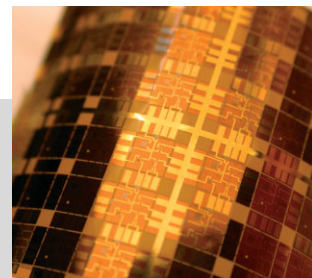


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Recent Developments in Polymer MEMS**

By Chang Liu*



Polymer materials, including elastomers, plastics and fibers, are being actively used for MEMS sensors and actuators. Polymer materials provide many advantages in terms of cost, mechanical properties, and ease of processing. In addition, polymers are being investigated for displays, memory, and circuitry. However, the incorporation of polymers for structural or functional purposes in MEMS systems raises new issues and challenges. This article provides a comprehensive review of the recent state of the art of polymer based MEMS—including materials, fabrication processes, and representative devices, including microfluidic valves and tactile sensors. Frequently used materials are reviewed, including polydimethylsiloxane (PDMS), parylene, nanocomposite elastomers, and SU-8 epoxy.

1. Background

The microelectromechanical systems (MEMS) area has been developed extensively during the past three decades.^[1–5] In the 1970s, with the advancement of semiconductor microelectronics processing, researchers investigated wet anisotropic chemical etching processes for forming three dimensional silicon geometries.^[6] In the 1980s, researchers adopted the Metal-Oxide-Semiconductor (MOS) process to realize polycrystalline silicon micromachining with silicon dioxide as a sacrificial layer material.^[7] This process leads to so-called surface micromachined devices, including electrostatically actuated motors^[8,9] and interdigitated finger capacitive sensors and resonators.^[10] In the 1990 s, many commercially successful MEMS products began to appear in the market, including digital light processor (DLP) from Texas Instruments, ink jet printer nozzles from Hewlett Packard, and solid-state accelerometers for air bag deployment from Analog Devices and Motorola (now Freescale). Government funding for MEMS

research in the US and in many other parts of the world leads to an explosive growth of MEMS processes and devices.^[11,12] Many substantially large sub-domains of MEMS emerged, including optical MEMS (e.g., mirrors, attenuators, phase shifters),^[13] RF MEMS (e.g., switches, resonators, capacitors, inductors),^[14] bioMEMS (e.g., microfluidics, medical devices, prosthesis implants), nanoelectromechanical systems—NEMS (e.g., resonators and biosensors),^[15] MEMS for harsh environment,^[16] and power MEMS (actuators, power generators, and micro chemical systems).^[17]

The MEMS field evolved from the semiconductor industry and is strongly tied to it in many ways. The predominant substrate material is silicon. The predominant surface thin film is polycrystalline silicon and silicon dioxide, widely used as the gate and insulation material in the MOS process. Often, MEMS devices are made in cleanrooms, similar to microelectronics devices. Photolithography is used to define both transistors and MEMS devices.

The MEMS field also contributes new knowledge and practice to the general area of microfabrication, stemming from its unique needs, such as the needs for functional materials (including piezoelectric and piezoresistive materials) and for three-dimensional features (such as cavities, throughwafer holes, flaps, and suspended beams and membranes). The MEMS field provided incentives for the conceptualization and sustained development of such processes as deep reactive ion etching, photodefinable SU-8 epoxy,^[18] and self-assembly.^[19]

Over the years, the MEMS field has steadily expanded its material base to include compound semiconductors,^[20,21] diamond,^[22–24] and ceramics.^[25,26]

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Polymer is a large class of material that includes three major categories: fibers, plastics, and elastomers. Since 1990s, polymer materials have been increasingly used in MEMS. Major motivations for incorporating polymers into MEMS include:

1) Many polymer materials provide greater mechanical yield strain than silicon (in single crystalline, polycrystalline, and amorphous forms). Though silicon is a mechanically strong material with a large Young's modulus, it is relatively brittle.^[27,28] Polymer materials, especially elastomers, can sustain greater degree of deformation. For applications where the MEMS devices are directly in contact with the elements, such as smart skins for tactile and flow sensing sensing, robust material is crucial for success.^[29,30]

2) Many polymer materials are of significantly lower cost to acquire. Further, the processing of certain polymers can be accomplished outside of the cleanroom confinement, lowering the cost of fabrication.

3) Polymer substrate can be obtained in non-wafer forms. In contrast, silicon substrates can only be obtained in wafer format. Polymer MEMS can have unlimited sizes.

4) Electronics and optoelectronics are migrating strongly towards polymer, including displays, photo voltaic devices,^[31,32] memory,^[33] and transistors.^[34–36] Sensors and actuators made by polymer MEMS could one-day become fully integrated with electronics in like material systems.

5) The silicon micromachining toolbox is relatively limited. Polymer MEMS increases the portfolio of microfabrication process drastically by allowing novel fabrication processes such as casting and molding, low temperature chemical vapor

deposition, embossing,^[37,38] spraying, screen printing, thick film processing,^[39] and stereo lithography.^[40]

6) Polymers provide unique chemical, structural and biological functionalities not available in any other material systems. For example, functional hydrogels can change volume in response to environmental pH and temperature.^[41,42] Poly carbonate films can have holes with controlled nanoscopic dimensions, produced by energetic ion track etching.^[43]

2. Polymer MEMS Devices

Polymer materials have been used in MEMS in several capacities, including substrates, structural thin films, functional thin films, adhesion and packaging, coating,^[44] and surface chemical functionalization.^[45,46] In this review, I will focus on materials for the first three functionalities—substrates, structural thin films, and functional thin films.

The following polymer materials are used in MEMS today with relative high frequency today: Parylene, polyimide, acrylics (PMMA), photopatternable epoxy, and polydimethylsiloxane (PDMS) elastomer. In addition, a number of other materials are also being used, including liquid crystal polymer (LCP),^[47] liquid crystal elastomer (LCE),^[48] biodegradable polymers,^[49,50] functional hydrogels,^[41] Paraffin,^[51,52] piezoelectric polymers, fluorocarbon thin films, and conductive polymers.^[53,54] The following Table 1 lists the materials and several representative demonstrated applications.

Table 1. Representative Polymer MEMS materials and applications.

Material	Representative processing methods	Applications
Parylene	Chemical vapor deposition	Micro pumps and valves; pressure and shear stress sensors; micro air vehicle wings; microfluidics
Polyimide	Spin coating, extrusion	Sensor substrates; microfluidics
Acrylics	Molding	Microfluid channels;
PDMS	Molding	Microfluidic channels, pumps, and valves;
Liquid crystal polymer	Chemical etching	Flow sensors
Biodegradable polymer	Molding	Drug delivery devices
SU-8 epoxy	Photo patterning, spin casting	Artificial haircell sensors
Polyurethane	Molding	Structures
Nanocomposite elastomers	Screen printing, molding	Conductors; sensors; actuators



Chang Liu received his M.S. and Ph.D. degree from the California Institute of Technology (Pasadena, CA) in 1991 and 1995, respectively. His Ph.D. thesis was titled "Micromachined sensors and actuators for fluid mechanics applications". In January 1996, he joined the Microelectronics Laboratory of the University of Illinois as a postdoctoral researcher. In January 1997, he became an assistant professor with major appointment in the Electrical and Computer Engineering department and minor appointment in the Mechanical and Industrial Engineering Department. In 2003, he was promoted to Associate Professor with tenure. His research interests cover MEMS, nanotechnology, sensors, and intelligent systems. He has 16 years of research experience in the MEMS area and has published over 200 technical papers. Prof. Liu received the NSF CAREER award in 1998 and the University of Illinois Xerox Award of Faculty Research in 2002. He is a senior member of the IEEE and a fellow in the Center for Advanced Studies at the University of Illinois.

A number of representative polymers and their MEMS applications are discussed in more detail in the following, to illustrate representative techniques and opportunities.

a) PDMS Elastomer

Elastomers such as PDMS and polyurethane have been used in microfluidics extensively. PDMS provides excellent and proven biocompatibility.^[55] It can be processed by cast molding, spin coating, screen printing,^[56] or drilling. Since many of these processes do not require photolithography, PDMS processing is widely used among biologists and chemists. The PDMS material is popular in both micro- and nanofabrication arenas. In nanotechnology area, it is an established material for micro contact printing, a technique for direct deposition of molecules on surfaces.^[57,58]

Due to its simple processing, optical transparency, and biocompatibility, PDMS is widely used for microfluidic devices.^[59–61] PDMS can be cast at room temperature and then thermally annealed—the PDMS device would replicate the structures on the surface of the mold. The molded PDMS piece is then attached to flat surfaces to form microfluid channels. Multiple layers of molded PDMS can be integrated with spatial registration to form functional components, such as valves,^[62] pumps,^[63] and mixers.^[62,64]

PDMA can be bulk cast, spin cast, or micro patterned by modified screen printing method.^[56] When spin casting, the thickness can be controlled by the spin speed and the viscosity of PDMS precursors. Due to finite viscosity, the thickness resulting from spin casting is generally on the order of tens of μm . The modified screen printing method (Fig. 1) involves building a sacrificial screen printing mold (step a and b). The mold may be made of common photoresist. The polymer precursor is cast onto the front surface. A squeegee is then used to remove excess PDMS precursor (step d), leaving precursors only in recessed regions (step e). After curing and crosslinking of the precursor, the sacrificial layer is removed, leaving only the cured PDMS patterns (step f).

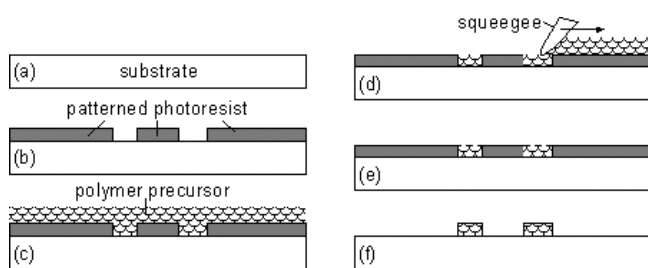


Figure 1. Modified screen printing method for PDMS patterning.

Other applications of PDMS include pneumatic actuated manipulator,^[65] optical pressure sensors,^[66] and scanning probe nanolithography.^[67]

b) Parylene

Parylene is in fact the generic name for a unique polymer series. The basic member of the series, called Parylene N, is poly-*para*-xylylene, a linear, highly crystal material. A ther-

malset polymer, Parylene is the only polymer that can be deposited using chemical vapor deposition (CVD) method. The CVD process is performed in a dedicated equipment involving three distinct steps: vaporization of the solid dimer, pyrolysis of the dimer into stable monomers, and polymerization in room-temperature chamber. It generally involves elevating the temperature of solid dimers (di-*para*-xylylene) to approximately 150 °C to induce sublimation, and coating the vapor phase dimers onto the job piece located in a vacuum chamber.

Parylene C is the second commercially available member of the series. It is produced from the same monomer modified only by the substitution of a chlorine atom for one of the aromatic hydrogens. Parylene C, with a low permeability to moisture and other corrosive gases, is ideal for coating critical electronic assemblies.

The Parylene film offers very useful properties for MEMS applications, including very low intrinsic stress,^[68] low dissipation factor, a frequency-invariable dielectric constant (for Parylene N), room temperature deposition, conformal coating, chemical inertness, and etch selectivity.^[69] Parylene can be deposited conformally at room temperature, with thickness ranging from a few thousand nanometers to a few tens of micrometers. In macroscale, Parylene has been used to apply protective coating for preservation and insulation.

Parylene has been used for microfluidics channels,^[70,71] valves,^[72,73] sensors (e.g., acceleration sensors,^[74] pressure sensors,^[75] microphones,^[76] ultrasonic imaging devices,^[77] and shear stress sensors^[75]) and large area structures.^[78]

Notable providers of Parylene material and/or processing equipment include Specialty coating systems (SCS) Corporation, Comelec Corporation, and Uniglobe Kisco Corporation.

c) Nanocomposite Elastomer

Nanocomposites are an exciting new material under intense investigation.^[79] The electrical properties of many plastics and elastomers can be modified by additive particles (doping). Traditional PDMS materials are transparent and insulating, serving primarily structural roles (e.g., as microfluid channel walls). Nanocomposite elastomers can be formed by embedding conducting particles (such as carbon blacks, carbon nanotubes and graphene sheets). If the concentration of embedded particles reaches a concentration beyond the percolation limit, the conductivity of the material changes significantly. The percolation limit is a function of both the polymer matrix and the additive particles. It is advantageous to have low percolation limit to preserve the mechanical elasticity of the material. The figure below shows the measured resistivity of four types of nanocomposite materials—multiwall carbon nanotube (MWNT) in PDMS matrix, MWNT in polyurethane (PU) matrix, carbon black (CB) particles in PDMS, and CB in PU matrix (Fig. 2 and 3).

The resistivity of the nanocomposite elastomer is a function of the applied strain—matrix deformation changes the effective concentration and therefore the conductivity. As such, the nanocomposite elastomer serves as a strain gauge.

In addition, the composite material may be made with other types of particles to afford richer variety of functions to the

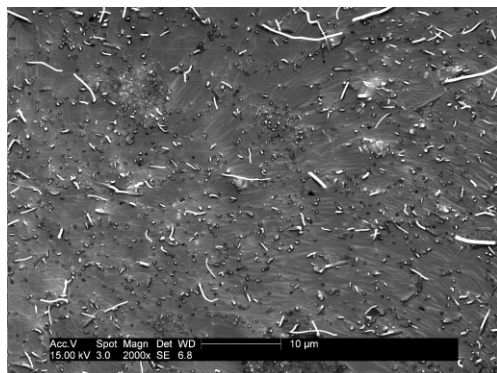


Figure 2. Scanning electron micrograph of the cross-section of an elastomer matrix with well dispersed carbon nanotubes.

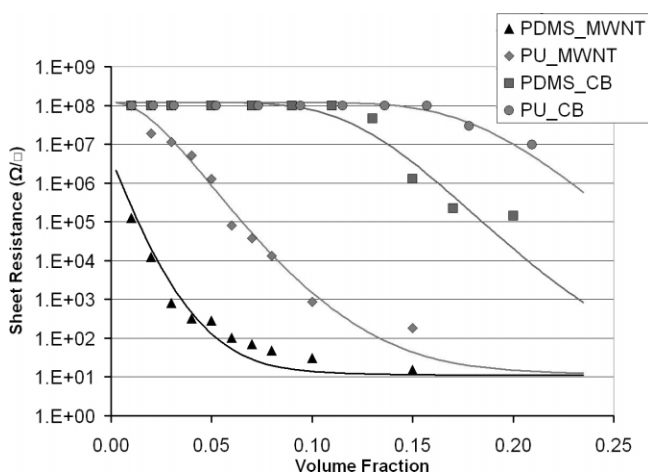


Figure 3. Plot of measured sheet resistance of four types of samples as a function of CB and MWNT volume fractions with model curves based on Novak's percolation model.

matrix itself. For example, PDMS with expandable microspheres have been used for actuation.^[80]

Nanocomposite elastomers can be patterned using precision screen printing technology^[56] and then integrated with non-conductive elastomers in multilayer soft lithography processes to form functional soft MEMS devices. Conductive elastomer structures can also form capacitors for both sensing and actuation. Such soft-MEMS systems may incorporate structures, sensing (strain gauge and capacitive sensing) and actuation (capacitive and pneumatic).

d) SU-8 Epoxy

The SU-8 is a negative tone, near UV photo-resist first invented by IBM in the late 1980s,^[81] with the main purpose of allowing high aspect ratio features (> 15) to be made in thick photosensitive polymers. The photoresist consists of EPON® Resin SU-8 (from Shell Chemical) as a main component. The EPON resin is dissolved in an organic solvent (GBL, gamma-butyrolactone), with the quantity of solvent determining the viscosity and the range of achievable thickness. Processed

layers as thick as 100 μm can be achieved, offering tremendous new capabilities for masking, molding, and building high aspect ratio structures at low cost.

High aspect ratio microstructures are often needed in MEMS, as fluid channels, injection needles, pillars, filters, gratings, throughwafer holes, etc. In this respect, the cost of SU-8 lithography is considerably lower than that of other techniques, notably LIGA process (for photoresist) and the deep reactive ion etching (for silicon). SU-8 has been integrated in a number of micro devices, including microfluid devices,^[82] artificial haircell flow sensors^[83] (Fig. 4), SPM probes,^[84] manipulators,^[85] and micro needles for drug delivery.^[86]

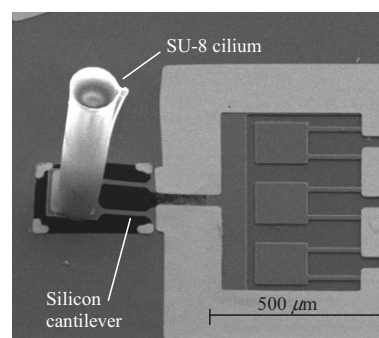


Figure 4. Scanning electron micrograph of an artificial haircell flow sensor, with a 700 μm tall SU-8 cilium resting on a silicon cantilever.

3. Representative Application

3.1. PDMS Microfluidic Devices

Biological microfluidics devices are under intense investigation for automated laboratory-on-chip biochemical analysis^[70,87,88] and drug screening.^[89] PDMS is widely used in the microfluidics area. Here, PDMS provides unmatched advantages, including optical transparency (for easy monitoring and interrogation of flow and contents within), gas permeability (for removing trapped gas bubbles while confining liquid volumes), simple processing (molding and reversible bonding), elasticity (for leak-free valving), and low cost (for disposable lab chip applications). A PDMS microfluid chip for protein analysis is shown in Figure 5.^[90] In contrast, silicon is opaque, gas impermeable, and much more costly to process.

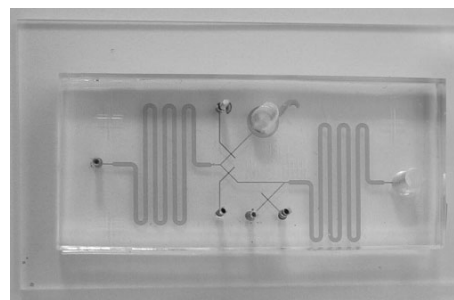


Figure 5. A microfluid lab-on-chip device for protein detection.

A representative process for molding PDMS microfluidic channel is illustrated in Figure 6. A first wafer substrate is provided (step 1), followed by the deposition of a photosensitive resist layer (step 2). The photoresist is photolithographically patterned (step 3) and developed. PDMS precursor is poured on top of the first wafer (step 4), cured, and then separated (step 5). The PDMS piece containing the inverse of the molded feature (e.g., channel in this case) is then attached to a second wafer to form enclosed channels (step 6).

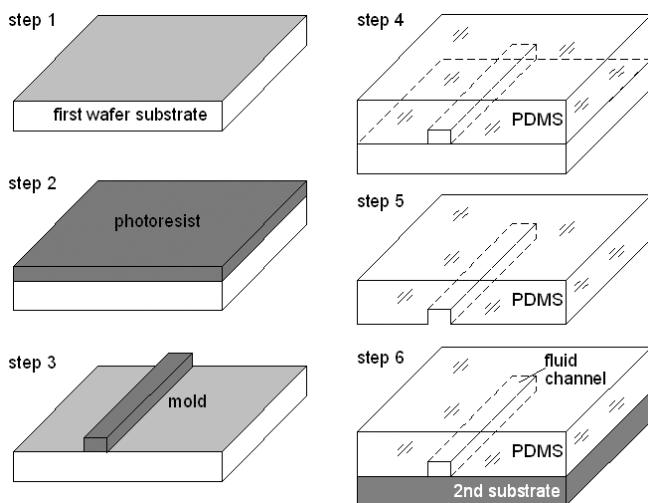


Figure 6. Process for fabricating microfluidic channels using PDMS.

One important reason why PDMS is heavily used in microfluidic is the ability to form valves, which are one of the most crucial elements in controlling the switching of flow. Valves made of silicon, silicon nitride and other hard, inorganic materials have been developed. However, these do not provide reliable seal in the presence of surface roughness and particles. In comparison, the elastomeric valves can provide much robust sealing, can hold against large backpressure with high power pneumatics, and can be controlled in multiplexed fashion for array devices.^[61,64] The PDMS also provide a relative easy solution for chip-to-world interconnection.

3.2. Parylene Valves

Parylene has been used for making microfluidic channels and valves. A recent work demonstrates that both normally closed and normally open fluid check valves have been made in one monolithic process.^[73] Further, the authors employed both normally closed and normally open valves in back-to-back configuration in a dual-valve microfluidic system. The detailed processing flow (Fig. 7) uses a silicon wafer with backside anisotropically etched cavities (step a). The front and backside of the silicon is covered with silicon dioxide. The frontal silicon oxide is removed, followed by deposition and patterning of a 1st parylene layer (step b). A photoresist layer

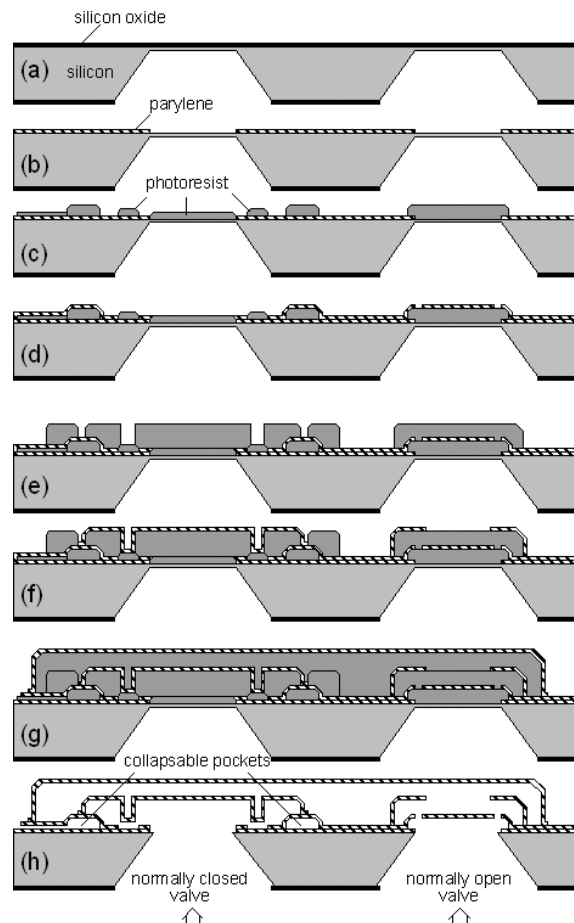


Figure 7. Fabrication process for a dual-valve unpowered microflow system using parylene as structural layer.

is deposited by spinning (step c) and photolithographically patterned. The wafer is once again coated with a parylene layer (2nd layer), which is then patterned to expose selective regions (step d). Another photoresist layer is deposited and patterned (step e), followed by the deposition and patterning of a 3rd parylene layer (step f). The last photoresist layer is deposited and patterned (step g) and then coated with a 4th parylene layer. The 4th and 3rd parylene layers are etched to open selective etch holes for removal of the sacrificial photoresist. After the photoresist removal by wet acetone bath, the parylene structures are left behind (step h). Lastly, a last parylene layer is deposited (not shown), which pulls vacuum in collapse pockets and initiate normally closed valves.

3.3. Polymer Tactile Sensing Skin

Tactile sensors are immensely important for future applications in robotics, interactive electronics, telemedicine and health care. While silicon micromachined tactile sensors provide high spatial resolution, high sensitivity and direct integration to signal-processing electronics,^[2,91] the long term me-

chanical reliability is unresolved due to the brittleness of the silicon MEMS materials. Using silicon, it is also difficult to make flexible or stretchable tactile sensors—packaging of such sensors on robotics hands or manipulators with curved surfaces is prohibitively difficult.

Polymer based tactile sensor is attractive due to many reasons. Polymer materials are mechanically robust and chemically resistant. The dimensions of future tactile sensing skin are limited by the finite sizes of silicon wafers in the case of silicon micromachining.

Multimodal tactile sensor on flexible polyimide substrate capable of sensing the hardness, roughness, temperature and thermal conductivity of the object in contact has been developed.^[29] The sensor is constructed using a polyimide substrate (Fig. 8) and consists of multiple sensor nodes arranged in an array format. Each node in turn consists of four elements: a thermal conductivity measurement unit (element A), a temperature measurement unit (element B), and two membranes

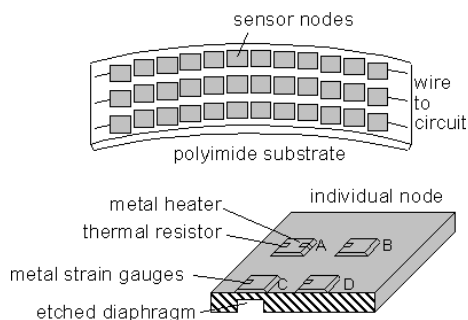


Figure 8. Schematic diagram of the polyimide multimodal tactile sensor.

with metal strain gauges for measuring surface roughness and contact force (elements C and D). The two membranes also work in tandem to provide measurement of the hardness without knowledge of the contact force. The finished sensor, shown in Figure 9, does not contain signal processing electronics at the current stage.

Element A consists of a micro patterned metallic resistive heater and a thermal resistor. Electric current supplied to the resistive heater causes ohmic heat generation, which is transferred to a nearby temperature sensor (made of Ni) by ther-

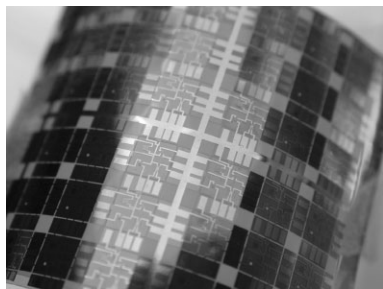


Figure 9. Optical micrograph of a patch of polyimide multimodal tactile sensing skin.

mal conduction via the substrate. The heat is sensed by the thermal resistor located 10–50 μm away. The steady-state read out of the thermal resistor is a function of the thermal conductivity of the object in contact, as it provides a parallel thermal conductive path.

Elements C and D use metallic strain gauge elements (NiCr) to detect strain developed in the polyimide substrate when the sensor is in contact with an object. The membranes for elements C and D are different. Since the two elements are very close, their contact force is approximately the same; however, amount of strain developed differs according to the membrane thickness. The thickness of membrane associated with element C is made smaller by oxygen plasma etching with a metal masking layer.

The sensor was able to identify objects by integrating multiple modalities of sensory input and perform texture classification,^[92] imitating the behavior of human sensing skin.

4. Opportunities and Challenges

There are significant challenges yet to be solved. Major concerns of polymer materials include temperature stability, performance shift over time, tolerance of high electric field, and chemical/environment stability.^[93] Many polymers also exhibit electric charging and low dielectric breakdown fields. For example, electrostatic actuators on polymers show hysteresis due to charging. For sensor applications, crosstalk is expected to be a primary issue. For example, resistors made of nanocomposite elastomers may incur resistance changes in the presence of changes of stress/strain, temperature, humidity, and chemical environment.

The thermal, mechanical and chemical properties of many polymers need to be carefully understood in the context of polymer MEMS in order for these materials to be used in broad commercial applications.

Technology for polymer MEMS processing needs to be further advanced to increase the appeal of polymer MEMS. These technologies in demand include large area processing (e.g., roll to roll process), heterogeneous polymer-semiconductor integration, and electronics packaging. It should be noted that polymer MEMS does not indicate the fact that the device is entirely made of polymers. In fact, heterogeneous integration of organic and inorganic materials is often necessary and desired. For example, it is often necessary to integrate signal conditioning and signal processing electronics directly with sensors. By integrating the circuits and sensory elements in close proximity, one reduces the noise and increases the detection threshold. For large area sensor skin, the ability to integrate electronics and sensors is indispensable to reduce lead routing complexity.

The number of polymer materials that have been incorporated into MEMS applications is still relatively small compared to the polymer materials available. Many polymer materials can potentially find applications in MEMS in the future. These candidates include conductive polymers,^[94,95]

electroactive polymers^[96] such as polypyrrole,^[97–99] photopatternable gelatin,^[100] shrinkable polystyrene film,^[101] shape memory polymers,^[102] and piezoelectric polymers such as polyvinylidene fluoride (PVDF).^[103,104] Future work will require close collaboration between experts in the following three areas: device, microfabrication, and materials.

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