures were repeatedly bent and electrically characterized. The samples were sequentially bent through $0^\circ - 90^\circ - 180^\circ$ and brought back to their initial flat positions ($0^\circ$), with resistance ($R_{\text{meas}}$) being measured at each bending angle. The time for each characterization cycle was 3.5 min. Performance of samples after such extreme bending exposures is an important consideration for interconnects in many polymer applications, ranging from e-skin to flexible displays.

The experimental data in Figure 13 shows the resistance characteristics of 2.5 $\mu$m wide SIMSIP and control Au-interconnect/polyimide samples, which were subject to 50 bending cycles. Both types of samples were electrically conductive through the entire duration of the tension tests, and the $R_{\text{meas}}$ of the SIMSIP sample remained almost constant. In contrast, a gradual increase in $R_{\text{meas}}$ with repeated cycling was observed for the control sample. The statistical variance between cycles was found to be greater or equal to 1.2 for the SIMSIP samples. In comparison, it was as large as 1,071 for the control samples.
Figure 6-13 Cycling loading bending of flexible 2.5 µm Au-interconnects, (a) Resistance ratio of Au-interconnects 2.5 µm wide during tension cycling loading, (b) Resistance ratio of Au-interconnects 2.5 µm wide during compression cycling loading
Similar to cyclic loading in tension, a cyclic loading experiment for compression bending was also performed on 5µm wide Au-interconnect/polyimide samples. The $R_{\text{meas}}$ values of the SIMSIP samples illustrated in Figure 6-14 display no significant variation with this cycling history. However, the compression testing greatly affected the electrical resistivity of the control samples with all control samples exhibiting catastrophic failures before the third bending cycle. The FESEM pictures (Fig. 6-15) show the effects of the compressive stresses on the SIMSIP and control samples. The SIMSIP samples do not show any structural defects under FESEM after 50 bending cycles in compression mode. The control sample is completely serrated at the metal-polymer dislocation point due to the compressive bending forces. This same type of defect was seen in both control samples tested for cyclic compression bending.

The resistance $R$ of a uniform sample of length $L$ and cross-sectional area $A$ is given by Equation 6-1:

$$R = \frac{\rho L}{A}$$ \hspace{1cm} \text{Equation 6-1}

where $\rho$ is the material resistivity. From this equation, it follows that the resistance of interconnect samples can change with bending due to: (1) changes in $\rho$, (2) changes in $L$, (3) changes in $A$, and (4) loss of sample uniformity (e.g., necking down, cracking). The electrical properties observed during cyclic testing certainly establish that the SIMSIP samples do not experience a loss in sample uniformity in either tension or compression. This conclusion is also supported by FESEM micrographs. The behaviors seen in the SIMSIP samples under tension and compression are fully explicable in terms of an increase in $L$, and a decrease in $A$ through Poisson’s ratio ($\rho$) in tension, and the converse in compression.
Figure 6-14 Cycling loading bending of flexible 5 µm Au-interconnects, (a) Resistance ratio of Au-interconnects 5 µm wide during tension cycling loading, (b) Resistance ratio of Au-interconnects 5 µm wide during compression cycling loading.
Figure 6-15 FESEM images of Au-interconnects after compression cycling loading, (a) Control 2.5 µm wide Au-interconnect, (b) SIMSIP 2.5 µm wide Au-interconnect
6.4 SIMSIP Nano Fabrication Technique (Derivative)

Existing techniques are able to support the surface-embedding of micro-metal features. However, there is no current application for these techniques when the metal features are less than 2 µm wide. As current technologies follow Moore’s law (Stokes, 2003) regarding size, cost, density and speed of components, applications using existing methods will decrease as the components in future electronic devices shrink from micron to nano dimensions. For example, the feasibility of using nano-antennas is now being studied by a few research groups because of their possible application in nano-sized communicating devices (Ziaei, et al., 2008). Also, the next generation of antennas needs to provide functionality and physical flexibility (Tiercelin, et al., 2006). A test of the robustness of the SIMSIP technique will be to be performed in order to assess its application for the surface-embedding of nano size metals.
Figure 6-16 SIMSIP Nano validation images, (a) optical image of the Au geometrical pattern design in the polyimide film, (b-d) AFM and FESEM studies show a complete transfer of Au metal patterns with 2 µm features wide (100 nm thick)

A derivative (SIMSIP Nano) of the novel fabrication technique (SIMSIP-Quartz) is obtained by replacing contact photolithography with electron beam lithography (e-beam). The e-beam writer is capable of producing nano-size patterns in the e-beam resist (Fig. 6-16 (c)). This will leave nano-metal features on the quartz substrate after the lift-off process (Fig. 6-16 (b)).

One experimental run of the SIMSIP Nano fabrication technique was successfully completed for surface-embedding 1.5 mm-long Au-interconnects (35 nm thick). The FESEM picture (Fig. 6-16 (c)) shows Au metal interconnects approximately half-a-micron wide (600 nm). However, a continuous hill type with a step height (~80 nm) similar to the thin micro-size metals was observed, as shown in the AFM image (Fig. 6-16 (d)). In addition, the electrical resistivity of the
nano Au-interconnects was around $2.45 \times 10^{-8}$ ohm-m (Baptiste, 2004) before and after surface-embedding (Fig. 6-17). As a result, the SIMSIP Nano fabrication technique can be used for surface-embedding nano-metal patterns into a thin flexible polyimide film.

![Figure 6-17 Electrical conductivity of SIMSIP Submicron Au-interconnects](image)

**6.5 SIMSIP vs. Existing Fabrication Techniques**

We find that there are three important issues when using mother substrates in the fabrication of surface embedded metal patterns in flexible polymeric substrates. First, the transferable thin metal pattern should have a moderate adhesion to the mother substrate. The adhesion has to be strong enough to withstand the metal patterning process but also be weak enough to allow for easy removal of the metal/polyimide material from the mother substrate after the curing processes. Second, the processing steps must have the ability to allow for chemical bonding between the metal and the polyimide film. Last, the technique must have potential for large-scale manufacturability.
Table 6-2 shows a comparison among existing fabrication techniques for flexible electronics. As we can see from the table, SIMSIP overcomes many of the disadvantages associated with the other three techniques. For example, SIMSIP eliminates the need for sacrificial metal stack layers (Lim et al., 2006) to ensure complete transfer of micro-metal structures. SIMSIP can easily accommodate the use of molecular monolayers to enhance metal/polymer bonding (Lee et al., 2005) if required, but it proved to be unnecessary when we embedded Au, Cu, and Ag into polyimide. The SIMSIP technique is capable of producing flexible paper-like metalized films without any defects (e.g., delamination and buckling) on the patterned metal features, unlike the direct deposition process on top of film (Xiang et al., 2005; Suo and Li, 2006). SIMSIP also eliminates problems associated with interconnections which are typically observed when using fully-embedded techniques (Befahy et al., 2007; Kim et al., 2008).
Table 6-2 Comparison of different fabrication techniques used for flexible electronics

<table>
<thead>
<tr>
<th>FABRICATION</th>
<th>PROS</th>
<th>CONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top of Film – Direct Deposition</td>
<td>-Simple process</td>
<td>-Adherence problems</td>
</tr>
<tr>
<td></td>
<td>-Potential for continuous process</td>
<td>• Delamination and buckling</td>
</tr>
<tr>
<td></td>
<td>-Supports micro and nano elements</td>
<td>-Not fully bendable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Step heights on surface</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Subject to wear and tear</td>
</tr>
<tr>
<td>Fully Embedded</td>
<td>-Fully bendable</td>
<td>-Complicated process</td>
</tr>
<tr>
<td></td>
<td>-Supports micro and nano elements</td>
<td>-Interconnection problems</td>
</tr>
<tr>
<td></td>
<td>-Good resistance to wear and tear</td>
<td>-Batch process</td>
</tr>
<tr>
<td>Surface Embedded</td>
<td>-Planar surface</td>
<td>-Uneven surface</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIMSIP</td>
<td>-Simple process</td>
<td>-Ability to fabricate nano features not jet verified</td>
</tr>
<tr>
<td></td>
<td>-Potential for continuous process</td>
<td>-Limited application</td>
</tr>
<tr>
<td></td>
<td>-Fully bendable</td>
<td>• Only attached metals to Polyimide</td>
</tr>
<tr>
<td></td>
<td>-Planar surface</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-Good resistance to wear and tear</td>
<td></td>
</tr>
</tbody>
</table>

6.6 Summary

This chapter presented the current implementation of the SIMSIP fabrication technique and electrical characteristics of SIMSIP Au-interconnects described in Chapters 4 through 5. An effective embedding of micro/ nano metal patterned films onto a polyimide film was achieved with the SIMSIP fabrication technique. FESEM studies validated the surface-embedding of metal (Au, Ag, Cu) patterns in the polyimide film. A flat surface topography of the SIMSIP samples could be observed when embedding metal patterns that were 100 nm thick. In addition, the electrical resistivity measurement results showed that metal patterns were completely transferred to polyimide film. Finally, the electrical conductivity of SIMSIP Au-interconnects remained constant when films were fully bent ($180^\circ$).
Chapter 7.

Conclusion

This research focused on developing a fabrication technique for surface integration of micro/nano metal structures into the surfaces of thin, flexible, paper-like polymer films. SIMSIP can be easily implemented to produce defect free, functional and fully bendable micro/nano metal patterns on thin polymer film in an economical manner. Future electronic applications may use this technique to manufacture electronic flexible devices that can be in intimate contact with curved surfaces (e.g., retinal implants) and able to withstand large and repeated mechanical deformations (e.g., RFID antennas). First, a summary of this research is presented in Section 7.1. Section 7.2 outlines major research contributions, which are followed by potential future research opportunities in Section 7.3. Finally, the broader impact of this research is discussed in Section 7.4.

7.1 Summary

In Chapter 1, we outlined our research motivations, which centered on the development of a thin, flexible, paper-like polymer films with surface-embedded micro/nano metal patterns which could be used in the production of new types of electronics, such as e-skin. A brief introduction to the desirable properties of flexible electronics was discussed. The perceived importance of new applications such as e-skin devices made out of a single layer of polymer film necessitated the development of a novel micro/nano fabrication process (SIMSIP).
In Chapter 2, previous research efforts in the area of flexible electronics were presented. We found that researchers have been investigating ways to attach electronics to flexible material (e.g., Au-interconnects). Also, several studies related to stresses in thin metal films (≤ 100 nm thick) on flexible materials were discussed. However, these studies showed that metal patterns (e.g., metal interconnects) on flexible films unless fully encased debonded under mechanical stresses.

Chapter 3 focused on the development of the fabrication process and its operational parameters for embedding Au metal patterns into a PDMS surface. Lithography and lift-off processes were developed for the fabrication of metal patterns on SiO₂ mother substrates. In addition, molecular monolayers were used in different fabrication steps in order to attach 5 µm-wide Au electrodes to PDMS. The experimental approach provided us with an understanding of the set of fabrication principles necessary to surface-embed thin metal layers (≤ 100 nm thick) into polymers.

Chapter 4 integrated the lessons learned through experimentation into novel fabrication techniques for surface-integration of thin metal patterns (≤ 100 nm thick) into polymers. First, a fabrication technique was developed for embedding Au metal patterns into PDMS. Then, a second fabrication technique (SIMSIP) was developed for embedding Au, Ag or Cu into a thin polyimide film. SIMSIP used the natural chemical bonding reaction between the metal boundary layer and polyimide material, and the low surface energy of Teflon (fluoropolymer) or the polished (surface roughness < 2 nm) quartz crystal surface as mother substrates in order to metalize polyimide films. Also, a derivative fabrication process from the SIMSIP technique
was developed for surface-embedding metal patterns with nano dimensions into a flexible polyimide film. As a result, the SIMSIP fabrication technique could be used for surface-embedding different metals with micro or nano dimensions directly into the surface of a fully flexible polyimide film without any defects.

Chapter 5 discussed the testing methodology for determining bending radii in flexible electronic devices (e.g., metal interconnects). The X-Θ system was developed to test the bendable characteristics of flexible substrates. This system was capable of overcoming the limitations of the non-uniform bending radius and the constantly changing sample length of the collapsing radius set-up. A manual X-Θ bending machine was designed and assembled to test the SIMSIP Au-interconnects ($L_0 = 10$ mm) at different bending angles ($0^\circ$, $45^\circ$, $90^\circ$, $135^\circ$, and $180^\circ$). Finally, the electrical resistance ($R_{\text{meas}}$) was reported in terms of the actual increase or decrease of surface stresses in the bent portion of the sample.

Chapter 6 presented the experimental results for surface-embedding thin (nano) metal layers ($\leq 100$ nm thick) on polymers using the novel fabrication techniques. First, Au-electrodes were successfully transferred into PDMS. Then, the SIMSIP technique was applied to metallize polyimide films with Au, Ag, and Cu metal patterns with different geometries. FESEM and AFM studies confirmed the successful transfer of metal features as small as 600 nm wide with no step heights on the surface of the polymer substrate. Lastly, there was no significant variation in the $R_{\text{meas}}$ response from the tension or compression bending of SIMSIP Au-interconnects. However, all control samples experienced debonding and breakage due to the surface stresses encountered during the X-Θ bending angle test.
In summary, the novel SIMSIP fabrication technique can be used to extend future research in micro/nano manufacturing techniques for flexible electronic devices. Although similar approaches exist in literature, the proposed SIMSIP fabrication technique provides a robust, lighter weight, economical, and reliable way of achieving flexible circuits/electronics. As a result, the SIMSIP fabrication technique will yield strategic advantages by accelerating the research and development cycle, and helping to create flexible, reliable, robust, and better performing electronic products.

7.2 Research Contributions

In this research, a novel fabrication technique for embedding 5 µm wide Au metal (≤ 100 nm thick) patterns into PDMS was developed and demonstrated. In order to make embedding metals into polymer a viable alternative for micro/nano manufacturing applications, a fabrication technique referred to as SIMSIP was created. This SIMSIP fabrication technique is capable of embedding metals with different geometric designs of submicron dimensions (< 1 µm) into the surface of a polyimide film.

The SIMSIP fabrication technique developed to embed metal patterns in polyimide film in this research is not limited to Au alone. It can be applied to Ag and Cu, which are less expensive. A thin metal thickness of 100 nm allows for successful embedding of metals without any step heights on the metallized surface. When the thickness is 30 nm, however, the metal does form a step height in the polyimide. Also, narrow metal patterns of 600 nm wide can be successfully transferred into a thin polyimide film. Moreover, the SIMSIP technique gives the same results with Teflon material as a mother substrate.
Based on the X-Ø bending test, SIMSIP Au-interconnects as small as 2.5 µm are fully functional under tension or compression bending stresses. The metal features remain embedded in the polyimide without any buckling or breakage. These interconnects do not degrade after a cycling loading of 50 runs, unlike all the control samples which were severely damaged during compression bending tests.

The practical implementation of the SIMSIP technique to flexible electronics will be ultimately governed by its ability to produce superior devices and circuits at lower cost. We believe the SIMSIP process is very capable of attaining this goal by using a roll-to-roll method. Figure 7-1 shows the conceptual diagram of a continuous low-cost, SIMSIP manufacturing process for producing metal interconnect/electrode structures in polymer films for flexible electronics. The production flow is based on a conveyor system transferring a Teflon sheet or Teflon-covered belt across multiple processing stations. This Teflon surface serves as the mother substrate for the production of metal-polymer flexible circuits. In the first process, which we term imprinting, the metal would be deposited and patterned with imprint lithography (Ahn and Guo, 2008). This would require the sub-steps of depositing the metal, applying the photoresist, soft-baking, imprinting with the required pattern, developing, and descumming. Alternatives to imprint lithography such as ink-jet (Ko et al., 2007; Calvert, 2001) and dip pen (Wang et al., 2008) lithographies could also be used to produce patterned metal features on the mother roll substrate in this figure. The successive steps are straightforward applications of SIMSIP: applying a continuous layer of polyimide liquid solution to the Teflon sheet (completely covering the patterned metal features), polymer curing, and separating the mother
roll substrate. Furthermore, the finished SIMSIP end product can be populated with circuit elements on the electrode pads of the metal-polyimide film using a surface-mount technology (SMT) manufacturing line. The process is also fully compatible with the neutral plane embedding, as the whole structure of devices, metal interconnects, and electrodes can be placed at the neutral plane with a final step of a second application of polymer.

![Conceptual diagram of the SIMSIP fabrication method used in a continuous very-low-cost manufacturing process of organic electronic devices](image)

We can expect such flexible electronic circuits, whose functions are currently being envisioned, to one day revolutionize the technological world in which we live.

### 7.3 Future Research Directions

A novel fabrication technique for embedding functional thin metal structures into a polymer was successfully created, and though the work outlined in this research was successfully demonstrated for polymer metallization of Au, Ag, or Cu metal patterns, many
enhancements to fabrication devices using the SIMSIP technique are still possible. Specific directions for future work are discussed below.

7.3.1 Thin-film Transistors (TFTs)

A thin-film transistor (TFT) is a special kind of field-effect transistor which is made by depositing thin films of a semiconductor active layer, a dielectric layer, and metallic contacts over a supporting substrate. A common substrate is glass, since the primary application of TFTs is in liquid crystal displays. This differs from the conventional transistor where the semiconductor material typically is the substrate, as in a silicon wafer. The best known application of thin-film transistors is in TFT liquid panel displays (LCDs), an implementation of LCD technology. Transistors are embedded within the panel itself, reducing crosstalk between pixels and improving image stability.

A logical extension of the SIMSIP fabrication technique is to embed TFTs into thin flexible polymer. Recently, a printable, flexible CNT-TFT device was fabricated on a standard transparent film (Vaillancourt, et al., 2008). However, the smallest feature size was 4 µm and the characterization was done on an unstressed device. Extending the SIMSIP process to this application will require solving the problems related to stacking the TFT components on the Teflon surface.

7.3.2 RFID Antennas

Radio-frequency identification (RFID) is the use of an object (typically referred to as a RFID tag) which has been applied or incorporated into a product, animal, or person for the
purpose of identification and tracking using radio waves. Some tags can be read from several meters away and beyond the line of sight of the reader. Most RFID tags contain at least two parts. One is an integrated circuit for storing and processing information, modulating and demodulating a radio-frequency (RF) signal, and other specialized functions. The second is an antenna for receiving and transmitting the signal.

The SIMSIP fabrication technique offers the opportunity to fabricate smaller, flexible, and skin like RFID antennas in a cost-effective manner. This will be an important improvement in the fabrication of RFIDs because their current manufacturing cost is one of the main obstacles to their use in product tracking. An example of sponsored research is the biomedical application of a flexible surface wetness sensor using a radio-frequency identification (RFID) device that is small, inexpensive, disposable, soft, wireless, and passive (Yang, 2008). The RFID components were fabricated and assembled in a flexible polymer film (Fig. 7-2). Now, the challenge is to develop a good design for a micro or nano RFID antennas.

7.3.3 Semiconductor Sensors (SCS)

Semiconductor sensors are semiconductor devices in which the semiconductor materials are chiefly responsible for sensor operation. They are differentiated from other solid-state sensors by their small size, and by the manufacturing techniques used to create them. Most semiconductor sensors are fabricated by processes that have been developed for integrated circuits (ICs). Currently, semiconductor sensors are on the order of micrometers (microns) in dimension.
The SIMSIP technique offers the opportunity to develop research on novel fabrication methods for flexible semiconductor sensors. The development of flexible semiconductor sensors in polymer film not only will contribute to their potentially low cost, but will also allow them to be integrated with other flexible microelectronics circuits (integrated sensors).

7.4 Conclusions

SIMSIP is a novel fabrication method for embedding metal patterns into flexible polymer substrates, demonstrated for Au, Ag, and Cu using different geometries and sizes in polyimide. Various geometries with designs as small as 600 nm in pattern width and 30 nm in metal thickness were used to demonstrate the range of the process. Excellent planarization is obtained for metal films greater than 100 nm in thickness. Film adherence was also demonstrated with the Scotch tape test, even without the use of self-assembling metal-polyimide bonding treatments. SIMSIP has considerable potential for being developed as a roll-to-roll continuous process for producing interconnect and metallization layers for skin-like flexible circuits or displays.

This research analyzed electrical resistance behavior, as a function of bending angle and bending history, for Au interconnects embedded into polyimide surfaces using the SIMSIP process. The SIMSIP samples were able to maintain an almost constant resistivity under tension and compression bending test conditions, even through 50 loading-unloading cycles. SIMSIP Au-interconnect samples displayed no buckling or dislocation defects after the bending tests. Control samples (Au-interconnects on top of polyimide surfaces), on the other hand, were significantly affected by tension and compression stresses.
These testing results demonstrate that SIMSIP fabrication method can provide thin flexible circuits with stable electrical resistance characteristics for bending angles up to 180°, even under cyclic loading conditions. Such interconnect/polyimide stability had only previously been seen for interconnects on the neutral plane. Obviously, the SIMSIP surface-embedded interconnects can also be positioned on the neutral plane by the addition of another layer of polyimide film on top, thereby providing further stability if desired. SIMSIP flexible circuits offer both the stability and durability characteristics necessary to advance the development of flexible electronics for applications ranging from antennas to displays.
References


Vita

Hector Carrion-Gonzalez

Hector Carrion-Gonzalez was born on October 14, 1969 in Seville, Spain. He received his baccalaurate degree in industrial engineering from the University of Puerto Rico (1992) and a master’s degree in industrial engineering with a concentration in manufacturing systems from the University of Michigan in Ann Arbor (1996). Hector has ten years of experience in industry. He worked in the pharmaceutical sector for Merck in Puerto Rico, where he was involved in the introduction of new products into the market. He also worked at Motorola as an engineer responsible for process improvements in the manufacture of engine controllers. At Motorola, he was also involved in the implementation of data integration projects that facilitated the execution of the production planning processes for semiconductor devices. He is a member of the Alpha Pi Mu Honor Society for Industrial Engineers. The focus of his current research is process modeling for novel nanofabrication techniques in the field of flexible electronics.