Published in final edited form as:

Adv Eng Mater. 2017 ; 19: . doi:10.1002/adem.201600592.

Flexible Thin-Film Electrodes on Porous Polyester Membranes for Wearable Sensors

Dr. Aveek Gangopadhyay,

Nanoscale Metrology Group, Engineering Physics Division, Physical Measurement Laboratory,
National Institute of Standards and Technology Gaithersburg, MD 20899, USA

Electrical and Computer Engineering Department, George Mason University Fairfax, VA 22030,
USA

Dr. Brian J. Nablo,

Nanoscale Metrology Group, Engineering Physics Division, Physical Measurement Laboratory,
National Institute of Standards and Technology Gaithersburg, MD 20899, USA

Dr. Mulpuri V. Rao,

Electrical and Computer Engineering Department, George Mason University Fairfax, VA 22030,
USA

Dr. Darwin R. Reyes*

Electrical and Computer Engineering Department, George Mason University Fairfax, VA 22030,
USA

Precision and personalized medicine intrinsically depends on the monitoring of biomarkers, and other physiologically relevant substances, that could shed light into the state of health of an individual. Wearable electronic devices are becoming more and more prevalent and a critical tool for real-time, continuous monitoring of body fluids containing biomarkers.^[1] For example, a recent study has shown that, specifically, eccrine gland sweat could provide metabolic information not previously thought possible.^[2] Therefore, measuring body fluids in real-time is highly valuable to monitor the health of a person. To this end, flexible thin-film electrodes deposited on polyester porous membranes are realized by using conventional photolithography. These flexible, gold electrodes show higher conductivities than their counter part on rigid substrates and demonstrated high conductivities when bent and twisted, demonstrating their potential use in the future as a component in wearable sensors for precision and personalized medicine applications and healthcare in general.

Latest advances in micro- and nanotechnology have made possible the proliferation of flexible electronic materials. Wearable sensors,^[1,3] foldable displays,^[4–6] flexible solar cells,^[7,8] and flexible electronic fibers^[9,10] are some of the major areas where flexible electronic technologies are of great interest. Flexible electronic devices must maintain their electrical and mechanical integrity when bent, twisted, folded, stretched, compressed, or deformed in any other way in order to demonstrate suitable performance. It is known that

* darwin.reyes@nist.gov.

electrical properties of thin films are influenced significantly by changes in mechanical loading conditions. Properties of thin films formed on flexible substrates have been reported, [11–13] but as new technologies and applications emerge, work on new materials is constantly required. Three types of substrates that are commonly considered for flexible applications are thin glass, metal foil, and polymers. However, metallic films formed on thin glass are brittle,^[14] while metal foils have limitations of withstanding multiple bending cycles.^[15] The flexible nature of polymeric substrates makes them of significant importance as a material for practical flexible electronics.^[16]

In this work, we compare the effect of stress (e.g., bending and twisting) on the conductivity of Au films deposited on thin films of the polyester poly(ethylene terephthalate) (PET), with and without pores, to assess their capabilities as a future component in wearable electronic devices. Both PET membranes (porous and non-porous) are approximately 11 μm thick. The porous membranes we used, contain pores with an average diameter of 1.2 μm at a density of 10^5cm^{-2} . We patterned 50 nm thick Au electrodes on the PET membranes by low temperature photolithography. The patterned membranes were subjected to different radii of curvature ($R=1\text{--}5$ mm) of convex bending with respect to the Au patterned side. We first compared the scanning electron microscopy (SEM) images of an Au electrode on PET membranes before (Figure 1a and c) and after (Figure 1b and d) mechanical loading. SEM image of porous PET/Au, with and without the thin film, is shown in Figure S1a (Supporting Information). Image of the transparent PET (without the thin film) is not clear due to reflection of light during SEM imaging. Bending the non-porous PET completely fractured the Au film, along the width of the electrode, thus, breaking its continuity (Figure 1c and d), which was confirmed by the complete loss of electrical conductivity. No further characterization was possible with the Au thin films deposited on the non-porous PET membrane. (An optical image of the complete fracture along the width of the electrode is shown in Figure S1b of the Supporting Information.) Bending the porous PET, however, did not result in catastrophic damage, but only generated small surface cracks (Figure 1b) that did not completely penetrate nor disrupt the continuity of the film. Having pores drastically reduces the tension in the PET membrane so that a hard, creasable polymeric film becomes readily foldable upon itself and conforms to objects. Therefore, the porous PET membrane becomes a sympathetic (compliant) substrate that increases the ability of the Au thin-film to withstand mechanical loading and high stress conditions while maintaining reliable electrical properties.

In order to measure electrical properties and reliability of this system, we assessed the conductivity of the Au film electrodes on the porous PET membrane as a function of bias voltage and frequency under various mechanical loading conditions. When flexible membranes are bent, twisted, or folded, the stress is translated to the thin-film it supports, which in turn affects the mobility of the electrons and extended line-defects on the surface of the Au films, and ultimately influences conductivity.^[17–20] Applied stress also affects grain boundary migration and coalescence, and the grain size, which is known to influence the mobile carriers within Au films.^[21–23] In general, the mobility decreases with increasing stress, which consequently decreases the conductivity of the Au film through the relationship in Equation 1

$$\sigma = nq\mu \quad (1)$$

where σ is conductivity of the film, n is the concentration of electrons, q is the charge of an electron, and μ is the mobility of electrons. The conductivity calculation is based upon the assumption of a uniform cross sectional area over the entire length of the Au film. However, the effective cross-sectional area may depend upon the defects in the Au film, such as the holes in the metal film propagated from the pores in the underlying substrate. The gap of the gold layer on the pore walls vary with the applied stress,^[16] and with bending of the PET membrane, cracks were formed on the surface. The combination of changing the inner pore-wall gap size and the formation of cracks may vary the effective cross-sectional area of the film. We believe the variation in the conductivity with stress to be a variation in the electron mobility^[23] due to the Au grain boundaries and defects, although the effective cross-sectional area could become a significant contributor at stresses greater than those investigated here.

Typically, we would expect increased conductivity in flexible electronic materials until stress causes the thin-film to fail (e.g., cracks, breaking). The influence of film stresses on the conductivity was determined by bending the PET membranes at different radii of curvature (1–5mm) in a convex or concave manner with respect to the Au film, while monitoring the impedance of the electrodes with a 10mV_{rms} AC signal swept from 0.01 to 60 kHz at varying DC bias voltages (Figure 2 and Figure S2, Supporting Information). The average conductivity of the Au was $4.5 \times 10^5 \text{ Sm}^{-1}$ in the absence of curvature. As the convex curvature stress was increased (Figure 2b), the average conductivity also increased to $4.8 \times 10^5 \text{ Sm}^{-1}$ at an $R=1\text{mm}$. With convex bending, we believe the shear stress stretched the top surface of the PET membrane, thus, reducing the transverse size of the pores on the PET, including those over which Au layer was deposited. This resulted in an increase in mobility of the electrons due to less interaction of the electrons with open pores in the electrode and, hence, an increase in its conductivity. Overall, the convex bending caused the conductivity to increase by 5–7%, with a slight decrease (<2%) with increasing DC bias (Figure 2c). We believe, joule heating is one of the reasons for the observed decrease in conductivity with increasing bias voltage, since this effect is commonly seen in many DC systems. Other factors that may also contribute to the decrease in conductivity at higher bias voltages are effects such as grain boundary migration and dislocation of bonds. On the other hand, when looking at the AC signal when sweeping from 0.01 to 60 kHz, at a fixed DC bias, we only observe a <1% change in conductivity. Therefore, we believe this shows that Joule heating has minimal or no effect on conductivity as an AC signal is swept. The convex bending was also cycled between flat and $R=1\text{mm}$ and analyzed at each R in order to assess the reproducibility and reliability of the Au film (Figure 2d). We observed a decrease of less than 4% in conductivity at later cycles.

The effect of stress from concave bending (Figure 2e), however, did not have the same trend as the convex bending, but rather resulted in a decreased conductivity for the Au film (Figure 2f) as the radius of curvature was decreasing. This is opposite to the trend observed during convex bending. At a 0.6V bias, the conductivity decreased by 14% from 4.6×10^5 to

$4.0 \times 10^5 \text{ Sm}^{-1}$ when the PET film is bent concavely to $R=1\text{mm}$. Reducing the DC bias increased the conductivity slightly due to less Joule heating (Figure 2g and Figure S3, Supporting Information). With concave bending of the electrodes, shear stress developed resulting in an increase in the depth of the pores. This geometrical increase in the dimension of the pores increases the size of the defects and dislocation of the Au electrode. We believe this decreased the mobility of the electrons in the Au thin-film and, hence, a decreased in conductivity was observed. Figure 2g shows the behavior of conductivity with an increase in bias voltages. The overall behavior in conductivity was found to be similar to the conductivity behavior observed when bent convexly (a small decline in conductivity with increased bias voltage). Repeated cycles of the concave bending (Figure 2h) resulted in a decreasing conductivity similar to convex bending with $<4\%$ of decrease in conductivity after five cycles.

We also investigated the effect on the conductivity as a function of planar rotation (or twist) along the length of the membrane, at various twisting angles (0° , 30° , 60° , and 90°) (Figure 3a). The electrical conductivity decreased with increasing planar rotation and increased with the bias voltage, which is similar to the results observed for the concave bending (Figure 3b). For a 0.6V bias, the conductivity decreased approx. 4% from 5.4×10^5 to $5.2 \times 10^5 \text{ S m}^{-1}$ when twisted from flat to 90° angle. Conductivity at other biased voltages was also measured (Figure S4, Supporting Information). The PET membrane experiences strain along the length of Au electrode when twisted. With increasing twist angles, the torque acting on the Au electrode increased, thus, increasing the size of defects on Au-film and decreasing the mobility of the electrons. An increase in DC bias is expected to decrease the conductivity in the same manner as previously described, due to Joule heating (Figure 3c). Performing multiple cycles of the planar rotation, gradually led to a minor decrease in the conductivity (Figure 3d). Unlike the concave and convex bending, the decrease in the conductivity was not uniform. After five cycles, the conductivity decrease was only approx. 0.5% at 0° , but approx. 5% at 45° and 90° . As the PET membrane was twisted, micro-cracks were formed in the electrode, and with each twist cycle these micro-cracks grew in size to some extent, introducing relatively small variations in the measured conductivity. Thus, due to the formation of micro-cracks with increasing number of twist-cycles, we observed a small change in the conductivity.

We compared the conductivity of Au electrodes on flat porous PET membrane with non-porous PET membrane and Ti/Au electrodes on rigid glass. Since, Au does not adhere to glass, a layer of 5 nm Ti is deposited prior to depositing the Au layer. We found that the conductivity on porous PET membrane/Au thin-film electrode was $>33\%$ greater than that of non-porous PET membrane and $>250\%$ greater than that of the Ti/Au on a glass substrate. The comparison with these two substrates illustrate the increase in conductivity of gold on the porous PET when compared to conventional rigid substrates requiring an adhesive layer (metal) for gold to stick on the substrate surface, and the difference when deposited without the need for such adhesive material (Figure S5, Supporting Information). Despite the bending and twisting stress imparted on the PET membrane/Au thin-film, their conductivities remained far greater than the Au thin-film on glass ($5.25 \times 10^5 \text{ Sm}^{-1}$ compared to $1.92 \times 10^5 \text{ Sm}^{-1}$, respectively).

In conclusion, we found that in non-porous PET membrane, the Au electrode breaks when it was bent to radius of curvature of 3mm or smaller. In contrast, porous PET membrane substrates can withstand harsh mechanical loading (radius of curvature down to 1mm and multiple bending cycles), while maintaining stable electrical properties and relatively large conductivities. When our flexible thin-film electronic system is compared with other published flexible electronic systems, we found that our conductivities are within the same range (10^3 to 10^4Scm^{-1}) as published by Kim et al.^[24] Also, the porous Au/PET membrane has shown conductivities of more than $4 \times 10^5 \text{Sm}^{-1}$, when flat as well as when it is subjected to mechanical loading (bending) and twist angles of up to 90° . We observed that our flat porous PET membrane/Au thin-film produces higher conductivities (>2.5 times) than the same design of 50 nm thin-film gold electrodes on glass substrate. The porous PET membrane device also shows robust conductivity behavior throughout the battery of tests that it was subjected to, showing overall changes of 7% or less. We believe that, in the future, this flexible electrode could be integrated in wearable devices, where it could produce similar robust results under bending and other type of conditions that wearable flexible electronic apparatuses are commonly exposed to.

1. Experimental Section

1.1. Fabrication of Au Electrodes

Porous and non-porous PET membranes were purchased from AR Brown-US.^[25] Standard photolithography and electron beam evaporation were performed in order to deposit 50nm Au electrodes on both types of PET membranes. We fabricated Au electrodes of the same geometry on glass substrates. After photolithography steps, we deposited 5nm titanium followed by 50nm Au layer on the glass substrate. A lift off step followed the Ti/Au deposition to finally obtain the pattern gold on PET. Since, Au does not adhere directly to glass (but adhere directly to PET), 5 nm of Ti was deposited as adhesion layer prior to the deposition of Au on the glass surface.

1.2. Conductivity Measurement

We used two-point probe method to measure the resistance of the Au electrode under different mechanical stress. We applied $10V_{\text{rms}}$ AC signal from 10Hz to 60 kHz and vary DC potentials from 0 to 0.6V (in step of 0.2). From the measured resistance, we calculated the conductivity of the Au electrodes. In our calculation, we assumed the geometric dimension of the Au electrode to be constant, which neglect the effect of any changes in the length, cross-section area of the Au electrode as well as of the porous.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors thank Asha Rani for assistance with SEM images. This work is performed in part at the NIST Centre for Nanoscale Science and Technology Nanofabrication Facility in Gaithersburg, MD, USA. Supporting Information is available online from the Wiley Online Library or from the author.

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Fig. 1. SEM images of an Au electrode on porous and non-porous PET membranes. (a) SEM image of porous membrane before mechanical loading (or bending) and (b) after multiple bendings. (c) Au on a non-porous PET membrane before mechanical loading, and (d) after multiple bendings (Scale bar=10 μ m).

Fig. 2.

Electrical behavior of thin-film Au electrodes under different mechanical loading. (a) Schematic of convex bending of Au electrode on PET. (b) Conductivity of convex bent electrodes as a function of frequency (DC bias = 0.6 V, 10mV_{rms} AC). (c) Conductivity of convex bent electrodes at different bias voltages measured at 1 kHz. (d) Conductivity of convex bent electrodes as a function of bending cycles (DC bias = 0 V; 1 kHz; 10mV_{rms} AC). (e) Schematic of concave bending of Au electrode on PET. (f) Conductivity of concave bent electrodes as a function of frequency (DC bias = 0.6 V, 10mV_{rms} AC). (g) Conductivity of

concave bent electrodes at different bias voltages measured at 1 kHz. (h) Conductivity of concave bent electrodes as a function of bending cycles (DC bias = 0V; 1 kHz; 10 mV_{rms} AC). The error bars are $<0.3 \text{ kSm}^{-1}$, which is within the size of the symbols. (■ Flat, ● 5 mm, ◆ 4 mm, ▲ 3 mm, ► 2 mm, ◄ 1 mm; solid on convex bending, hollow on concave bending) ■ PET Membrane, ■ Gold).

Fig. 3.

Au/PET electrode conductivity assessment under twist stress. (a) Schematic of a twisted thin-film Au electrode on PET. (b) Conductivity of twisted electrodes as a function of frequency (DC bias=0.6 V, 10mV_{rms} AC). (c) Conductivity of twisted electrodes at different bias voltages measured at 1 kHz. (d) Conductivity of twisted electrode as a function of number of angular cycles. (DC bias=0V; 1 kHz; 10mV_{rms} AC). The error bars are <0.1 kS m⁻¹ and are within the size of the symbols. (■ Flat, ● 30°, ◆ 60°, ◄ 90°, ■ PEI Membrane, ■ Gold).