2017

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**Flexible Polymer-Ceramic Composite Materials for High Sensitive
Pressure Sensing Applications in Harsh Environments**

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**Thesis submitted to the Benjamin M. Statler College of Engineering and
Mineral Resources at West Virginia University**

In partial fulfillment of the requirements for the degree of

**Master of Science in
Materials Science and Engineering**

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**Morgantown, West Virginia
2017**

**Keywords: tactile sensor, space, harsh environment, capacitive,
capacitance, composite, HfO₂ thin film, flexible electronics, robotics
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ABSTRACT

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Kavin Sivaneri Varadharajan Idhaia

Robotics aligned with completing physical activities in the space environments will require a new suit of solid-state sensors that are versatile and robust, and will provide precise information about contact events with various space assets. One of the vital sensing mechanisms is the “feel-of-touch” or “tactile/haptic” feedback to the robotic system. Current robotics tactile/force sensor use mechanical switches for the feedback to determine whether the end-effector is in contact, which does not provide sufficient information regarding the local force and point-of-contact for the robotic end-effector. To tackle these challenges, the current work focusses on the development of flexible tactile sensor arrays that conform to the geometry of the end-effector and provide information about contact location, force magnitude, and force type. The sensor arrays were also composed of robust materials sufficient for the desired space application; the sensor system was designed to withstand the harsh environment, temperature fluctuations, and desired sensitivity.

In this research, tactile sensor arrays were fabricated and tested, which were flexible, thick film, capacitive sensors that are composed of a 2:2 laminar polymer-ceramic composite. The composite was composed of four distinct layers, which consist of a polyimide support (Kapton film), patterned Pt electrodes, a compliant elastomer layer, and a ceramic dielectric layer (HfO_2). Three different capacitive sensor architectures were developed to study the influence of the dielectric HfO_2 layer on the sensitivity of the sensor. The baseline architecture was composed the compliant elastomer layer (Arathane 5753 A/B) sandwiched between the Pt electrodes. A bi-layer architecture was also fabricated with an additional HfO_2 thin film deposited onto the elastomer in order to magnify the capacitive response of the sensor structure. In a tri-layer architecture, the HfO_2 layer was sandwiched between elastomer layers to understand the influence of the additional elastomer layer on the sensitivity and pressure distribution across the sensor structure. These materials were tested over a wide temperature range from -60 to 120 °C. The fabricated sensor showed good sensitivity and cycle stability between 0 and 360 kPa. The influence of temperature variations on the capacitive and mechanical properties of the composites was also studied in detail. Thermomechanical loading cycles were performed with an in situ electrical acquisition to characterize the sensor. Chemical and structural characterization of the HfO_2 layer deposited on the flexible substrate was evaluated by a combination of conductive atomic force microscopy (c-AFM), raman spectroscopy, and x-ray photoelectron spectroscopy (XPS), and the optical properties were analyzed by ultra-violet visible spectrophotometer (UV-Vis).

Embedding strategies were proposed and developed to shield the sensors against the direct exposure to cosmic rays, atomic oxygen, ultraviolet rays, and damages caused by direct contact with other objects in space. The sensors were embedded in a 3D printed prototype which mimics the actual geometry of the gripper tool, a silicone layer was used to provide the mechanical compliance and to support the top plate holding the sensor. The embedded prototype was tested in a mechanical analyzer to study the capacitive response and analyze the influence of the residual capacitance from the silicone layer and the top plate. The final prototype was built and demonstrated with the customized electronics and a software program to directly read-out the pressure/force signal from the sensor.

Dedication

I would like to dedicate this work to my family, advisors, friends and especially to God without whom none of this work would be worthwhile.

Acknowledgment

First, I would like to express a great deal of thanks to my research advisor, Dr. Edward Sabolsky, for providing me the opportunity and dedicating countless hours to the furthering of my research goals. Without his advising and guidance, completion of the project would not have been possible. I would also like to thank Dr. Thomas Evans, my co-advisor, for providing his continuous support in the fulfillment of research goals. I owe a great deal of thanks to Mrs. Kathy Sabolsky for providing her help and expertise in the lab whenever I needed it. I would also like to thank my other committee member, Dr. Konstantinos Sierros for providing his support in the project and letting me use the equipment in his lab. I would also like to acknowledge Mr. Ozcan Ozmen, Mr. Gunes Yakaboylu, Dr. Tugrul Yumak, Mrs. Mina Aziziha, and Dr. Matthew Johnson for their expertise and assistance in materials characterization. Special thanks to Mr. Harley Hart who spent countless hours assisting and training me in the cleanroom for handling sophisticated equipment and Dr. Qiang Wang who helped me in the XPS characterization. I would also like to acknowledge Dr. Powsiri Klinkhanchorn, Mr. Eric Loy, and Mr. Patric Lewis for their help and support in electrical characterization. I finally would like to thank all my family member and especially my cousin, Mr. Keerthi Sivaneri for their love and unwavering support throughout my life.

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Chapter 1 – Introduction

1.1. Statement of Problem – Challenges in Tactile Sensing for Space Robots

The advancement of technologies in the field of telecommunication, weather monitoring, navigation, and space exploration increased the demand for launching satellites in the last decade. A survey shows there is a steady increase in the launch of geostationary satellite vehicles and the demands keep steadily increasing since 2005 [1]. In 2016, the Satellite Industry Association (SIA) posted revenues of \$261 billion which accounts for 77% of the space economy with an average growth above 9% per annum since 2007 [2]. In 2016, the satellite industry reported \$127.7 billion was spent on satellite servicing which accounts for ~49% of the overall expenditure [2]. The projections clearly show that the demand for satellite servicing is increasing due to on-orbit failures “to a great extent”.

The advancement in robotic technology has been proven to be an effective option to service, decommission, refuel and to address various issues of satellite servicing which can make a satellite inoperable. In addition to servicing the satellite, robotic technology was researched to handle convoluted tasks in outer space which involves risking the life of an astronaut [3,4]. Additionally, space robotic technologies can also be applied to autonomous berthing systems of spacecraft and the robots working in tandem with human interactions to handle complex tasks in space which require reliable, robust and high sensitive sensor system in the robotic skeleton. Among various sensors embedded within a robotic skeleton, tactile/haptic (pressure mapping) sensing is one of the vital sensing capabilities required within robotic end-effector manipulators, since spatial

awareness is one of the essentials to remotely handle an operation in space. Tactile sensor play a major role in performing simple operations like grasping an object and moving it (low dexterous) to delicate operations (high dexterous), such as docking a spacecraft without human intervention, servicing a satellite (changing the repaired parts), refueling (changing solar cell/batteries) or decommissioning an object in space.

Based on the application, research has been focused on the development of various tactile sensor technologies for several years. Commercially available sensors are incompatible for space applications due to the harsh environments of space including cosmic ray bombardment, temperature fluctuation, electrical and volumetric constraints [5]. Current space robotic tactile feedback utilizes a wide range of technologies such as force/torque sensors, strain gauges, mechanical switch, flexibility modeling and motor current/voltage calculations [6]. Capaciflector, a capacitive proximity sensor, was used for contact prediction and force quantification by the embedded spring elements. Due to the spring elements, the sensor experiences high drift and poor resolution; this is not viable for space application where a robotic system handles sophisticated tasks. Additionally, these technologies provide information only on whether the contact is made and quantifies the force based on a predefined model which cannot be accurate. This might lead to over/under gripping an object which is unable to detect with the current technologies. Furthermore, current technologies do not provide information regarding point-of-contact, force magnitude, slippage of the object during grappling.

To overcome the limitations, more advanced technologies have recently been proposed for tactile/haptic feedback or pressure mapping of robotic end-effector [5,7]. The sensor must be designed in such a way that it should consider several factors such

as mechanical, environmental, and volumetric restraints. The environmental restraints are low vacuum pressure ($10^{-7} - 10^{-8}$ Torr), temperature fluctuations between -60 and 120°C, cosmic ray and ionic/electron bombardment [8,9]. The design should also incorporate the ability of the sensor to be embedded within the end-effector to protect from charging and radiation effects of the space environment. Finally, the sensor should be able to operate with minimal power, hardware requirements while providing a reliable feedback.

There are various physical and electrical mechanisms that were reported in the fabrication of tactile sensor technology [10-12]. Piezoresistive, piezoelectric, and capacitive sensing is the most common electronic mechanisms used to develop tactile/pressure-sensing devices [13-17]. The early pressure mapping sensors were fabricated on rigid (nonflexible) substrates which are limited to the planar end-effector geometry and certain pressure/force. To overcome this limitation, research has been focused on developing tactile sensors on various flexible substrates composed of polymers, metal foils and fabrics [18-30]. To achieve all the requirements of tactile sensors with high spatial resolution, and pressure mapping under low operating power conditions which conforms given geometry of the end-effector, microelectromechanical systems (MEMS) are a viable platform to develop advanced flexible tactile sensors. To realize the local forces and point-of-contact on the end-effectors, a very precise sensing mechanism should be applied. Among various sensing mechanisms discussed above, piezoresistive is the most widely researched area in flexible tactile sensor and there are commercially available flexible piezoresistive tactile sensors which use conductive carbon ink composite as the active sensor material [4]. Though the sensors work in the moderate

force regime (100 – 300 N), it is also very important to sense low force regime (0.1 – 100 N) while performing a delicate and high dexterous tasks. The limitations with commercially available piezoresistive sensors are drift, hysteresis, high nonlinearity, and temperature stability, which require frequent calibration and the life cycle of the sensor is limited by operation and frequency of usage. To overcome the limitations and drawbacks of the piezoresistive sensors, capacitive sensing modality has been introduced [7-20]. The mechanism of the capacitive sensor is the measure of change in capacitance (ΔC) as the change in distance (d) between two parallel plates (electrodes) with respect to applied pressure/force. The active sensing area is defined by the area (A) of the electrode, the separation distance between the electrodes which is a dielectric material. The nominal capacitance of the parallel plate sensor without load is given by,

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (1)$$

where ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m), ϵ_r is relative permittivity (ratio of complex frequency dependent absolute permittivity of the material to ϵ_0). The change in capacitance is induced by a change in distance between the elastomer layer (when an elastomer is used as active sensing material), which can be evaluated by a change in strain (ϵ) of the elastomer layer, the equation can be rewritten as,

$$\Delta C = C_1 - C_2 = \frac{\epsilon_0 \epsilon_r A}{d_1} - \frac{\epsilon_0 \epsilon_r A}{d_2} = \frac{\epsilon_0 \epsilon_r A \epsilon}{d_2} \quad (2)$$

If d_1 is pre-strain thickness and d_2 is post strain thickness, the induced strain equation can be deduced by,

$$d_2 = \left(d_2 - d_1 / d_1 \right) d_1 + d_1 = \epsilon d_1 + d_1 = d_1 (1 + \epsilon) \quad (3)$$

d_2 is the change in capacitance equation,

Capacitive sensors are robust with design flexibility, high sensitivity, good repeatability and temperature stability. Commercially available capacitive sensors require sophisticated electronic circuits to be designed and incorporated in order to measure the small change in capacitance which adds up to extra cost for incorporating the device. XSensors® developed a capacitive pressure measurement using conductive fabric and foam dielectric material [6]. Muhammad et al. incorporated a capacitive sensor in a CMOS using silicon substrates which are not conformable and limited by end-effector geometry [13,14]. Pritchard et al. fabricated flexible pressure on polyimide film with Parylene – C as active sensing element which operates in low pressure regime [11]. Dobrzynska et al. fabricated flexible polymer sensor using common metallization and micromachining process, and the capacitance was in the pF (10^{-12} Farad) range and the change in capacitance (ΔC) was in the fF (10^{-15} Farad) range, which requires highly sensitive and sophisticated electronics to read out the sensors. Lee et al. reported the fabrication of capacitive tactile sensing array using polydimethylsiloxane (PDMS) and air gap as active dielectric layer [16]. Cheng et al. fabricated a tactile sensor that can be incorporated into a flexible printed circuit board with a sensing range of 250 kPa [17]. The sensors showed drift during the calibration cycles and capacitance was generally low, which makes the electronics even more sophisticated and causes many anomalies during operation cycles. The materials used in these works demonstrated relatively high thermal expansion and low stability under high and low temperature (<0°C) regime. Designing and fabricating a sensor with good spatial resolution, stability under a wide temperature range, and low power consumption is still in its early stage of development. Weadon et al. reported thick

film tactile sensor fabricated by 0:3 connectivity ceramic:polymer composite material as active sensing material with good sensitivity; however, the hysteresis and drift were high due to the porous polymer-ceramic microstructure [21-22].

1.2. Goals of Research

The primary goal of this work is to design, fabricate and characterize a robust tactile sensor which can provide accurate information of force exerting on the end-effector, point-of-contact within the end-effector and to provide real-time force mapping while the end-effector is in operation. Also, the sensors should be able to accommodate the temperature fluctuations and provide consistent information on the force and spatial information of the end-effector. To avoid the harsh environments of space, the sensors need to be embedded within the end-effector geometry. To achieve all the goals, the following tasks were accomplished in this research work:

- Reviewed the trends in tactile sensing technology and the work done in the area of capacitive force/pressure sensors for use of the technology quantification.
- A single layer polymer dielectric capacitive force sensor was developed and evaluated with the help of thorough literature survey and experimental procedures. procedure and This work provided the baseline understanding and working mechanism relating to the molecular, micromechanical, thermal and electrical properties to specific attributes of the sensor character, such as sensitivity, drift, hysteresis, and noise.
- Using the analysis from the single layer sensor, an advanced and sophisticated 2:2 connectivity laminar polymer-ceramic composite capacitive sensor architectures were developed to improve the sensitivity, reduce noise, hysteresis

and other anomalies. The three different multi-layer sensor architectures are: baseline architecture, composed of compliance elastomer layer sandwiched Pt electrodes supported on flexible (Kapton film) substrate; bilayer architecture, with an additional HfO₂ layer deposited on the elastomer layer; trilayer architecture, with the HfO₂ sandwiched between the elastomer layers.

- The proposed advanced sensor architectures were realized by fabrication of the new composites and alternation to processing methods and thin film deposition techniques. The resulting composites were characterized to evaluate the various attributes of the composite material such as cyclic loading and stability, thermomechanical effects, and long-term static (quasi-static) loading.
- Chemical and structural characterization of the different layers of the multi-layer composite deposited on the flexible substrate was evaluated by a combination of conductive atomic force microscopy (c-AFM), raman spectroscopy, and x-ray photoelectron spectroscopy (XPS), and the optical properties were analyzed by ultra-violet visible spectrophotometer (UV-Vis).
- Finally, an embedding prototype was designed and tested to accommodate for the laminar composite sensor within the gripper tool. The fabricated sensor was made to be incorporated into the NASA's ARM gripper tool. Characterization of the sensor embedded within the gripper tool was evaluated to demonstrate the importance of each embedding element.

1.3. Organization of Work

This research work is composed of four chapters, which introduce, examine, and discuss the above-mentioned research goals and objectives. The first chapter states the

need for developing advanced sensor technology in the field of robotics to address the issues and challenges in space servicing missions and to motivate the research to fulfill the need. This chapter also discusses the former work done in the area of tactile/force sensor and arrays, and current technologies applied to develop a high sensitive sensor. A thorough literature review of mechanisms and technologies used in the development of tactile sensor was discussed and the knowledge base was used to develop the sensor technology in this work.

The second chapter discusses the development of a single layer flexible tactile sensor technology that could be applied to achieve the desired force magnitude and spatial information. The design, fabrication, and testing of the single layer tactile sensor were discussed and addresses the issues in the fabrication process to further develop the thick film single layer sensors. This section also serves as a baseline to develop and build an advanced composite material which has better sensitivity even in a low pressure regime. Additionally, this section serves as a knowledge base to experimentally understand the mechanism of the tactile sensor and the parameters that need to take into account to develop a highly sensitive sensor.

In the third chapter, an advanced laminar polymer-ceramic composite material was proposed to boost the sensitivity and address various challenges in tactile sensor technology. To prove the hypothesis, an experimental matrix was developed to fabricate three different architectures and these architectures were tested at exact working conditions and pressure regimes. Furthermore, to study and understand the intrinsic properties of the different layers deposited on the polymer substrate, each layer was characterized and thoroughly analyzed with the combination of spectroscopies and

microscopes. This chapter was concluded by identifying the best working sensor architecture by analyzing the materials properties.

The embedding strategy was developed and implemented in the fourth chapter of the research. Various parameters were analyzed both theoretically and experimentally to embed the sensor with minimal error in the force feedback during the operation. The experimental matrix was tested and analyzed to prototype the developed tactile sensor.

Chapter 2 – Single Layer Capacitive Sensor:

2.1. Introduction

In this section, an attempt was made to fabricate a single flexible capacitive sensor and to address various challenges in the fabrication process. A literature review was completed to understand the technologies used in the fabrication of flexible capacitive tactile sensors. In an effort to fully understand the various aspects of fabrication of flexible capacitive sensor, a single layer sensor design was proposed, fabricated and characterized. The sensor architecture was fabricated by coating a metal thin film on both sides of a Kapton film. The main purpose of this work is to evaluate the various sources of errors during the fabrication and characterization of the sensor. By identifying and improving the error, it will be useful to choose the appropriate fabrication route to further develop the various aspects of the sensor including sensitivity, robustness, and stability. The secondary goal of this task is to analyze the mechanical and dielectric property of the active sensing material which attributes to the sensor response, cyclic and thermal stability.

2.2. Evaluation of Methods to Coat Metal Electrode on Polymer Substrate

2.2.1. Experimental Procedure

Before fabrication of the sensor, the adhesion/wettability of metallic electrode on Kapton film was thoroughly evaluated by conducting a series of experiments. DC magnetron sputtering technique was used to deposit Pt thin films on the Kapton substrate due to the following reasons: i) sputtered atoms have suitable energy to nucleate and grow on the polymer substrate without application of external energy (thermal energy) to

the substrate; ii) the sputter deposited film will have better density and the grain size which will be smaller; iii) the thickness of the thin film can be monitored and controlled at angstrom ($\text{\AA}$) level; iv) the uniformity of the film can be preserved for a larger area; v) DC magnetron source will allow for operation at relatively low pressure and the plasma will assist the directionality of the sputtered atoms, that helps to preserve the high energy elastic collision of atoms for a longer area; vi) the target material was sputtered consistently and an inert gas (argon) was used, thus preserving the stoichiometry of the deposited film.

Kapton film of 1 mil ($25\ \mu\text{m}$) purchased from DuPont (Hayward, CA, USA) was used as the substrate to deposit the metal electrodes. The thickness of the Kapton film was chosen in such a way that it is easy enough to handle the flexible substrate during the fabrication process while providing high enough capacitance to easily measure the change in capacitance with conventional electronics. A 2 mil ($50\ \mu\text{m}$) Kapton film was easier to handle but the capacitance of the sensor will be reduced by one half of the thinner film. The Kapton film was carefully supported on a 4" diameter silicon wafer to avoid the wrinkling and also providing a uniform surface during the fabrication process. The static on the Kapton film plays an important role in determining the adhesion of the sputtered metal thin film to the substrate. In this work, we used a low-static Kapton film to improve adhesion of metal thin film during deposition. The Kapton film was further cleaned by bath sonication process in succession with acetone, isopropanol and deionized water for 2 min in each solution. Between each wash, the substrate was dried on a hot plate for 2 min at 120°C and finally blown on the main surface with dry nitrogen. Owing to its excellent electrical properties, better wettability and adhesion to amorphous

substrates, platinum (Pt) was chosen as the metal electrode. A lift-off process was used to pattern the Pt electrodes on the Kapton substrate. AZ 5214 photoresist (Microchemicals, Ulm, Germany) was spin coated on the Kapton film substrate using Laurel Technologies 400 spinner (North Wales, PA, USA) at 500 rpm for 10 sec, followed by 2000 rpm for 30 sec to coat 2 μm thick layer. The substrates were soft baked for 2 min at 110°C on a hotplate.

The desired electrode pattern was transferred to the Kapton film using a photomask purchased from UTZ Technologies (Little Falls, NJ, USA) using a Suss Microtech MA6 (Garching, Germany) mask aligner. The pattern was developed with AZ 300 MIF developer solution (Microchemicals, Ulm, Germany) for 1.5 min and rinsed several times by soaking in deionized water and dried by blowing dry nitrogen. The rinsing of the film with solvents was carried out very carefully, where over soaking of the film in solvents will cause delamination of the photoresists which tends to lead to poor adhesion of platinum electrodes. The patterned Kapton film substrates were removed from the silicon support and dried on a hot plate at 100°C for 1 min to thoroughly dry the patterned Kapton film substrates before introducing into the vacuum chamber. This process is critical because the physisorbed water molecules on the substrate will increase the evacuation time in the vacuum chamber.

The Pt electrodes of desired thickness were sputtered on the patterned Kapton film substrates by CVC 610 DC Magnetron sputter station equipped with 99.99% pure 2" platinum target (Kurt J. Lesker, Jefferson Hills, PA, USA) under ultra-high pure argon atmosphere. Generally, the substrate is maintained at a higher temperature or a very thin "seed" layer (10 – 20 nm) of Cr, Al or Ti metal will be sputtered before sputtering Pt or Au

on an amorphous polymer substrate to improve the adhesion of Pt or Au thin film. The additional seed layer i.e., a very thin layer of Ti/Al/Cr will get incorporated into the parallel plate capacitor structure which affects the effective dielectric permittivity of the sensor structure. In this case, the seed layer cannot be used because the active dielectric layer (Kapton film) needs to be sandwiched between the Pt electrodes. It has been shown that the deposition pressure, sputtering power, and target-substrate distance play a significant role in determining the adhesion of metallic thin films on polymer substrates. The target-substrate distance was kept at a minimum (2") distance to preserve the energy and momentum of the sputtered atoms for improved nucleation on the surface of the substrate since larger target-substrate distance will decelerate the sputtered atoms by causing inelastic collision of atoms before reaching the substrate. The sputtering pressure was maintained at 6 mTorr throughout the experiment, because higher pressure (>8 mTorr) would increase the rate of sputtering which encumbers thickness control and uniformity during the deposition, whereas, low sputtering pressure (<3 mTorr) would reduce the elastic collision among the sputtered atoms, and thus reduce the number of high energy sputtered atoms reaching the surface of the substrate. The substrate rotation was maintained at a contact velocity of 2°/sec, to achieve uniform film thickness across the area of the substrate. A series of experiments were conducted by varying the sputtering power and thicknesses of the Pt thin film deposited on Kapton substrate to analyze the precise working parameter which provides desired properties of the electrode layer.

The chamber was evacuated below 5×10^{-6} Torr before introducing inert argon gas to remove all the contaminants in the chamber. The deposition pressure was maintained at 6 mTorr by a throttle valve with a constant flow of 30 sccm of high purity argon gas.

Initially, DC power source of 60 W was ramped at a rate of 1 W/sec and the target was pre-sputtered for 30 sec to avoid surface contaminants of the target. After sputtering for 600 sec, the Pt film immediately started to peel off from the substrate after removing the substrate from the chamber. To investigate the effect of sputtering power on the adhesion of thin film on a polymer substrate, the power was increased to 100 W. Adhesion test was performed by sticking a high strength silicone adhesive tape on the sputtered film and peeled-off at a faster rate. This qualitative analysis shows the film deposited at high power had good adhesion on the Kapton film substrate. This corresponds to the fact that increasing the power, increases the energy of the sputtered atoms which enhances the transport and diffusion of atoms on the surface thus improving the nucleation frequency resulting in better adhesion. So, the sputtering power was maintained at 100 W for the experiments that were conducted thereafter.

Table 1: Deposition parameters for depositing Pt thin films on Kapton film substrate.

Target	Power	pAr	Deposition	Deposition	Sputtering	Thickness
Material	(W)	(sccm)	Pressure	Rate	Time (s)	(nm)
			(mTorr)	(nm/sec)		
Platinum (Pt)	100	30	6	0.75	135	100
					280	200
					400	300
					535	400
					670	500

Pt electrodes were sputtered with varying thicknesses from 100-500 nm to analyze the effect of electrode thickness, wettability and microcracking of the Pt layer during loading cycles of the sensor. The sputtering parameters to deposit Pt electrodes of thicknesses from 100-500 nm are shown in table 1. The patterned substrates were sonicated in an acetone bath for 5 min to lift-off unexposed areas (lift-off process). After lift-off, the patterned substrates were rinsed several times with DI water and dried by blowing nitrogen. The sputtered Pt films on Kapton films were analyzed in a dynamic mechanical analyzer (DMA) to evaluate the wear and microcracking of Pt layer. The Pt layer was supported by a high modulus silicone compliance layer to avoid direct metal contact on the surface of the Pt layer. The loading cycles were performed at a rate of 120 kPa/min up to 360 kPa for 200 cycles in an ambient atmospheric condition. The samples were imaged in the scanning electron microscope (SEM) to evaluate the wear and microcracking of the Pt layer due to mechanical loading cycles.

2.2.2. Evaluation of Microcracks and Defects of Pt Layer

High resolution JOEL SEM (Peabody, MA, USA) was used to image the surface of the Pt coated Kapton film samples that underwent mechanical loading cycles in the dynamic mechanical analyzer. Since the 100 nm Pt layer showed cracks and delamination after the cyclic loading at the macroscopic scale, the SEM micrograph of the sample is not shown in the study. Scanning electron microscope (SEM) micrographs of these Pt films are presented in figure 1, which shows the Pt films deposited onto the Kapton film substrate for thicknesses of (a) 200 nm and (b) 300 nm. The key aspect of these micrographs is the uniform color representing no defects in the films, and thus, a stable electrode performance during loading and unloading cycles. In contrast, the thicker

electrode films (400 and 500 nm) showed significant cracking and pore formation during loading cycles, which is represented in the SEM micrographs shown in figure 1 (c) and (d).

Figure 1: SEM image of 200 nm (a), 300 nm (b), 400 nm (c), and 500 nm (d) platinum electrode deposited on flexible polyimide Kapton film.

The importance of this analysis cannot be understated since the life cycle and longevity of these sensors would be greatly limited during loading due to these defects. Avoiding cracks is vital for better sensitivity and provides low noise-to-signal ratio because of the change in capacitance (that lies in tenths of pF). The cracks developed form local

voids which also contribute to a change (a lowering) of the capacitance during repeated use and requires frequent calibration of the sensor arrays. The change can be negligible for only a few cracks, but a larger population of cracks contributes to a significant change in capacitance which is not tolerable for the proposed application.

2.3. Fabrication of Single Layer Sensor Architecture

2.3.1. Sensor Design and Fabrication

The single layer sensor was fabricated on a Kapton film which acts as a flexible polymer substrate, compliance layer, and the active dielectric medium. The active sensing area of the single layer sensor design was fabricated to 8 mm diameter circular nodes and the electrical contact pads were also embedded in the design as shown in figure 2. The sensor fabrication process was completed in a class 1000 cleanroom. The thickness of the Pt layer was chosen to be 300 nm since it showed good performance without cracking under long-term loading cycles.

Figure 2: Sensor design of single layer architecture.

The flowchart of the batch fabrication process of the sensor is shown in figure 3. The top electrode was sputtered on one side of the Kapton film by a conventional lift-off process as discussed in section 2.2.1. The ground Pt electrode was accurately aligned with the top electrode using a mask aligner and patterned by the similar fashion. After

completing the lift-off process, electrical contacts were made by “cold” soldering Teflon coated silver wire of 100 μm thickness using a silver epoxy and drying the epoxy in an oven at 65°C for 15 min. Cold soldering technique was used to avoid melting of the Kapton film since conventional soldering’s temperature is higher than 350°C. A thin layer of insulating epoxy was coated on top the electrical contact as a reinforcement to the silver epoxy due to the low bonding strength of the silver epoxy.

Figure 3: Fabrication process flowchart of single layer sensor architecture.

Electromechanical characterization of the single layer sensor architecture was performed using a Dynamic Mechanical Analyzer Q800 (DMA) (TA Instrument, New Castle, DE, USA) equipped with the temperature controlled chamber in tandem with an LCR meter (889B, BK Precision, Yorba Linda, CA, USA). Voltage was kept constant at 1 V_{AC} and the signal was maintained at 200 kHz throughout the characterization. The sensor was placed on the silicone coated static arm and a silicone compliance layer of 1/8th inch thickness was placed on the active sensor area to evenly distribute the pressure across

the active sensing area. The characterization temperature was maintained at 30°C and the pressure was ramped from 0 to 360 kPa at a rate of 20 kPa/min.

2.3.2. Discussion

2.3.2.1. Dielectric Characterization of Kapton Film

An effort to obtain a better understanding of electrical properties of the sensor architecture, the dielectric properties of the Kapton film was analyzed thoroughly by comparing the experimental results with the theoretical values. For simplicity, the sensor structure is considered as a classical parallel plate capacitor in which a pair of electrodes was separated by a dielectric medium and the equation representing the parallel plate capacitor is,

$$C = \frac{\epsilon_0 \epsilon_r A}{d} = \frac{\epsilon A}{d} \quad (4)$$

where C is the capacitance, ϵ_r is the relative permittivity (dielectric constant), ϵ_0 is the permittivity of free space, $\epsilon = \epsilon_r \epsilon_0$, A is the surface area, and d is the distance between parallel plates (in this case its thickness of the dielectric layer). Since the Pt layer is deposited directly on the Kapton film, the contribution of permittivity from vacuum (or air) is negligible.

To understand the dielectric properties of the Kapton film under different frequencies, the sensor was ramped between 100 Hz and 200 kHz at 1 V_{AC} signal. The frequency dependent capacitance response with respect to time is shown in figure 4 where the sensor was held at room temperature under zero applied pressure. Over the given time period, the capacitance signal at lower frequency was very noisy due to lower

polarization response time; however, at higher frequencies, the capacitance signal got smoother and a flat band response has been achieved. The capacitance signal gets smoother as the frequency increases from 100 Hz to 200 kHz, where 200 kHz signal provides a smooth linear line representing the rapid polarization response at higher frequencies. This trend is typically observed for an amorphous polymer dielectric material and it is a common behavior and expected to occur.

Figure 4: Frequency dependent capacitance response as a function of time for the single layer sensor architecture at 30°C under zero applied pressure.

The reported dielectric permittivity of Kapton film under ambient conditions at 1 V_{AC} with 1 kHz signal ranges from 2.9 to 3.4. To compare the experimental dielectric permittivity with the reported values, the capacitance obtained at 1 kHz signal was plugged into the equation 4 to calculate the dielectric permittivity of the sensor

architecture. The dielectric permittivity of the Kapton film obtained by plugging the known values from the experiment in equation 4 is 3.23 which lies within the range of the reported values. Since the 200 kHz signal has the lowest signal-to-noise ratio, it was chosen for further electromechanical characterization of the sensor.

2.3.2.2. Electromechanical Characterization of Single Layer Sensor Architecture

Mechanical loading cycles of the single layer sensor architecture were performed on five different sensor samples. The sensor was supported on silicone coated static arm of the dynamic mechanical analyzer and a silicone compliance layer of 1/8" thickness was placed on the active sensing area of the electrode to evenly distribute the pressure across the surface area and to avoid metal-on-metal contact of the dynamic arm with the static arm. The sensor was normalized by holding the sensor at maximum pressure (360 kPa) for 5 h. The sensor was ramped between 0 and 360 kPa at a rate of 20 kPa/min and the electrical response (capacitance) was simultaneously recorded with BK Precision's 889B bench LCR meter. The capacitance response as a function of applied pressure at room temperature of a single layer sensor architecture is shown in figure 5. The capacitance response cannot be seen at the low pressure regime due to the high modulus nature of the Kapton film. At the high pressure region, above 60 kPa, the sensor response is linear up to 360 kPa. The change in capacitance (ΔC) for the pressure regime is ~ 0.3 pF which states that the sensitivity of the sensor is 0.08 pF/100 kPa or 80 fF/kPa. The sensitivity of the sensor was relatively higher than the sensors reported by Pritchard et al. and Muhamed et al., where the sensors were fabricated by a complex process involving multiple layer deposition of metal electrodes and polymer dielectric thick films. Furthermore, Pritchard et al. used a seed layer to deposit the electrode on the polymer

substrate. Muhamed et al. fabricated a complex architecture containing hollow micro bumps which utilized the voids inside those bumps as an active dielectric medium which questions the robustness of the sensor.

Figure 5: Capacitance response (ΔC) as a function of applied pressure from 0 to 360 kPa for the single layer architecture at room temperature.

Chapter 3 – Polymer-HfO₂ Laminar Composite Sensor Architectures

3.1. Introduction

In this section, an advanced composite material was introduced to address various issues such as sensitivity, cyclic stability, hysteresis, drift, the capability of the active sensing material to withstand wide temperature fluctuation and outgassing of polymer due to low pressure atmosphere of space. To tackle these parameters, a 2:2 polymer-ceramic laminar composite material was proposed which has four distinct layers: i) flexible polyimide substrate (Kapton film), ii) Pt thin film as electrode layers, iii) stress-sensitive elastomer (Arathane 5753 A/B), and iv) high dielectric ceramic (HfO₂) thin film layer. The proposed sensor architectures will overcome the drawbacks of nanoparticles infiltrated polymer-ceramic composite while improving the capacitive response of the sensor. The laminar architecture has active sensing layers deposited on the each other providing better distribution of force across the sensing area. Thus, providing advantages of increased capacitance with improved cyclic stability and sensitivity.

Three different sensor architectures were designed, fabricated, and characterized with combination of atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), raman spectroscopy and uv-vis spectroscopy to understand the material properties of the different layer of the deposited films. Electrical characterization of the HfO₂ thin film and sensor composites were performed in a temperature controlled environmental chamber in tandem with an LCR meter for electrical acquisition. Thermomechanical characterization of the sensor architectures was performed in a dynamic mechanical analyzer (DMA) equipped with a furnace and a liquid nitrogen

cooling system for temperature control. The sensors were analyzed between the temperature range of -60 and 120 °C with a periodic interval of 30°C.

3.2. Experimental Procedure

3.2.1. Sensor Design and Fabrication

The active sensing area of the tactile sensor was fabricated to 8 mm diameter. The cross-sectional schematic of the three different sensor architectures is shown in figure 6. The baseline architecture was composed of a bottom 500 nm Pt electrode patterned on 3 mil (75 μm) Kapton film (Hayward, CA, USA) substrate. A 10 μm thick Arathane 5753 A/B two-part epoxy (Huntsman Advanced Materials, The Woodlands, Texas, USA) elastomer was coated over the bottom Pt electrode. The top electrode was a separately patterned on a Kapton film substrate, and this electrode substrate was laminated over the bottom Arathane /electrode layer. For the bilayer architecture, the elastomer and an additional 100 nm HfO_2 thin film layer was deposited over the elastomer. The top electrode was the same Pt sputtered film supported on the Kapton film substrate, as in the baseline design. The tri-layer architecture included the 100 nm HfO_2 thin film sandwiched between the elastomer layers. The bottom HfO_2 /Pt electrode layers possessed the same architecture as the bilayer structure previously described. The difference included the extra 10 μm thick Arathane layer that was cast over the top 500 nm Pt electrode patterned on the Kapton film substrate. The different architectures were developed to compare the effect of elastomer thickness, the HfO_2 on the sensitivity, shielding of HfO_2 thin film, and the effect of porosity on the sensitivity.

Figure 6: Schematic of cross-section of three different sensor architectures.

The sensor fabrication was completed in a class 1000 cleanroom. The fabrication flowchart is shown in figure 7. The first step in the fabrication process was depositing/patterning the Pt films on polyimide (Kapton) film for the bottom and top electrodes. A 3 mil (75 μm) thick Kapton film (with silicone adhesive layer) was carefully supported on a 4" diameter silicon wafer. The Kapton film was cleaned by sonication in succession with acetone, isopropanol and deionized water for 2 min in each solution. Between each wash, the substrate was dried on a hot plate for 2 min at 120°C and finally blown on the main surface with dry nitrogen. A lift-off process was used to pattern the Pt electrodes on the Kapton substrate. AZ 5214 photoresist (Microchemicals, Ulm, Germany) was spin coated on the Kapton using Laurel Technologies 400 spinner (North Wales, PA, USA) at 500 rpm for 10 sec, followed by 2000 rpm for 30 sec to coat 2 μm thick layer. The substrates were soft baked for 2 min at 110°C on a hotplate. The desired electrode pattern was transferred to the Kapton film using a photomask purchased from UTZ Technologies (Little Falls, NJ, USA) using a Suss Microtech MA6 (Garching, Germany) mask aligner. The pattern was developed with AZ 300 MIF developer solution (Microchemicals, Ulm, Germany) for 1.5 min and rinsed several times by soaking in deionized water and dried by blowing dry nitrogen. The Pt electrodes of 500 nm thickness were sputtered on the patterned Kapton film by CVC 610 DC Magnetron sputter station

equipped with 99.99% pure 2" platinum target (Kurt J. Lesker, Jefferson Hills, PA, USA) under ultra-high pure argon atmosphere. The chamber was evacuated below 5×10^{-6} Torr before introducing argon gas. The deposition pressure was maintained at 6 mTorr by a throttle valve with a constant flow of 30 sccm of high purity argon gas. DC power source of 100 W was ramped at 1W/sec and the target was pre-sputtered for 30 sec to avoid surface contaminants. The patterned substrates were sonicated in an acetone bath for 5 min to lift-off unexposed areas (lift-off process). After lift-off, the patterned substrates were rinsed several times with DI water and dried by blowing nitrogen.

Figure 7: Fabrication process flow chart of baseline, bilayer and tri-layer architecture.

Arathane 5753 A/B was used as a stress-sensitive elastomer which is a two-part epoxy with a broad temperature stability, and the material complies with NASA's low

outgassing space standards. Arathane 5753 A/B was mixed in 1:5 (Part A: Part B) and stirred carefully with a glass rod until the two-part epoxy forms a cloudy viscous solution. A Mayer rod (RD Specialties, Webster, NY, USA) was used to cast a uniform layer of elastomer of desired thickness on the substrate. The elastomer was cast by pipetting ~5 ml of Arathane 5753 A/B on the substrate and dragging the Mayer rod across the substrate at an approximate rate of 0.1 cm/sec. The thickness of the casted film was determined by the thickness and spacing of the wounded wires. A Mayer rod with a standard thickness of ~10 μm was used in this work. The casted elastomer was cured in a vacuum oven at 95°C and a vacuum pressure of 20 mm-Hg for 10 h. After curing, the thickness of the Arathane layer was measured with a stylus profilometer and the thickness was reduced to 9.2 μm due to evaporation of solvents in the elastomer.

Deposition of the HfO_2 thin film was carried out by pulsed laser deposition (PLD) (Neocera's Pioneer 180, Beltsville, MD, USA) using a 99.95% pure ceramic HfO_2 target (QS Rare Elements, Syracuse, NY, USA). The main chamber was maintained below 1×10^{-7} Torr. The sample was loaded into a load lock chamber and transferred to the main chamber after it reached a pressure of 5×10^{-6} Torr. In this PLD system, a KrF excimer laser system (Coherent Inc., Santa Clara, CA, USA) with a 248 nm wavelength was used. The target-substrate distance was exactly maintained at 2" and asymmetric rotation of both target and substrate was employed to achieve better film uniformity. The top electrode was fabricated in the same way as described above on Kapton film. Interconnects for the different sensor architectures were fabricated using silver micro-wire of 150 μm thick coated with 50 μm polymer insulator and two-part conductive silver epoxy (cold soldering) purchased from Alfa Aesar (Haver Hill, MA, USA).

3.2.2. Microstructural and Surface Characterization of Deposited Films

The microstructure of each layer of multilayer sensor architecture was characterized by an Agilent 5500 SPM atomic force microscope (AFM). The AFM has a tip radius of 2 – 5 nm and the tip is made of antimony doped silicon. Tapping mode conductive-AFM (c-AFM) technique with a resonant frequency of 320 kHz was employed to measure the surface morphology of the elastomer and HfO₂ deposited on rigid and flexible substrates. An 8 V bias voltage was applied to the tip during the imaging to compensate for the charge on the dielectric material. AFM image analysis was conducted using Gwyddion 2.47 software.

3.2.3. Chemical and Structural Characterization

Elemental composition and chemical state of elements present in HfO₂ and Arathane were characterized x-ray photoelectron spectroscopy (XPS) (Physical Electronics PHI 5000 VersaProbe, MN, USA). The analysis was performed on the HfO₂ layer deposited on Arathane layer with Al monochromatic source of 24.6 W power and energy 117.4 eV energy with an incident angle of 45° on the sample. Both a survey scan and a detailed scan was taken, and the data analysis was performed in PHI MultiPak data reduction software. Peak shift was corrected by adjusting carbon peak at 284.6 eV before data reduction and analysis. Atomic percentage concentrations were calculated using the Hf 4d, Hf 4f, and O 1s peaks.

Raman microscopy (Renishaw InVia, IL, USA) was used to analyze the chemical composition of the thin films. A green laser source (532 nm wavelength) was used to characterize HfO₂ thin film deposited on flexible substrates. Due to the fluorescence

effect, the laser power was decreased to 0.1% to reduce the dominance of fluorescence signal from the polymer layers. The data were deconvoluted and analyzed in WIRE software.

3.2.4. Optical Properties of Arathane Layer and HfO₂ Thin Film

The optical properties of the HfO₂ and Arathane films were analyzed using UV-Vis spectrophotometer (Agilent's Varian Carry 300 double beam). The spectral range of the analysis was from deep ultra-violet (190 nm) to far infra-red (900 nm). All the measurements were completed at room temperature.

3.2.5. Dielectric Characterization of HfO₂ Thin Films and Sensor Architectures

Dielectric characterization of the HfO₂ thin film deposited on Pt coated Kapton substrate was performed at a temperature between -60 and 120°C with LCR meter (Agilent E4980A precision) in an environmental chamber (Sun Systems, Titusville, FL, USA). A 200 nm platinum ground electrode was sputtered on a 75 µm thick Kapton film supported on a silicon wafer (100-ohm resistivity, University Wafers, Boston, MA, USA). HfO₂ thin films were deposited on the ground electrode with the same parameters used for depositing on Arathane surface, 50 nm thick top platinum electrodes were deposited on the HfO₂ layer using 1000 µm diameter by a shadow mask purchased from UTZ (Little Falls, NJ, USA). Electrical interconnects were made using silver micro-wire and conductive silver epoxy as discussed above. A Faraday cage (VWR International, Randor, PA, USA) assembly was setup in the environmental chamber to avoid electrostatic fluctuation during characterization. All electrical measurements were completed with 1 V_{AC} signal with a frequency ranging from 20 Hz to 2 MHz. Frequency dependent dielectric permittivity and

dielectric loss ($\tan \delta$) loss were calculated from capacitance and dissipation factor, respectively, using a parallel plate capacitor relation.

3.2.6. Electromechanical Characterization of Sensor Architectures

Electromechanical characterization of the sensor was characterized using a Dynamic Mechanical Analyzer Q800 (DMA) (TA Instrument, New Castle, DE, USA) equipped with the temperature controlled chamber in tandem with an LCR meter (889B, BK Precision, Yorba Linda, CA, USA). Voltage was kept constant at 1 V_{AC} throughout the characterization. The sensor was placed on the static arm and a silicone compliance layer of 1/8th thick was placed on the active sensor area to evenly distribute the pressure across the active sensing area. Three different loading cycles were performed for each sensor architecture: (a) pressure was ramped from 0 – 360 kPa with the ramp up and ramp down the rate of 20 kPa/min for temperature ranging from -60 – 120°C with 30°C temperature interval, (b) sensor was loaded to 20 kPa pressure increment and held at that pressure for 1 min for temperature ranging from -60 to 120°C with 30°C in temperature interval to analyze the drift in capacitance/elastomer, and (c) cyclic loading of sensor at -60°C, 30°C, and 120°C.

3.3. Discussion

3.3.1. Microstructural and Surface Characterization of Deposited Films

Conductive atomic force microscopy (c - AFM) was used to analyze the surface morphology of the Arathane elastomer and HfO₂ thin film. The surface morphology study was performed to analyze the surface roughness and effect of a change in roughness of HfO₂ thin film based on the surface morphology of the substrate. Tapping mode AFM was

used with a frequency of 320 Hz to avoid damage to the sample, and the required DC bias was applied to the tip to neutralize the surface charging of sample due to high insulating nature of the sample.

Figure 8: (a) 3-D surface morphology of Arathane elastomer cast on Pt coated Kapton substrate and (b) 2-D topography image with watermarks showing the porosity in Arathane surface.

The 3-dimensional surface morphology of Arathane elastomer is shown in figure 8a where the average roughness value across the surface is 12.34 nm. Since the Arathane film was cast, the surface has an irregular pore structure consisting of alternating ridges and valleys, which are defined as pores in this study. The 2-dimensional phase contrast topography image (figure 8b) of the Arathane elastomer illustrates the peaks (yellow watermarks) and ridges (red watermarks) in the Arathane elastomer. The pore size was measured as the differential height between the top of the peak and bottom of the ridge, and the average pore size is found to be ~30 nm. During deposition of the HfO₂ thin film, the HfO₂ conforms to the surface of the Arathane, and seals the pores and makes the surface smoother for bilayer architecture which helps to reduce the discrepancies in sensor response. The interface between the Arathane and HfO₂ thin film has porous polymer-ceramic composite structure. To compare the change in roughness

of HfO_2 thin film with respect to substrate roughness, the same deposition parameters were followed to deposit the film on a sapphire substrate and figure 8c shows the 3-D surface morphology of HfO_2 on a sapphire substrate with an average surface roughness value of 0.38 nm. Figure 8d shows the 3-D surface morphology of HfO_2 deposited on Arathane surface, where the roughness of the thin film increased from 0.38 nm (HfO_2 on sapphire) to 4.48 nm due to the irregular porous structure of the Arathane surface.

Figure 8: 3-D surface morphology of room temperature as-deposited HfO_2 thin film on (c) sapphire substrate showing the random distribution of grains due to amorphous nature of the film and (d) Arathane surface where the roughness of the film increased and the grains are clustered due to the roughness of Arathane surface.

For the pressure sensing application, a smoother surface is preferred due to the following reasons: i) the capacitance is sensitive to thickness change between parallel plates, which will be reflected in the change in average roughness between the interface of parallel plates (for example, if there is 1 nm difference in the thickness across sensing area, the ΔC will deviate ~ 18 pF) ii) a rougher surface will result in the discontinuity of top electrode which will affect the overall dielectric property of the sensor and the sensitivity, iii) the pores on the surface may act as active site to develop cracks during loading and unloading cycles, and iv) the ridges and peaks may lead to differential stress concentration locations, which may later tend to develop a crack in the dielectric coating

and potentially short-circuit the sensor (and also reduces the cyclic stability). The stress concentration at the interface between Arathane/electrode layer in baseline architecture is minimal due to the thicker Arathane (9.2 μm) which dominates over the surface roughness which is 12.34 nm.

3.3.2. Chemical and Structural Characterization

XRD was completed on the HfO_2 thin film deposited on sapphire and Kapton substrate (not shown in this work) at room temperature, and both spectra showed a singular broad amorphous peak centered on $28.34^\circ 2\theta$. The amorphous nature of the as-deposited HfO_2 thin film was reported by Li et al. and indicated that crystallization temperature of HfO_2 thin films occurs above $\geq 200^\circ\text{C}$ [24-26]. Since the melting point of the Arathane elastomer is 180°C , the deposition of the HfO_2 thin film was processed at room temperature. X-ray photoelectron (XPS) was employed to analyze the chemical states and the atomic concentration of hafnium and oxygen present in the HfO_2 thin film deposited on the Arathane surface. Furthermore, the depth-profile analysis was performed using *in-situ* argon sputtering to analyze the stoichiometry of HfO_2 through out the thickness and to analyze chemical states and bonding of elements present at the interface between Arathane and HfO_2 layer. Figure 9a shows the XPS survey scan with distinctive peaks for hafnium and oxygen in the HfO_2 thin film; the binding energy (B.E.) of hafnium and oxygen core level correspond to amorphous HfO_2 and are in good agreement with the reported literature [27-29].

Figure 9 (a): XPS survey scan of HfO_2 deposited on Arathane elastomer at room temperature by PLD technique.

The oxygen at binding energy 980.3 eV is assigned as an Auger peak. The C 1s core level arises from the adventitious carbon contamination on the surface and the C 1s core level at (B.E.) 284.6 eV which was used for spectral correction. Figure 9b shows the detailed scan of the depth-profile analysis Hf 4d, O 1s and C 1s core levels. The detailed scan of Hf 4d, O 1s, C 1s was taken at a periodic interval of 0.5 min of Ar sputtering until the HfO_2 layer is entirely removed. It can be inferred from figure 9b that the intensity of hafnium and oxygen peak starts to significantly decrease at 1.5 min of sputtering and the C 1s peak at B.E. 283 eV appears after 1.5 min of Ar sputtering, which represents the C

1s core level of Arathane elastomer which is due to the interface between Arathane and HfO_2 since the interface thickness is ~ 30 nm as evaluated by AFM.

Figure 9 (b): Detailed depth-profile XPS scan of O 1s, C 1s, and Hf 4d core levels showing the change in the intensity of respective with respect to sputtering time.

Deconvolution of Hf 4d, Hf 4f peaks O 1s was performed to distinguish the individual core levels and spectral features which were shown in table 2. Figure 9c shows the deconvolution of Hf 4d core levels with two peaks centered at B.E. 212.93 and 223.93 eV, which represents Hf $4d_{5/2}$ and Hf $4d_{3/2}$, respectively, which are distinctive spin-orbit doublet characteristics of HfO_2 [28]. If the chemical state for an oxide shifts to lower B.E., then this indicates the composition is oxygen deficient; the deconvoluted Hf 4d core levels lies within the range of stoichiometric HfO_2 [27,41]. In addition to Hf 4f core levels, Hf 4d core levels are used in the calculation of O/Hf ratio in the HfO_2 thin film because Hf 4f core levels might affect the accuracy of O/Hf ratio estimation due to the difference in the B.E. of O1s core levels [27]. Figure 9c shows the deconvoluted Hf 4f core levels which are split into two asymmetric doublets peaks which represent Hf $4f_{7/2}$ and Hf $4f_{5/2}$ at B.E. 16.30 and 18.30 eV, respectively. These results all agree with stoichiometric HfO_2 [27]. The peak at B.E. 18.30 eV is a characteristic peak for Hf in HfO_2 [41]. Figure 9d shows

the deconvoluted O 1s core level with a singlet peak at B.E. 529.80 eV representing the lattice oxygen in HfO₂.

Table 2: Spectral features of various chemical states present in HfO₂ thin film and Arathane elastomer.

Spectral Features				
Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Peak Assignment
Hf 4f _{7/2}	16.30	1.37	11133	Hf(IV) in HfO ₂
Hf 4f _{5/2}	18.30	1.91	15300	Hf(IV) in HfO ₂
Hf 4d _{5/2}	212.93	4.14	29327	Hf(IV) in HfO ₂
Hf 4d _{3/2}	223.93	4.41	19515	Hf(IV) in HfO ₂
O 1s	529.80	1.72	11549	Lattice oxygen in HfO ₂
C 1s	282.82	1.2	3245	C-C/C-H bonding in aliphatic groups
C 1s	282.31	1.13	3105	C-C bonding in aromatic groups
C 1s	284.23	N/A	N/A	C=N terminating group
C 1s	287.43	N/A	N/A	N=C=O in isocyanate group

The O 1s spectra were taken after 0.5 min of Ar sputtering to avoid hydroxyl and carbon surface contaminants. The singlet peak of O 1s represents the presence of oxygen only at lattice HfO₂ without any surface contamination such as carbon and hydroxyls. After 0.5 min of Ar sputtering to remove the surface contaminants, the ratio of atomic concentrations oxygen to hafnium in the HfO₂ thin film was found to be 1.97 by evaluating the ratios of FWHM core levels of Hf 4d, Hf 4f, and O 1s.

Figure 9 (c): Deconvoluted peaks of Hf 4f and Hf 4d analyzed after 0.5 min of Ar sputtering to remove the surface contaminants showing the doublet nature of native Hf core levels in the HfO₂ thin film.

Figure 9d represents the deconvoluted spectra of C 1s core level of Arathane elastomer after completely removing the HfO₂ layer. Arathane is composed of carbon bonding in aromatic, aliphatic and isocyanate functional groups. The C 1s core levels were deconvoluted into four distinctive carbon bonding to their respective functional groups. The peak at B.E. 282.82 eV represents carbon bonding in C-C/C-H (aliphatic groups); peak at B.E. 282.31 eV represents carbon bonding in phenyl (aromatic) groups; the two broad peaks at 284.23 and 287.43 eV represents carbon bonding in C=N and N=C=O (isocyanate group), respectively, which is shifted slightly (0.3 eV) towards left because of the additive homopolymer which is an aniline group. The ratio of the area under the peak 282.31 eV to the overall peak area is 0.47 which confirms the dominance of phenyl group since the Arathane has two phenyl groups and linked with vinyl groups which have peak area ratio of 0.27. The peak area under isocyanate groups has the

lowest value (0.26), and this represents the termination functional groups in the elastomer.

Figure 9 (d): Deconvoluted peaks of O 1s analyzed after 0.5 min of Ar sputtering to remove the surface contaminants showing the singlet nature of oxygen in the lattice of HfO₂ and C 1s analyzed after sputtering for 3 min to completely remove HfO₂ layer showing four distinct peaks for carbon bonding in Arathane elastomer.

Raman spectroscopy analysis was performed to investigate the phonon vibration modes in the amorphous HfO₂ thin film. The spectra shown in figure 15 shows phonon vibration modes for the amorphous HfO₂ thin film. The carbon signals from Arathane elastomer were recorded separately and subtracted. The theoretical and computational analysis suggests HfO₂ has a total of 36 vibration possible phonon vibration modes among which 18 phonon vibration modes (9A_g + 9B_g) are distinctive Raman active, 15 are infrared active, and the three remaining belong to acoustic vibration modes [29-30]. The peaks represented in the figure 15 correspond to A_g mode at wavenumbers 258 cm⁻¹, 381 cm⁻¹, 498 cm⁻¹, 577 cm⁻¹ and 677 cm⁻¹, B_g mode at wavenumber 241 cm⁻¹ and the peak at 133 cm⁻¹ represents mixed vibration mode (A_g+B_g), which agree with the reported theoretical calculation and experimental value [29,30]. Usually all the 18 vibrations modes

should appear for the HfO_2 thin film, but in this case, there are only 9 vibration modes present. This can be expected for an amorphous thin film which has very short-range crystalline symmetry (or order). The observed peaks are broader which indicates the film has short range symmetry arising from its amorphous nature. Although the peaks are broad, the peaks correspond to the monoclinic HfO_2 , that indicate the favorable monoclinic phase for HfO_2 , and this agrees with the theoretical models as well as experimental results [31,32].

Figure 10: Raman spectrum of the amorphous HfO_2 thin film deposited on Arathane surface by PLD technique. The labeled vibration modes are classified into A_g , B_g and A_g+B_g modes observed in HfO_2 . The broad nature indicating the short-range order of amorphous HfO_2 which coincides with peaks of monoclinic phases

3.3.3. Optical Characterization of HfO₂ and Arathane

UV – Visible spectrophotometer was used to analyze the optical properties and the band gap of the Arathane and HfO₂ thin film. Since the thickness of Arathane elastomer is two orders of magnitude higher than HfO₂ thin film, the intensity of wavelength from HfO₂ thin film passing through both Arathane and HfO₂ significantly decreases and makes the bandgap analysis difficult. To overcome the anomaly, a background spectra of the Arathane elastomer was measured separately and subtracted from the HfO₂/Arathane spectra.

Figure 11: UV-Visible spectroscopic analysis showing (a) Transmission spectra of HfO₂ thin film which has optical transmission above 90% upto 5.3 eV and Arathane elastomer which has broad optical transmission and drops from 1.3 to 3.3 eV with a sharp transition at 3.4 eV, (b) Tauc plot showing the indirect band gap of HfO₂ thin film extrapolation of the sharp transition point.

Figure 11a shows the UV-Vis transmission spectra comparison for the Arathane and HfO₂ thin films (with background subtracted). The transmission of the Arathane is 90% at 1.3 eV and gradually falls until 3.4 eV above, which it more abruptly falls, reaching ~0% at about 4.3 eV. The transmission spectra of Arathane has two transition states, a broad transition regime from 1.3 to 3.4 eV, which is due to the presence of conjugated π

bonds in the polymer chain and the second region which occurs at 3.4 eV is due to the bandgap transition edge. However, the sharp transition at 3.4 eV shows us bandgap should be greater than 3 eV which is true for semiconductors. The transmission of the HfO₂ is above 90% up to 5.3 eV, above this, there is an absorption edge. To investigate the bandgap of HfO₂, we use the method of Tauc et al. which fits the above bandgap behavior of the optical absorption. The bandgap is related to the difference between the photon and bandgap energy and is expressed as:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g), \quad (5)$$

where α , h , and ν are the measured absorption coefficient, Planck's constant and the frequency, respectively and E_g is the bandgap and A is a constant of proportionality. The n is a parameter which denotes the nature of a transition, where n is 2 (1/2) for indirect (direct) allowed transitions [33,34]. Plotting the measured data for the HfO₂, we find that the plot for $n=2$ gives very linear behavior above bandgap indicating an indirect bandgap with a value of 5.3 eV (figure 11b) by extrapolation. HfO₂ is a wide band gap dielectric insulator with band gap ranging from 5.0 – 6.0 eV [35-37]. The highest reported bandgap of amorphous HfO₂ thin film is 5.68 due to simultaneous secondary plasma assisted rapid oxidation of Hf metal during deposition which cannot be used due to thermal constraints of the substrate [37]. Vescio et al. reported similar bandgap (5.34 eV) of HfO₂ thin film deposited on polymer substrate by inject printing of monoclinic HfO₂ particles [40]. The bandgap of the HfO₂ particles falls within the range of stoichiometric HfO₂ thin film [35 – 40].

3.3.4. Dielectric Characterization of HfO₂ Thin Film and Sensor Architectures

The dielectric properties of the HfO₂ thin film were measured with metal – insulator – metal structure on 200 nm Pt coated Kapton substrate as discussed in section 2.5. It was found that the dielectric properties of HfO₂ thin film deposited on Pt coated silicon substrate overlaps with the film of similar thickness deposited Pt coated Kapton substrate which shows the dielectric properties of HfO₂ thin film can be retained when deposited on Pt coated polymer Kapton substrate. The dense Pt layer also acts as a seed layer and supports the nucleation of sputtered HfO₂ film. In addition, the Pt also reduces the lattice strains which affects the dielectric properties. All measurements were taken between -60 and 120°C in 30°C step using an environmental chamber. The electrical response was acquired by a computer directly from the LCR meter with 1 V_{AC} as test signal and the AC frequency was ramped from 20 Hz to 2 MHz.

Figure 12a and 12b shows the change in capacitance and dielectric permittivity as a function of frequency in logarithmic scale at each temperature interval. The average dielectric permittivity for HfO₂ thin film measured in this work at room temperature (30°C) was found to be 32.05 and the average dielectric permittivity from -60 to +120°C was 31.60. The decrease in dielectric permittivity of the HfO₂ was linear between 20 Hz and 10 kHz with a change of 0.5. There is a sudden drop in dielectric permittivity from 20 kHz to 100 kHz which is ~3 and the permittivity drops linearly up to 1 MHz. It is evident from the figure 12b that increasing the temperature increases the dielectric permittivity of the HfO₂ thin film, and increasing the frequency decreases the capacitance and dielectric permittivity. The prior properties of HO₂ thin film occurs due to the short-range order

(amorphous nature) of the HfO_2 thin film where an increase in temperature will cause an increase internal field with respect to the applied electric field. The increase in internal field decreases the number polarizable particles per unit volume due to direct effect of volume expansion [42]. As the number of polarizable particles per unit volume decreases the dielectric permittivity increases with increase in temperature. The later (increasing frequency decreases permittivity) occurs due to polarization response time of the AC electric field. Increasing the frequency increases the polarization rate of the dipoles, and this results in the decrease of dielectric permittivity with increase in frequency [40,42].

The change in dielectric loss as a function of frequency at specific temperature is shown in figure 12b. We observe the dielectric loss is higher at lower frequencies and starts to gradually decrease as the frequency is increased. The dielectric loss is high in low frequency regime because the electronic polarization occurs very rapidly (order of 0.1 nanoseconds) whereas the ionic polarization happens in milliseconds and the dipole polarization happens even longer. Due to the difference in the response time and the alignment of dipoles the tangential loss is high at low frequency. The effect of temperature is negligible at higher frequencies because the dipoles gains sufficient energy to orient themselves irrespective of temperature. Whereas at low frequency, the tangential loss is temperature dependent because higher temperature assists in orienting the dipoles and reducing the gap between electronic and dipole polarization time. From the above result, it is evident that the capacitance, dielectric permittivity and dielectric loss begins to stabilize at frequency 100 kHz and stable at 200 kHz.

Figure 12 (a): Capacitance of HfO₂ thin film deposited on Pt coated Kapton substrate as a function of frequency from -60 to 120°C measured at 1 V_{AC} signal.

The dielectric properties of the three sensor architectures were compared to study the effect of the HfO₂ layer. All the measurements were performed in a similar setup as discussed above and the electrical response was measured at 1 V_{AC} and the frequency was kept constant at 200 kHz, as explained above. Figure 12c shows the dielectric permittivity of baseline architecture bilayer and trilayer architecture from -60 to 120°C at 30°C interval. As expected the average dielectric permittivity of baseline architecture (Arathane elastomer) is 3.12, which is similar to that reported by the manufacturer [43]. The dielectric permittivity between -60 and 30°C is similar with a deviation of approximately 0.05 and there is a linear increase from 60 to 120°C. The polarization of a dielectric polymer (Arathane) is contributed by electronic, dipole and ionic polarization. Arathane elastomer has both polar and non-polar functional groups/ The temperature

dependent dielectric change is arising from the polar component of the elastomer. At lower temperatures, the dipole molecules are unable able to orient themselves so the dielectric permittivity is relatively low when compared with higher temperature region. However, in high temperature regime, the thermal expansion facilitates the orientation of dipoles, because as the temperature increases, the thermal energy decreases the ratio of the number of molecules to the effective length of the dielectric. In general, the dielectric permittivity of polar polymers tends to increase until the glass transition temperature (T_g) and the curve drop down above the T_g due to the indefinite orientation of the dipoles [44]. The coefficient of thermal expansion (CTE) also contributes to the change in permittivity. The CTE of the Arathane elastomer is 76 ppm/ $^{\circ}$ C which is low for a flexible elastomer. Assuming the thermal expansion occurs only in longitudinal direction due to the tensile stress acting normal to the direction of parallel plates, the temperature and polarization dependent permittivity (ϵ_A) of Arathane elastomer can be deduced by the following equations,

$$\epsilon_A = \epsilon_f = \frac{\epsilon_u}{1 - 2\epsilon_u \kappa \sigma_T} \quad (5)$$

where ϵ_f is the permittivity under thermal stress, ϵ_u is permittivity without stress, κ is electrostriction constant and σ_T thermal stress. The thermal stress acting in longitudinal direction can be written as,

$$\sigma_T = 2\sigma_{longitudinal} = 2E_A(\epsilon_S - \epsilon_A) \quad (6)$$

where the E_A is the elastic modulus of the Arathane, ϵ_A is the strain induced by thermal stress in Arathane and ϵ_S is the strain induced by thermal stress in the substrate. The strain of the Arathane elastomer and the substrate can be expressed as,

$$\epsilon_A = (\alpha_A V_A) \Delta T \quad (7)$$

$$\epsilon_s = \alpha_s \Delta T \quad (8)$$

where α_A and α_s is the thermal expansion co-efficient Arathane and substrate (Pt coated Kapton) V_A is the volume of Arathane and the volume is negligible for substrate since the thickness of the Pt layer is very thin.

Figure 12 (b): Dielectric permittivity and loss tangent ($\tan \delta$) of the HfO_2 thin film deposited on Pt coated Kapton substrate as a function of frequency from -60 to 120°C measured at 1 V_{AC} signal.

To estimate the dielectric response of the composite films that were formed we need specific information related to the microstructure of the Arathane layer and thickness of the HfO_2 thin film deposited on the Arathane layer. The microstructural characterization shows the Arathane layer has a porous structure with an average pore depth of ~30 nm. As a result of the porous surface microstructure, the HfO_2 layer forms a diffuse interface

during deposition on the Arathane layer. The thickness of the diffuse layer is ~30 nm which was corroborated by XPS depth profiling characterization. The depth profile shows the presence mixed core levels consisting of Hf, O, and C after sputtering ~70 nm through the HfO₂ layer. The Hf and O core levels disappear after sputtering ~30 nm which shows the interface layer consisting of Arathane/HfO₂ composite stretching through the ~30 nm thickness. The relative porosity is unknown, but we will assume at this point the porosity level is stretching 30 nm thick.

It is assumed that dielectric response of the bilayer architecture arises from the Arathane layer, diffused polymer/HfO₂ interface, and the HfO₂ thin film which is assumed to be 70 nm. First, the polarization of polymer is caused by external stress by the inverse of electrostrictive effect (or piezodielectric effect) [45]. When an electric field is applied at the diffuse interface, both the polymer and HfO₂ particles experience a change in polarization; the direction of polarization is approximated using Rayleigh's mixing law which defined as the influence of a cubic array of spherical objects in a secondary medium. Much work was performed in this area with the contribution from Mossotti, Lorenz, Clausius, and Maxwell-Garnet [46-49]. Weadon et al. provided a model for the dielectric permittivity of ceramic particle filled polymer which was used for the permittivity of the diffused layer [30, 31]. The temperature dependent dielectric permittivity (ϵ_c) of interface (ceramic filled polymer matrix) is given by [46],

$$\epsilon_c = \epsilon_1 + 3V_f\epsilon_1 \frac{(\epsilon_2 - \epsilon_1)}{\epsilon_2 + 2\epsilon_1 - V_f(\epsilon_2 - \epsilon_1)} \quad (9)$$

where ϵ_1 and ϵ_2 are the permittivities of Arathane (polymer filler) and HfO₂ particle, respectively, V_f is the volume fraction of Arathane elastomer matrix. The third layer is

HfO₂ thin film with an effective thickness of 70 nm, and the significance of the dielectric permittivity arising from the HfO₂ thin film was discussed previously. Since the dielectrics are stacked in the longitudinal direction, it is considered as the dielectrics in series; the thickness of the low permittivity material is a magnitude order higher than high permittivity HfO₂ and the contribution is low. The overall dielectric permittivity (ϵ_B) of the bilayer architecture is given by combining the equations 4 – 8 and given by,

$$\epsilon_B = \epsilon_A + \epsilon_C \quad (10)$$

The dielectric permittivity calculated using the simple model discussed above (under zero pre-strain and thermal stress) is ~9.7 which is close to the measured value of 8. The dielectric property of the bilayer architecture is almost twice the value measured for the baseline architecture as shown in figure 12c. The dielectric permittivity of the bilayer architecture at a temperature between -60 and 0°C is 7.1 and increases quadratically up to 90°C. As explained in baseline architecture discussion, the dielectric permittivity changes due to electronic, dipole and ionic polarization. It is also evident from the characterization result of the HfO₂ thin film, the dielectric permittivity increases with proportional to temperature. At low temperature, the Arathane elastomer has a negligible change in thermal stress and the slight dielectric permittivity (0.1) change is wholly due to polarization effect of Arathane and HfO₂ as discussed. As the temperature is increased, the dipoles, as well as, the thermal stress increases, so there is a significant change in dielectric permittivity at a temperature from 30 to 120°C.

Figure 12 (c): Dielectric permittivity of three different sensor composites as a function of temperature measured at 1 V_{AC} and 200 kHz signal.

In the trilayer architecture, the mechanism of change in dielectric permittivity with respect to temperature is similar to the composite discussed in bilayer architecture. The difference between the bilayer and trilayer architecture is the presence of additional Arathane layer on top of the HfO₂ layer. So, the effective permittivity becomes,

$$\varepsilon_T = 2\varepsilon_A + \varepsilon_C \quad (11)$$

The contribution from dielectric permittivity of the Arathane layer is doubled since the thickness of the Arathane layer is the same. This additional low permittivity Arathane

layer reduces the effective dielectric permittivity (ϵ_T) of the trilayer architecture. Figure 12c shows the thermal drift becomes more linear due to the additional Arathane layer which reduces the thermal drift.

3.3.5. Thermomechanical Response of Sensor Architectures

The three different sensor architectures were analyzed from 0 to 360 kPa at a rate of 20 kPa/min and temperature ranging from -60 and +120°C at an interval of 30°C in a temperature controlled dynamic mechanical analyzer. The sensors were soaked for 10 min at characterization temperature under zero load to stabilize the layers of the sensor material. In baseline architecture, the Arathane elastomer acts as the compliance layer which contributes to mechanical strain under applied pressure and as an active dielectric material as discussed. The change in capacitance of the sensor is directly proportional to the change in strain of the Arathane elastomer. Since the baseline architecture is fabricated only with Arathane elastomer as an active dielectric and compliance layer, conventional capacitive sensor model (equation 2, chapter 2) was used to correlate the change in capacitance with respect to applied load.

Figure 13a shows that the ΔC with respect to applied pressure with an error bar representing the average of data points from 10 different runs. The glass transition temperature (T_g) plays an important role in the thermomechanical behavior of the Arathane elastomer which is -69°C. The elastomer does not undergo viscoelastic change since the viscoelastic transition occurs at a temperature above 140°C. It can be inferred at the low temperature regime (-60 to 30°C), the relationship is linear and there are no noticeable differences between low and high modulus region due to the thermal stress is negligible (discussed in section 3.4) at low temperature. When the temperature is

increased and moves farther away from the T_g , the Arathane elastomer experiences noticeable change in modulus of elasticity from where there is a significant change from low to high modulus region. Weadon et al. modified Spriggs equation to analyze the modulus of porous material which was adopted to analyze the transition point in Arathane elastomer [21]. To find the transition point from low to high modulus, stress-strain data points are plotted and a linear trendline is plotted for both the low and high modulus region. The trendline is plotted by fitting a linear line to consecutive data points for both the regions until the coefficient of determination reaches a value of 0.98 [21]. With respect to the fitted trend line, a third line was generated to determine the intersection of the stress-strain curve which is the transition point from low to the high modulus.

Figure 13 (a): Thermomechanical loading of baseline architecture is shown as ΔC as a function of applied pressure at a temperature from -60 to 120 °C 30 °C interval.

Figure 13b shows the graphical determination of Arathane elastomer's transition from low to high modulus region at 60°C. The transition point is where the porosity of the Arathane elastomer is compressed and transitions to a high modulus region. The effectiveness of the model was corroborated by taking the first and second derivatives of the stress. Figure 13c and 13d show the first and second derivatives of the stress, respectively, which clearly shows the transition point from the low to high modulus occurs at ~50 kPa. It is evident from the porosity analysis that the linear increase in ΔC at 60°C from 0 to 50 kPa occurs due to the low modulus (collapsing of pores) and the linear response from 50 to 360 kPa is due to pressure applied at high modulus region. A similar analysis is applied for the sensor response at 90 and 120°C and the transition is found to be at 60 kPa and 120 kPa, respectively.

The ΔC of baseline architecture at various working temperature is shown in table 3. The change in sensor response from low to high temperature for the sample applied pressure is due to thermal drift which affected the dielectric permittivity as explained in section 3.4. From the thermomechanical analysis, it is significant to understand the ΔC is attributed to both the elastic modulus and thermal stress of the active sensor material (Arathane elastomer). From the analysis of the baseline architecture's response, the ΔC is better than a reported sensor which was applied the same principle which has ΔC in femto-Farad (10^{-15} Farad) region [9-13]. The dielectric permittivity of the Arathane elastomer is higher and the elastic modulus of Arathane is also higher which is responsible for the better sensitivity and increased capacitance.

Figure 13: Applied stress versus the % of strain and the first and second derivatives to pressure the transition point from low to high modulus region of Arathane elastomer (baseline architecture) at room temperature loading (30°C). The plots shows are (b) determination of transition point by splitting the angle between two slopes, (c) transition point is shown as the first derivative of pressure, and (d) transition point is shown as the second derivative of pressure.

The sensor response of bilayer architecture is shown in figure 14 and the overall ΔC from 0 to 360 kPa as a function of temperature is tabulated in table 3. As explained in section 3.4, the HfO_2 layer boosts the capacitance of the bilayer architecture by increasing the dielectric permittivity of the active sensing layer. The sensor response for bilayer architecture is also divided into low and high modulus region, which was calculated by the same method used for baseline architecture. At temperature from -60 to 30°C, the transition point from low to high is at 90 kPa. The additional HfO_2 layer is also responsible for the increased modulus because the modulus of a ceramic layer (HfO_2) is higher than polymer [37, 39]. The low modulus region of the bilayer architecture is increased when

compared with the baseline architecture due to the interface (Arathane/HfO₂) which acts more like a ceramic particle filled polymer composite. The modulus from collapsing the HfO₂ particles increases the strain in low modulus region. The low to high modulus region for 60 and 120°C occurs at ~60 kPa. At high temperature, the collapsing of ceramic particles at the Arathane/HfO₂ interface occurs rapidly providing a quicker response in the ΔC when compared with low temperature region. The linear response in the high modulus region which from 90 to 360 kPa at -60 to 30°C and 60 to 360 kPa at 60 to 120°C shows the displacement occurs only in the Arathane layer because the modulus of HfO₂ layer is very high (21 GPa) when compared with the Arathane and the mechanical effect from HfO₂ layer is negligible [50]. If there is a differential strain in the HfO₂ film, then the sensor response will be noisy and it will show a hysteresis behavior because the differential strain will be a catalyst to form micro/nano cracks in the film. This is another reason why the surface of the Arathane layer should be smoother (roughness <300 nm) and should have minimal pores [29].

Table 3: Average sensor response across the applied pressure regime as a function of temperature.

Temperature (°C)	ΔC (pF)		
	Baseline	Bilayer	Trilayer
-60	0.263	31.824	6.09
-30	0.303	31.836	7.039
0	0.399	35.842	8.081
30	0.411	37.484	8.289
60	0.519	39.508	8.539
90	0.637	42.941	8.856
120	1.093	46.247	9.469

Figure 14: Thermomechanical loading of bilayer architecture is shown as ΔC as a function of applied pressure at a temperature from -60 to 120°C with 30°C interval.

The sensor response of trilayer architecture is shown in figure 15. The additional Arathane layer decreases the capacitance of the sensor due to the increased thickness of low permittivity Arathane layer as explained in section 3.4. In the case of trilayer architecture, the transition from low to high modulus region is at 70 kPa for temperature between -60 and 90°C, which was similar to the trend as seen in the bilayer architecture. The transition at temperature 120°C is at 30 kPa, the reduced transition region is because the Arathane layer moves close to the viscoelastic region. The sensor response is more linear when compared with bilayer architecture because the compliance layer to distribute the pressure is thick (20 μm). The displacement in the compliance layer is large to overcome the displacement in the pores which was reflected in the sensor response as a linear function. The second Arathane layer is cast over the smoother HfO_2 film, which

reduces the internal stress at the interface since the Pt layer is not in direct contact with the HfO_2 layer.

Figure 15: Thermomechanical loading of trilayer architecture is shown as ΔC as a function of applied pressure at a temperature from -60 to 120°C with a 30°C interval.

3.3.6. Thermomechanical Cyclic Loading and Drift Analysis

Thermomechanical cyclic loading analysis was performed to study the thermal drift and hysteresis of the three sensor architectures at -60, 30 and 120°C. The sensors were soaked at respective characterization temperature for 10 min to stabilize and the pressure was cycled between 0 and 360 kPa with an interval of 60 seconds between cycles to study the time-dependent thermal drift and quasi-static viscoelastic behavior of the sensor material. In general, all amorphous polymers show some degree of viscoelastic character and the viscoelastic nature of these polymers is a time-dependent behavior which is

defined by the dynamic modulus. In the case of baseline architecture, the Arathane elastomer behaves as an elastic material at -60 and 30°C, since the quasi-static loading shows the whole elastic modulus of the material as shown in figure 16a. However, the sensor tends to show large drift and hysteresis at 120°C which indicates the loading scheme was not quasi-static anymore. It indicates the loading rate schedule was occurring at a rate where it overcomes the stress-strain relationship.

The change in capacitance shows the viscoelastic behavior of the Arathane elastomer because the pressure was kept constant the loading rate was not altered. The viscoelastic behavior of the polymer (in this it is an elastomer) is attributed by three primary variables which affect the molecular and sub-molecular interactions in the polymer chain which are: i) the length of the polymer chain which was generally defined by the average molecular weight of the polymer, ii) mobility of the polymer and iii) interactions between the sub-molecules or intermolecular interactions between different functional groups in the polymer chain [51]. The Arathane elastomer has two phenyl groups linked by a vinyl group and terminated with an isocyanate group as discussed in XPS analysis of the elastomer. The phenyl group acts as the backbone of the elastomer, the vinyl and the isocyanate groups provide the elastic modulus to the polymer. Since the Arathane elastomer has a long polymer chain the slip-link between molecules tends to occur at a larger rate [52]. The rate of the slip occurs at low temperature is less when compared with high temperature. The thermal applied loading will increase the mobility and interactivity of the molecules in the amorphous polymer matrix [53].

Figure 16 (a): Thermomechanical drift analysis of baseline sensor architecture at -60°C, 30°C and 120°C.

In the bilayer architecture, the thermomechanical response is due to Arathane elastomer, HfO₂ particle filled elastomer matrix and the HfO₂ thin film layer. In this work, the effect of modulus from the HfO₂ thin film is considered negligible because the elastic modulus of HfO₂ is very large (8 – 21 GPa) [50]. The phase change within HfO₂ due to change in temperature is approximately zero since the film is amorphous [36]. The modulus of the bilayer architecture is approximated to the Arathane and the interface between Arathane/HfO₂ thin film. Similar to baseline architecture at -60°C the effect of temperature on the viscoelasticity of the active sensing material is negligible and it preserves the elastic modulus limit within the applied pressure regime in the quasi-static loading region. The sensor has slight thermal drift at 30°C because the HfO₂ particles at the interface tend to collapse at a faster rate within the polymer indicating the loading rate scheme was not quasi-static. The pores are collapsing at a rate which overcomes the stress versus strain relationship of the elastomer, thus, affecting the capacitive response which was reflected as the hysteresis in the figure 16b. A similar effect can be seen at 120°C, but the collapsing of the pores occurs at a much faster rate which was reelected as a linear slope when the pressure was rapidly increased to 360 kPa, and this took approximately 12 – 15 secs to stabilize and no hysteresis effect can be seen further.

Figure 16 (b): Thermomechanical drift analysis of bilayer sensor architecture at a) -60°C , b) 30°C and c) 120°C .

As shown in figure 16c, the time-dependent hysteresis effect of trilayer architecture is similar to that of bilayer architecture, the additional Arathane elastomer layer does not seem to alter/affect the sensor response for the cyclic loading scheme. The sensor remains under quasi-static loading at -60°C as seen in baseline and bilayer architecture. At 30°C , the trilayer architecture behaves similarly to the bilayer architecture under thermomechanical loading cycles. When the temperature increased to 120°C which approaches the viscoelastic transition temperature (140°C), the capacitive response from Arathane layer dominates. Since the HfO_2 layer is sandwiched between Arathane layer, the pseudo-viscous transition occurs only at the Arathane layer. The pseudo viscoelastic property of thermosetting elastomers we computationally modeled by Zoberi et al. stating that elastomers that can retain their original elastic limit at a given temperature after removal of force/pressure [54]. In figure 16c, we can see the slope linearly increases at high pressure loading cycle, showing the dominance of pseudo-viscous flow region. However, during the material relaxed and does not show thermal drift at 0 kPa which shows the Arathane elastomer can regain its elastic modulus state.

Figure 16 (c): Thermomechanical drift analysis of trilayer sensor architecture at a) -60°C, b) 30°C and c) 120°C.

Chapter 4 – Embedding of Sensor and Future Work

4.1. Introduction

An embedding strategy was introduced to integrate the developed sensor arrays with the robotic end-effector in order to demonstrate the response of the sensor in the actual working environment. The NASA Goddard Space Flight Center (GSFC) has been developing autonomous robotic systems to dock in earth-orbiting satellites by grappling the “marman ring” which is mounted on all satellites for deployment into space. It is vital for the robotic system to be aware of contact force, the spatial distribution of forces across the end-effector and time dependent hysteresis to appropriately grasp the marman ring to dock the satellite. In this work, the prototype was designed to accommodate the developed sensor array on of the GSFC’s robotic end-effector manipulator.

Figure 17: NASA GSFC’s robotic gripper tool designed to dock the satellite by grasping the marman ring. The cross-hair locations are proposed to embed sensor arrays.

The GSFC’s marman ring gripper as shown in figure 17 was designed concretely for initial grappling of satellites in earth orbit, sanctioning for secure docking of the robotic equipment for refueling and rehabilitates. During the docking process, the contact surface

between the end-effector and the marman ring experiences a high force, metal-on-metal contact and strict geometry constraints. It is difficult for the embedded sensor to realize the high force acting on the end-effector since the polymer compliance layer is $\sim 10\text{ }\mu\text{m}$ thick and the coarse machined metal surface will create point/line stress concentrations on the sensor which will potentially damage the sensor over time. To avoid the potential damage to the sensor, and to evenly distribute the force across a large area, an additional rubber compliant layer was implemented. The compliant layer with a high modulus of elasticity was chosen to protect the sensor from metal-on-metal contact while providing an adequate mechanical support without pressure gradient across the compliant layer. The marked locations as shown in figure 17 are proposed to embed the sensor array into the gripper. For simplicity, a single node sensor was chosen to initially prove the proof-of-concept.

4.2. Experimental Procedure

The GSCF's marman ring gripper tool was used for prototyping and demonstrating the embedding of the sensor arrays. To avoid restructuring and manufacturing of a new gripper tool, the existing gripper tools was redesigned by simply providing a small cavity to accommodate the sensor array. The etched cavity was used to accommodate the sensor array, the rubber compliant layer and the baseplate holding the compliance layer and sensor array in their locations during operation. Various embedding depths and thicknesses of compliance layers were proposed to study the effect of those variable in the sensor responsible. Two different embedding depths of $1/4$ and $1/2$ inch were proposed. Temperature and corrosion resistant silicone of $1/8$ and $1/16$ inch was used as a high modulus compliant layer to distribute the force across the sensor. The model of

designed prototype is shown in figure 18 representing the embedding cavity to accommodate the sensor and the compliance layer of variable thickness with respect to

Figure 18: Redesigned GSFC's gripper tool prototype with dimensions matching the contact points shown in figure 17. In this figure the blue represents the bulk material, the grey represents the cavity made to a depth of 0.5" to provide an area for embedded sensor and compliance layer, and the red circles are machined to accommodate shoulder screws.

Since it is inconvenient, as well as, uneconomical to redesign the entire gripper tool, the actual embedding area was modeled. The proposed models were fabricated by 3D printing technology. Owing to its excellent temperature and chemical resistance, mechanical properties, co-polyester was used a filler material to 3D print the designed test prototype. The baseplate was also 3D printed with locations on 4 ends to accommodate shoulder screws. Shoulder (frictionless) screws were used in order to reduce the effect of friction between the baseplate holding the sensor package and the screws. Bilayer sensor architecture from chapter 3 was used to embed within the

prototype for high pressure characterization. Figure 19 shows the different steps of embedding process where a thin layer of silicone elastomer was placed right underneath the active sensing area to protect from the micro roughness of the prototype surface; the sensor with micro silver leads was approximately placed at the center; the top compliance material was placed and encased by the top plate. To understand the effects of different layers used in the embedding of sensors, the sensor was characterized: i) as bare sensor, ii) within the gripper prototype with a silicone compliance layer, and iii) complete embedding with the baseplate.

Figure 19: Embedding of single node sensor in 3D printed prototype for characterization in Shimadzu. a) sensor supported in the silicone layer just underneath the active sensing area; b) a compliance layer was covered over the entire sensor area to protect for direct metal-on-metal contact; c) completed embedded sensor prototype with shoulder screws supporting the top plate.

The packaged embedded sensor prototypes were characterized by applying a mechanical load and simultaneously acquiring the capacitive response from the sensor. The mechanical loading cycles were performed by Shimadzu AGS-X mechanical analyzed stand. The capacitive response was logged by BK precision's 889B bench LCR meter with a logger program customized to record capacitance every second for the simplicity of data analysis. The test setup of embedding prototype was shown in figure 20 where the upper arm is the dynamic arm which provides the known mechanical loading and the test prototype was placed on the static (lower) arm.

Figure 20: Mechanical loading setup for high pressure characterization in Shimadzu. The upper arm is the dynamic arm where the prototype is supported on the static arm.

The mechanical loading was applied with a constant rate of pressure to precisely control the loading rate, and to promote safety and avoid accidental overloading of the equipment. Furthermore, it provides a direct correlation with the capacitance change as a function of time which helps to plot change in capacitance with respect to applied pressure. A constant loading rate of 1 N/sec was used to test the bare film sensor up to 120 N of force for bare sensor film. A rate of 2 N/sec was used to apply a final load of 250 N for both the sensor with silicone compliance layer and the complete embedded sensor with the baseplate. The data acquisition rate of Shimadzu was completed at 10 Hz, whereas the electrical acquisition was varied with an average rate of 1 Hz. A two-step data analysis process was followed to correlate and plot the sensor response (ΔC) as a

function of applied pressure. First, the force data from the Shimadzu was interpolated as a function of time to provide approximate data for capacitance time stamp from the LCR meter. The applied force across the sensor face was assumed to be perfectly distributed across the active sensing area without any parallel contact of the active clamp of the gripper tool. This assumption will lead us to straightforwardly converting the applied force into pressure since the pressure acting on the active sensing area accounts for the capacitance response. However, this assumption shows up as a seeming loss of sensitivity as an additional force is applied but the sensor response (capacitance) does not change accordingly.

The sensor was tested in an alternative order to prevent any progressive damage due to the loading schedule from improper correlation with a specific embedding design. Two sensor samples were first embedded in each of the gripper prototypes with 1/8th inch silicone compliance layer and point loading operation was performed by alternating the samples followed by testing the same sensor by changing the thickness of the compliance layer to 1/16th inch thickness. The second test was performed with the baseplate which supports the elements in the embedding cavity by holding them together. Same test runs were performed for both the compliance layer thickness. All specimens were tested as bare film supported on electrically insulated testing clamp at last since this testing process was expected to damage the sensor. All specimens were tested a total of 5 runs and embedded within the same gripper tool prototype.

4.3. Discussion

The sensor response (capacitance) as a function of applied stress (force/area) for the sensor embedded with 1/16th inch silicone compliance layer and fully embedded prototype for shown in figure 21. The sensor response (capacitance) of the bare film loading shows a sporadic result and could not be able to plot by combining with the other data. The bare film loading shows the sensor reached failure point after reaching ~1 MPa pressure. This indicates that the applied force is induced local stress concentration on the sensor and the micro-roughness between the deposited layers in the sensor architecture will further influence and acts as the favorable sites for stress concentration regions which leads to short-circuiting the sensor.

Figure 21: Sensor response (capacitance) of bilayer sensor architecture as a function of applied pressure embedded in the prototype with 1/16th inch silicone layer and fully embedded prototype.

The sensor response of the bilayer architecture embedded in the prototype with 1/16th inch silicone compliance layer was improved and was consistent with the loading cycle. It is evident from the data shown in figure 21 that the silicone compliance helps to distribute the applied force more uniformly across the surface of the sensor and prevents point loading which damages the sensor. The result shows the presence of two distinct linear regions: 0 – 2 MPa and 2 – 5 MPa, which is consistent with the previous discussion, where the thermomechanical characterization of the sensor in chapter 3 shows a similar trend in the data due to low and high modulus region of the elastomer. Furthermore, the sensor response was similar to the fully embedded prototype where the initial capacitance under zero load was increased to ~64.6 pF from ~62 pF due to the existing residual stress when the sensor was tightened with the shoulder screws to lock into its location. The sensor response slightly varies for the fully embedded prototype where the low to high modulus transition occurs at ~1.25 MPa since the applied force also absorbed by both the compliance layer and the top plate.

Figure 22 shows the sensor response of the same sensor embedded in 1/8th inch compliance layer and fully embedded prototype. The initial capacitance under zero load for 1/8th inch compliance layer is increased due to thicker compliance layer which promotes more residual stress across the sensor area. However, the trend in sensor response was similar to that of 1/16th inch silicone compliance layer with a slight decrease in the sensitivity. The initial capacitance of the fully embedded prototype is increase as expected with an increment of ~4 pF and the sensor response was also decreased similar due to diffused absorption of the stress in the top plate and the compliance layer. This

indicates thinner compliance layer with a minimal thickness of the top plate will be more efficient in protecting the sensor while preserving the sensitivity of the sensor.

Figure 22: Sensor response (capacitance) of bilayer sensor architecture as a function of applied pressure embedded in the prototype with 1/8th inch silicone layer and fully embedded prototype.

Chapter 5 – Conclusion

5.1. Sensor Composition

A single layer sensor architecture and a laminar polymer-HfO₂ composite material consisting of three variables, each being optimized for various parameters. In this section, some of the important findings, and necessary considerations for the design of a robust, high sensitive, laminar thick-film sensor composite for harsh environment applications are summarized below:

- **Deposition of amorphous HfO₂ thin film on the flexible substrate:** Amorphous HfO₂ thin film with excellent dielectric permittivity was successfully deposited at room temperature on a flexible polymer substrate by a laser ablation process from a ceramic HfO₂ target. The HfO₂ thin film was deposited on Pt coated Kapton film substrate shows an average dielectric permittivity of ~29 which was close to the theoretical dielectric permittivity of HfO₂ thin film [33]. However, we report the first ever HfO₂ thin film deposited on a polymer substrate along with an excellent dielectric permittivity.
- **Performance of the laminar polymer-ceramic composite for the capacitive sensor:** From the thermomechanical characterization results, the bilayer and trilayer sensor architectures reported in this work showed the highest performance for a capacitive sensor. The sensor response (capacitance change) for the bilayer and trilayer sensor architecture is approximately 56 and 18 pF, respectively. The change in capacitance is an order magnitude higher than the reported literature [11-18]. Among the bilayer and trilayer architecture, bilayer shows more response

than the trilayer, however, the trilayer has better stability over the bilayer architecture. Depending on the application and working environment these sensor architectures can be employed. For instance, at a very noisy (electronic noise) environment, bilayer architecture is preferred over the trilayer architecture owing to its better signal-to-noise ratio. In the case of high temperature fluctuation environments, trilayer architecture is preferred to promote stability of the sensor.

From the experimental and characterization results, one must consider the following while designing and fabricating a capacitive pressure sensor for harsh environments,

- **Selecting a flexible substrate:** The flexible substrate used for harsh environment application should be able to withstand wide temperature fluctuations, chemical resistant during fabrication, low outgassing under low pressure (vacuum atmosphere), and must have minimal surface roughness and defects. Kapton (polyimide) is one of the best available candidate for the polymer substrate, Mylar (polyethylene terephthalate) can also be used other harsh environments but the applications is limited to earth's atmosphere due to relatively higher degassing under vacuum atmosphere.
- **Electrode deposition and techniques:** The metal electrode used to deposit onto the polymer substrate should have excellent adhesion to the substrate without any intermediate (seed) layer. The seed layer might affect the capacitive response from the sensor. Owing to its excellent electrical conductivity across wide operating temperature and chemical resistance, Pt is a viable option to be used as an electrode for depositing on the polymer substrate. Sputtering is proven to be an effective technique to deposit Pt electrode on a polymer substrate with the desired

thickness without depositing a seed layer such as Ti, Al, or Cr. The advantages of sputtering are: room temperature deposition is feasible, uniform film deposition across a large area, good thickness control, and stoichiometry of the thin film can be preserved. In addition to the advantages, it is easy for mass production in an industry. Thickness characterization showed the thickness of the Pt layer should neither be thick nor be thin, should lie in a range where the adhesion is good and the film conforms the geometry of the flexible polymer substrate.

- **Selecting a polymer elastomer layer:** The compliant polymer used as an elastomer for the sensor composition should be able to withstand temperature between -60 to 120°C. The polymer should not undergo phase transition within the temperature regime. The polymer should have low or negligible modulus transition under the wide operating temperature to improve the linearity of the sensor response (capacitance). The polymer should have very low polydispersity index (<0.1) to reduce/avoid viscoelasticity effect during operation. During curing, the polymer should have very low shrinkage to improve adhesion on the substrate and to avoid pores in the complex microstructure. Furthermore, the dielectric strength, as well as dielectric permittivity of the cured elastomer, should be as high as possible.

5.2. Embedding Strategy

Embedding strategy was developed to protect the sensor from direct metal-on-metal contact simultaneously providing uniform stress distribution across the surface of the sensor. A single node sensor with 8mm diameter was embedded and tested in high pressure mechanical loading cycles to analyze the effects of different layers of embedding

materials. A compliance is required to protect the sensor from point loading which renders the sensor useless and to distribute the force uniformly across the area of the sensor. The complete embedded prototype has lower sensitivity than just the loading on compliance layer. This is attributed to the top plate which engrosses the applied force. The study shows the using a compliance layer with high modulus material along with minimal thickness will be an excellent option to protect the sensor as well as improve the sensitivity and stability.

Future Work:

Several sensor architectures were developed, tested and discussed in this work with significant improvements having been made; however, there is always more scope for further advancement. A diffuse layer between the elastomer and HfO_2 thin film was discussed in chapter 3, which should be minimized to improve the stability and linearity of the sensor. The Arathane elastomer has a sharp transition between low and high modulus region which affects the sensitivity of the sensor. Porosity in the three-dimensional polymer network during curing cycle is one of the main reason for the drift, hysteresis, and modulus transition. To avoid this transition, the Arathane elastomer can be densified under high pressure at a temperature close to the viscoelastic transition region. This densification cycle can be applied either before or after dielectric layer deposition to study the effect of the defects induced in the dielectric layer in sensitivity. Further development can be made by choosing an alternative elastomer matrix which has good temperature stability and compression strength still providing enough compliance for high sensitivity.

Embedding prototypes can be enhanced by adding multiple node sensors to improve the spatial awareness and locating the point-of-contact information. The surface of the top plate can be beveled with actual sensor surface area to measure the shear force or to find if a grasped object slipping from the robotic end-effector. The silicone compliance layer thickness should be further decreased to the improve the sensitivity of the sensor.

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