Novel MEMS Devices Based on Conductive Polymers

by Seiichi Takamatsu and Toshihiro Itoh

Recently, conductive polymers have received considerable attention as a new material candidate for electronic devices[1-3] because they conduct electricity, while most plastics are dielectric. Since Nobel laureate Hideki Shirakawa and his colleagues invented polyacetylene in the 1970s,[4] the development of highly conductive polymers has accelerated for new polymer-based electronics. In the early developmental stages, these polymers had low conductivity and stability in a natural atmosphere with oxygen and moisture; however, recently organic conductive materials have reached conductivity levels >1000 S/cm which is the same as indium tin oxide (ITO).[3] Additionally, new chemically stable materials have been invented, such as polyaniline,[5] polypyrrole,[6] and polythiophene.[3] Due to the historically low conductivity levels, conductive polymers have been used for antistatic layers on TVs or photos, which do not require high conductivity levels. Currently, advanced applications, such as electrodes for a high functional capacitor, have been emerging.[3,7] In the near future, further applications, such as electrodes or sensing elements in highly functional devices or sensors, are expected. In addition to the basic electronic characteristics, improvements in mechanical flexibility have occurred. On the other hand, inorganic materials are typically brittle and can therefore be only used for applications involving mechanical rigidity.[8]

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)[3] is a conductive polymer in which electrons are removed with a dopant, and electricity flows according to the hole transportation phenomenon shown in Fig. 1a. Among the various highly conductive polymers, PEDOT:PSS is most promising because it has the highest conductivity (<100 ohm/sq) and environmental stability. Additionally, its transparency is as high (98% at a thickness of 100 nm) as that of a conventional transparent electrode such as ITO.[3,9]

There are several recent examples of conductive polymer applications for highly functional electronic devices. Conductive polymers have been used as the flexible polymer electrode on the piezoelectric organic polymer, polyvinylidene difluoride (PVDF).[10] The piezoelectric film with the conductive polymer acts as a speaker with transparency and flexibility. Similarly, conductive polymer electrodes have been studied as organic light emitting diodes (OLEDs) according to their transparency.[11] A strain sensor was developed with PEDOT:PSS according to the piezoelectric function, which involves changes in electric resistance with applied pressure.[12] Light transmissive display elements were also constructed based on the electrochromic function, which involves color changes from reversible electrochemical reactions.[13] Memory elements were also constructed based on reversible electrochemical reactions.[14] Due to these attractive features, conductive polymers are highly functional organic electronic devices.

By contrast, human–machine interface devices are in high demand because of the widespread use of personal mobile computers, tablet computers, and smart phones.[15] These portable devices require highly sophisticated sensors to detect human motions. For example, keyboards, touch screens, and motion-based games and sports controllers are embedded with these mobile information tools. These systems are comprised of microelectromechanical system (MEMS)-based sensors for pressure, acceleration, and gyroscopic sensing, which are highly functional and lightweight.[16,17] Several applications use these small MEMS devices. However, many other applications, such as keyboards and large area-sensing devices cannot use conventional MEMS devices, and therefore new MEMS devices are required. One of the device requirements for large-area specific applications is a device area with a width that is several tens of centimeters for a keyboard because human fingers are 2 cm wide, and widths greater than 20 cm are necessary for a keyboard to have 10 × 5 keys.[18] The other requirement is high flexibility to sustain human touch or shaking.[8] Because conventional MEMS devices are fabricated on a silicon wafer that is less than 30 cm wide,[15-17] new flexible and scalable materials should be used, and new processing technology should be developed for new MEMS devices.

Thus, to construct flexible large scale sensors for human machine interfaces, we have developed organic conductive polymer-based sensors. Development of the Bio Electromechanical Autonomous Nano Systems (BEANS) project was conducted under the supervision of the New Energy and Industrial Technology Development Organization (NEDO), where new types of hetero-functional integrated devices through innovative fabrication process are addressed.

To enable the development of conductive polymer-based MEMS devices, we have constructed a processing technology for a conductive polymer and demonstrated conductive-polymer-based human interface devices. First, we describe the microfabricated touch sensors, electrochromic pixel displays and biosensors that are fabricated with the MEMS fabrication process. These devices were constructed on centimeter-scale flexible plastic substrates. Second, for constructing the meter-scale large area devices, the fabric based touch sensors are fabricated with reel-to-reel

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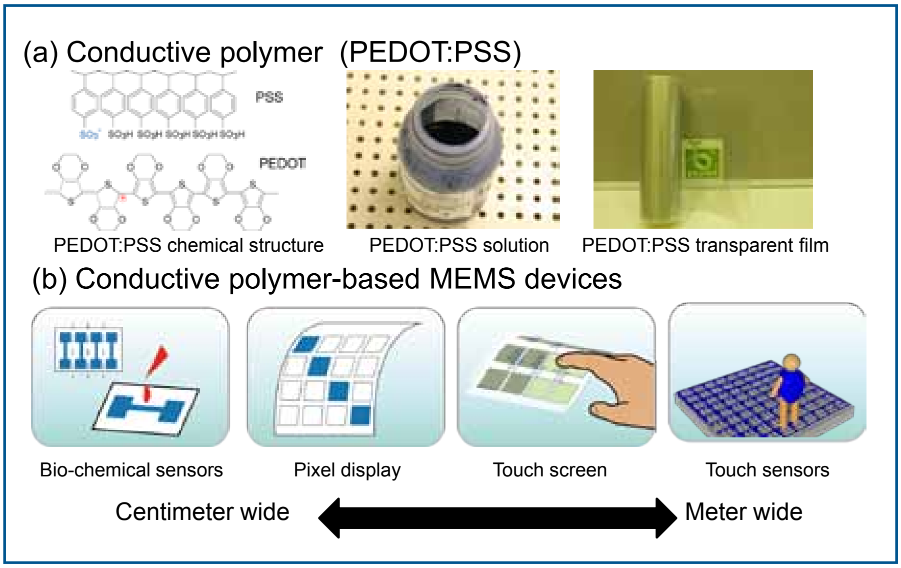

Fig.1. *Conductive polymer-based MEMS devices. Conductive polymer of PEDOT:PSS transfers holes for conduction. The PEDOT:PSS is coated with water-dispersion and the resultant film is transparent. The devices consist of bio-chemical sensors, pixel displays, touch screens, and large area touch sensors.*

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micro-processing of fibers. The resultant fibers are subsequently woven into sheets. We will present recent results from the conductive polymer-based devices from the BEANS project and possibilities for the new MEMS devices (ranging from centimeter- to meter-wide devices with high flexibility and functionality) that provide human motion sensing for information input and output at the nearest human contact point (Fig. 1b).

Flexible Conductive Polymer-based MEMS Devices on Plastic Films Constructed with the Parylene Peel-off Process

Flexible conductive-polymer-based sensors on the several centimeter scale plastic substrate, which has patterns that are hundreds of micrometer wide, are described in this section. While several micrometer scale electrodes are constructed in several millimeters of silicon wafer area with micromachining technology and are used as highly functional and reliable pressure and acceleration sensors for conventional silicon-based MEMS devices, several centimeter-square-area devices are required for display elements and touch screens, which are defined by the human finger, eyes, and other human body parts. To cover this large area and achieve flexibility, a relatively cheap and bendable conductive polymer is used as the main material for specific MEMS sensors for touch screens, display elements, and chemical sensors. This function has been achieved with flexible plastic substrates.

For a touch screen, which is a flexible application, a transparent strain sensor array with a conductive polymer (PEDOT:PSS) is proposed.[12] Because PEDOT:PSS is transparent and has a conductivity that changes with tension according to the piezoresistive effect, the display can be observed with highly sensitive PEDOT:PSS sensors. Additionally, because conductive polymers, including PEDOT:PSS and polyaniline, display the electrochromic phenomenon, which exhibits coloration from pale blue to dark blue at low electronic potentials (< 2 V), display elements have been developed.[13] However, this phenomenon is slow (the coloration duration is more than 1 s); therefore, its application is limited to electronic papers and sign boards, which operate at slow frequencies. Additionally, conductive polymers can be adapted for electrochemical transistors, which change their resistance by 10 to 100 times based on the electrochemical potential and the concentration of ions. Biochemical sensors are constructed with ion-based transducers.[19] A biochemical sensing mechanism is a unique feature of organic conductive polymer-based devices.

To develop these conductive polymer-based devices, a fabrication process with a conductive polymer micro-pattern must be addressed. The difficulties for forming the conductive polymer-patterned substrate are that the conductive polymer is not easily processed with conventional a microfabrication technique, *i.e.*, photolithography and etching, because the conductive polymer film is easily diluted with the water-based developer used in lithography and deteriorated by alcohols that remove the photoresist. Therefore, we have constructed a Parylene peel-off process, in which the dry lift-off layer of the patterned Parylene is used for defining the pattern of the conductive polymer.[20]

An example of the fabrication process for a conductive polymer based pattern that includes pixels and the wiring pattern is provided in Fig. 2a. In the fabrication process, the Parylene film is first deposited on the plastic substrate, and a negative pattern is formed on the Parylene with photolithography. After oxygen plasma etching, the negative Parylene pattern remains on the plastic substrate. Second, PEDOT:PSS water-dispersion is coated on the substrate and dried at 65 C°, which is the minimum Parylene glass transition temperature. If Parylene is heated to higher than the glass transition temperature, the Parylene sticks on the plastic substrate, resulting in mechanical lift-off failure. Finally, the Parylene is mechanically removed by peeling off the Parylene with the undesired part of the PEDOT:PSS film, as shown in Fig. 2a. The pixel and wiring pattern of PEDOT:PSS remains on the plastic substrate. Therefore, the conductive polymer can be patterned at the photolithography resolution and does not lose its conductivity in the drying process. Additionally, the patterning resolution of PEDOT:PSS was as low as 20 µm, while a 1 µm-wide pattern cannot be formed with this process (Fig. 2a). With the Parylene peel-off method, conductive polymer-based MEMS devices have been fabricated and characterized (Fig. 2b).

We developed the PEDOT:PSS-based strain-sensor array as a transparent touch screen, which is especially useful for flexible displays. The optical, mechanical, and electrical characteristics of the sensor sheet were evaluated and compared with an indium-tin-oxide (ITO) film. The light transmittance of the 130 nm-thick PEDOT:PSS film reached 92%, which is in the same range as that of the ITO with a thickness of 360 nm. The sensor sustained bending for 1,000 repetitions with a bending radius of 5 mm. As a strain sensor, the gauge factor was 5.2, which is higher than a conventional copper strain gauge. A touch input experiment was also performed. For this experiment, the sensor sheet was on a rubber base and was either placed on a flat surface or bent (20 mm bending radius) on a curved surface. The experimental results demonstrate that the sensor sheet can receive touch input information even when attached on a flexible display.

For the pixel display, the pixels and wiring are patterned with a PEDOT:PSS film, and the wiring area is covered with a Cytop insulation polymer, which is a fluorine resin. To assemble the pixel display, a polydimethylsiloxane (PDMS) rubber (Sylgard 184) composite was placed on

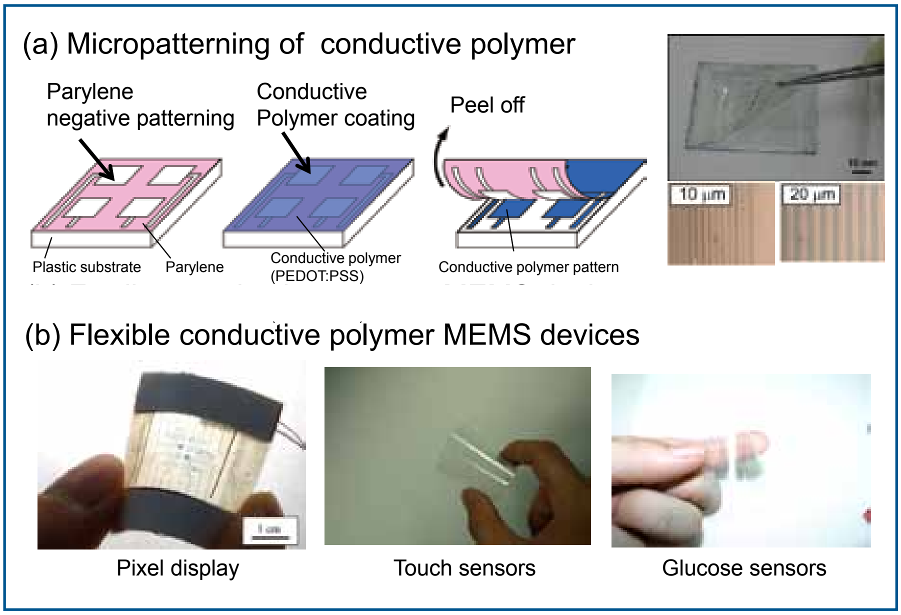

Fig. 2. *Micro patterning of conductive polymer and the resultant flexible devices. Conductive polymer is patterned with Parylene peel off method. The pixel display, transparent touch screen, and glucose sensor are fabricated.*

the plastic substrate with the patterned PEDOT:PSS and Cytop, and a 1 mM calcium chloride solution was poured in the well. An aluminum wire was placed in the solution. For the display demonstration, 1 V was applied to the wires connected to the pixels, resulting in the coloration. The picture in Fig. 2b presents the transverse display line.

Electrochemical glucose sensing is demonstrated in Ref. 19. The sensitivity of this sensor is 100 times higher than a conventional sensor, thereby allowing for the detection of low concentration glucose in saliva. This saliva-based sensor can easily sense glucose without causing pain, which occurs with conventional blood sampling.

Meter-Scale Conductive Polymer-based Fabric MEMS Devices Constructed with Reel-to-Reel Processing and Weaving

The previous section described portable human interface devices that are in the several-centimeter size scale. To expand the application of conductive polymer-based MEMS devices, we enlarge the device area. Certain applications, such as human position sensing, require meter-scale width sensors because human body parts are at the meter scale, while the conventional MEMS process is operated on wafers that are several inches in size (< 30 cm). For detecting human position with sensors, sensors that are 5-10 cm are required and it is also necessary to detect 10-20 times larger than this width, requiring a sensor that is more than 100 cm. Therefore, for detecting human position or other human motion, meter-scale sensors are essential. To achieve this sensor size, the most important task is the establishment of meter-scale fabrication processing. Existing MEMS fabrication tools can only create wafers that are less than 30 cm in width, due to the sputter and etcher processing tools.

To solve these device area problems, we have proposed a new manufacturing process that includes a continuous reel-to-reel nano/micromachining process for fiber substrates with organic electronic materials (Fig. 3a) and a large area integration process that weaves the resultant functional fiber substrates (Fig. 3b). These new machining tools have been developed under the NEDO BEANS project for exploring new MEMS fields.

For the development of meter-scale devices, we introduce the organic conductive polymer-based large area touch sensors in this feature article. The proposed sensors include an organic conductive PEDOT:PSS polymer and a UV-curable adhesive dielectric polymer that are coated on nylon fibers. These resultant fibers are woven. The sensors detect the induced capacitances between the fibers and human fingers. Because the surface capacitance detection method is used for smart phones and other portable systems for detecting human input from fingers, these capacitive sensors have been demonstrated to be suitable for commercial use. The sensor fabrication consists of a reel-to-reel coating process of the conductive and dielectric polymers with a die-coating and then weaving the resultant fibers.

The die-coating system consists of a winding machine that continuously transfers fibers, a die to coat the PEDOT:PSS and UV-adhesive, and a heater to dry the solvent, as shown in the Fig. 3a. The winding machine moves the fibers from left to right. To prevent the fibers from loosely hanging, they were transferred with a certain amount of tension using bobbins with pressure sensors. The machine was operational at speeds reaching 50 m/min. The machine in the middle of Fig. 3a contained dies and a heater or UV lamp for drying or curing. The dies consisted of reservoirs of PEDOT:PSS and UV adhesive and a nozzle for coating the fibers with these solutions. Because the dies surrounded the fibers with a gap, the wet film coated all surfaces of the fiber. A heater evaporated the solvent to dry the film, and a UV lamp was used for curing the UV adhesive. For the die-coating of the PEDOT:PSS, the film thickness was controlled from 53.5 to 338.4 nm by changing the gap between the fiber and dies from 17.5 to 97.5 µm. Larger gaps increase the thickness of the PEDOT:PSS film. The thickness of the UV adhesive also ranges from 5-40 µm. The traveling speed of the fibers during die-coating reached 50 m/min, which is fast enough for constructing long fibers for the fabric.

Next, the resultant long fiber (> 100 m) is woven with an automatic weaving machine, as shown in Fig. 3b. The width of the fabric is 1.2 m and the several meter sensors were continuously constructed by the machine. The required fabric length is easily obtained by cutting the fabric. The meter-scale sensor was woven, as shown in Fig. 3b.

The fabricated sensor consists of weft and warps, in which the PEDOT:PSS and UV adhesive are coated on the nylon fibers, as shown in Fig. 4a. Sensors detect the capacitance between the fiber and human finger, as shown in Fig. 4b. The large scale sensor system consists of sensor fabric, a capacitance meter in the conventional micro control unit (MCU) and a personal computer (PC) (Fig. 4c). Recently, the capacitance measurement circuit was embedded on the conventional MCU for the touch sensor for portable electronic devices, such as smart phones. For our experiment, capacitance measurement circuit in a MCU of Silicon Laboratories C8051F700 was used. The capacitance measurement pin was connected to the PEDOT:PSS electrode on the fibers by removing the UV curable adhesive and connecting the PEDOT:PSS layer with a conventional copper wire. The MCU measured the capacitance and transferred the data to the PC with a USB cable. Figure 4c shows the measured capacitance when the fiber was touched with a human finger, which changed from 34 pF to 36 pF. A capacitance change of 2 pF is conventional for the touch screens for cell phones and portable electronic devices. A keyboard with this touch sensor system is demonstrated in Fig. 4d.

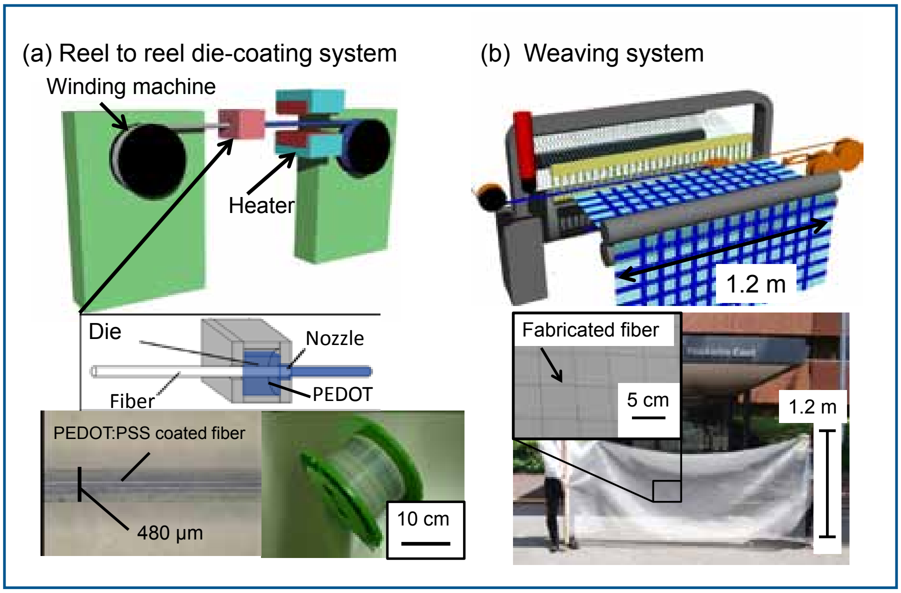

Fig. 3. *Reel-to-reel die-coating system and weaving system for the fabrication of large area touch sensors.*

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Conclusions

Flexible large-area conductive polymer-based MEMS devices were constructed. We first developed a Parylene peel-off process and subsequently used this process to fabricate touch sensors, electrochromic pixel displays, and biochemical sensors. Next, we demonstrated the feasibility of these human interface devices at the several-centimeter scale.

For the enlargement of conductive polymer-based MEMS devices, under the NEDO BEANS project, we developed a new manufacturing process that includes a continuous reel-to-reel die-coating process for fiber substrates with organic electronic materials and a large area integration system that weaves the resultant functional fiber substrates. We presented the developed meter-scale touch sensors and demonstrated them with keyboard input.

These conductive polymer-based MEMS devices will lead to flexible and large-area sensor applications for human information input and output.

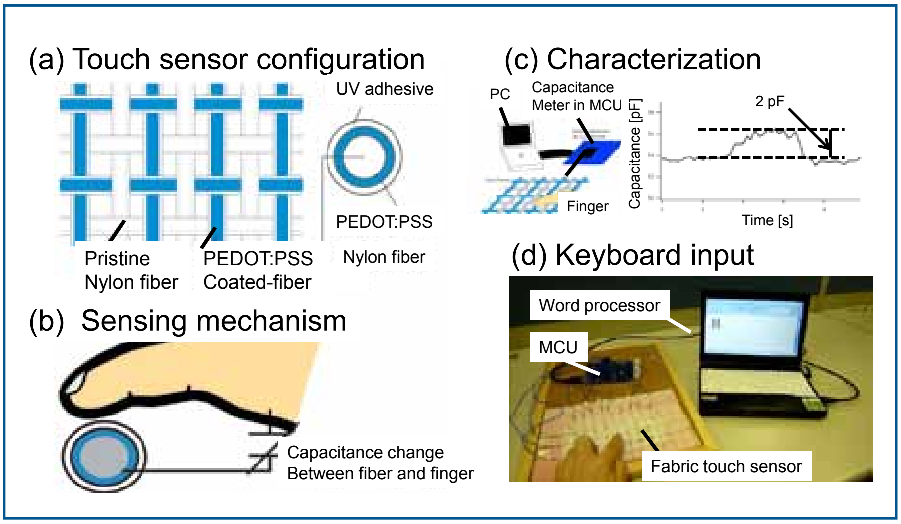

Fig. 4. *Meter-scale fabric touch sensors. Touch sensors consist of conductive polymer-coated fibers. Capacitance between fiber and human finger is measured for detecting human touch. The keyboard input is demonstrated.*

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