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Highly stretchable wrinkled gold thin film wires

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With the growing prominence of wearable electronic technology, there is a need to improve the mechanical reliability of electronics for more demanding applications. Conductive wires represent a vital component present in all electronics. Unlike traditional planar and rigid electronics, these new wearable electrical components must conform to curvilinear surfaces, stretch with the body, and remain unobtrusive and low profile. In this paper, the piezoresistive response of shrink induced wrinkled gold thin films under strain demonstrates robust conductive performance in excess of 200% strain. Importantly, the wrinkled metallic thin films displayed negligible change in resistance of up to 100% strain. The wrinkled metallic wires exhibited consistent performance after repetitive strain. Importantly, these wrinkled thin films are inexpensive to fabricate and are compatible with roll to roll manufacturing processes. We propose that these wrinkled metal thin film wires are an attractive alternative to conventional wires for wearable applications.
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Rapid growth in the fields of flexible electronics and wearable technology has created a surge of research into new materials and component designs in an effort to create electronics better suited for the human body.[1–6] Therefore, there is a critical need to develop wires that can withstand repeated large strains and can be manufactured into discreet, low cost, and dense arrays. Unlike traditional electronics which are planar and rigid, these new electrical components must conform to curvilinear surfaces and stretch with the body. These components, especially for body-worn consumer and medical applications, must also endure frequent exposure to moisture as well as large strains while maintaining favorable electronic properties. Conductive wires that exhibit constant conductivity under high dynamic strains are of great interest.[5] Such a stretchable wire would find application in many wearable systems because they would be used to electronically interface multiple components. Additionally, stretchable conductive wires can provide mechanical isolation for rigid components worn on the body where there is not yet a stretchable substitute. Active areas of research for creating these wires can be categorized into developing new composite materials, liquid metals, and mechanical design optimization of metal thin films.

In developing stretchable wires, one of the active areas of research has been in developing new electronic materials that are able to withstand strains greater than that of metal thin films, which are known to have fracture limits of around 1% strain.[7] For example, Chun *et al.* have shown that by mixing a silver nanoparticle and multi-walled carbon nanotube composite (Ag-MWNT) with polyvinylidenefluoride (PVDF), they were able to develop an elastic conductor with conductivities of up to 5710 S cm^{-1} at 0% strain and 20 S cm^{-1} at 140% strain.[8] Lee *et al.* have developed a highly transparent graphene and silver nanowire hybrid structure with a sheet resistance of 33 Ω/sq that was able to withstand a tensile strain of up to 100%.[9]

In addition to these solid materials, liquid metals have also been used as stretchable wires. One advantage that liquid metals have over solid materials is that they are able to flow and withstand large deformations while maintaining high electrical conductivities. For this reason, there has been much interest in exploring liquid metals, particularly eutectic gallium-indium (EGaIn). By injecting EGaIn into elastomeric microfluidic channels, a stretchable wire that could withstand strains of up to 600% is achievable.[10] Although the electrical performance is good under high, dynamic strains, EGaIn remains relatively expensive and difficult to handle. Therefore, widespread adoption of this technology has been slow.

Aside from altering the material properties for stretchable wires, mechanical optimization of the geometrical design of heterogeneous metal-polymer systems has been intensely investigated for developing stretchable wires from traditional electronic materials. One of the earliest design strategies implemented when fabricating flexible electronics was the "wavy" buckled structure.[2,6,11] The strategy behind buckled structures is that they can be stretched out and reversibly buckled back to its original state with a linear elastic response to an applied force. By utilizing "wavy" buckled structures in silicon, researchers were able to achieve strains of up to 20 times more than the fracture limits of silicon.[11] Research has shown that the structural configuration of thin films influences its performance allowing them to be mounted onto non-planar surfaces.[2,12] In one study, an encapsulated metal thin film patterned into a serpentine structure was able to withstand strains of up to 120%.[13] Gutruf *et al.* demonstrated that it was

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possible to finely tune the piezoresistive response of a gold thin film by implementing optimized serpentine designs.[14] Utilizing the serpentine structure, Jahanshahi *et al*. was able to achieve up to 40% elongation with gold wires in polydimethylsiloxane (PDMS) with a corresponding resistance change of 60%.[15]

In this work, we introduce self-similar wrinkled micro- and nanofeatures in gold thin films for use as stretchable wires. We have previously demonstrated that metal thin films deposited on shape memory polymers (SMP) buckle and create hierarchical, self-similar wrinkled structures. The buckling occurs because of the stiffness mismatch between the SMP and the metal thin film during the shrinking process. These wrinkled thin films have shown greatly decreased effective resistivity, when compared with planar as-deposited thin films, and are similar to the intrinsic properties of bulk gold.[16] Here, we show that these wrinkled metallic thin films can be transferred from the rigid SMP carrier film into elastomeric silicone. The hierarchal self-similar wrinkled structures provide large amounts of strain relief allowing an excess of 200% strain.

SMP is a class of polymers that are able to dynamically change shape when induced with external stimuli. Pre-stressed polystyrene is a SMP that shrinks 67% in area when heated above its glass transition temperature.[17] Figure 1 shows the process flow for fabricating the wrinkled thin film wires. Polystyrene (PS, Grafix) was rinsed with ethanol followed by deionized water. A shadow mask (Frisket film, Grafix) pattern was drawn using CAD software (Autodesk, Inc., CA) and laser cut (VLS2.30, Universal Laser Systems, AZ) into desired pattern and placed on top of a PS substrate. Finer line width traces are readily achievable by patterning using finer physical shadow mask features or patterning with photolithography.[16]

Electron beam evaporation (E-BEAM, CHA MARK 50, CA) was then used to deposit a 25 nm Au thin film through the shadow mask. After removing the shadow mask, the substrate was heated to approximately 150 °C to induce biaxial shrinking and wrinkling in the Au thin film. The wrinkled Au film was then immersed in an adhesion promoter solution, 5 mM (3-mercaptopropyl) trimethoxysilane (95% MPTMS, Sigma-Aldrich, MO)(MPTMS) to silanate the Au surface. After treating with MPTMS, an elastomeric silicone (Ecoflex 0030, Smooth-On, PA) was cured on top of the metal film subsequently reacting with the silane layer on the Au surface. After curing, the Ecoflex was placed into an acetone bath (55 °C) followed by a toluene wash to remove any residual PS.

After heat induced biaxial shrinking, the final dimension of the wires was estimated to be 1 mm wide and 15.5 mm long. The wrinkled thin film was then transferred onto Ecoflex, a silicone elastomer that is able to withstand strains of up to 900%. The final dimensions measured after transferring onto Ecoflex were 949 μm $\pm$ 38.6 μm wide and 14.9 mm $\pm$ 0.528 mm long within 9 samples. The overall thickness, including the Ecoflex layer, of the wrinkled thin film wire was approximately 1 mm. Importantly, the silicone support substrate could be thinned to hundreds of microns by spin casting.

Figure 2 shows scanning electron microscope images of the Au film at various stages of the fabrication process. Figure 2(a) shows an electron beam deposited Au film on a PS substrate. The fidelity of the transfer process can be seen in Figure 2(c) in comparison with the non-transferred wrinkled Au film in Figure 2(b). The introduction of larger wrinkles can be explained by the slight swelling and shrinking of the Ecoflex polymer during the organic solvent liftoff of the PS during the transfer process.

The electrical properties of the thin metal film were established through measurements of the sheet resistance of the wrinkled Au films using the van der Pauw method.[18] Before shrinking, our initial sheet resistance value was 183 Ω/sq $\pm$24 for 25 nm of gold evaporated onto PS. Upon shrinking, our metallic wrinkled wires displayed a significant decrease in sheet resistance. The value decreased by a factor of 2.6 to become 70 Ω/sq $\pm$4. Our wires also demonstrated minimal increase in sheet resistance after transfer onto a soft silicone elastomer, 85 Ω/sq $\pm$3. The subsequent folds introduce a higher probability of contacting adjacent structures, thus resulting in lower sheet resistance.[16,19] Figure 2(d) shows the sheet resistance from unshrunken to transferred samples for our wrinkled thin film wires.

Resistance was measured under increasing tensile strain in order to determine strain sensitivity of the wrinkled metallic wires. The measurements were conducted on a custom-made automated tensile stretching apparatus, which is a linear actuator apparatus that converts the rotational motion of a stepper motor into linear motion via a leadscrew.

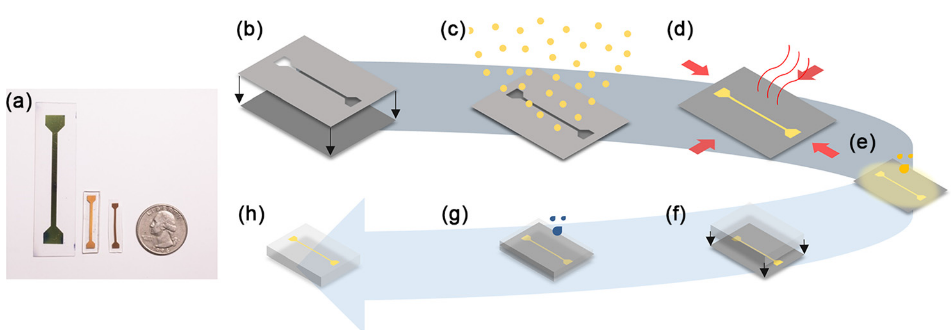

FIG. 1. Illustration of the fabrication of wrinkled thin film wires. (a) Image of the wire at various stages of the fabrication process: unshrunken, shrunken, and transferred from left to right (b) shadow mask is mounted onto PS substrate. (c) Electron beam deposition is used to deposit Au thin film. (d) After removing mask, PS substrate is heated to induce biaxial shrinking. (e) Substrate is treated with MTPMS adhesion promotor solution. (f) A silicone elastomer is cured on the PS substrate. (g) Organic solvent bath is used to lift-off the PS substrate. (h) Final wrinkled thin film wire.

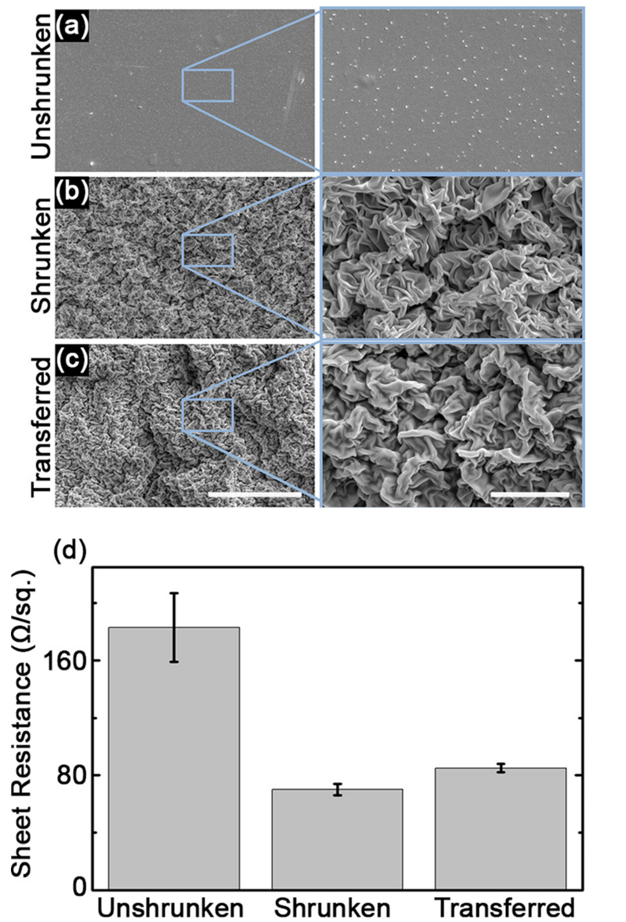

FIG. 2. Scanning electron microscopic images of the metallic wrinkled wires. (a) Au film deposited on PS substrate. (b) Shrunk wrinkled Au thin film on PS substrate. (c) Transferred wrinkled Au thin film on Ecoflex substrate. Left hand column scale bar is 30 μm and the insets are 5 μm. (d) Sheet resistance measurements of the unshrunken, shrunken, and transferred Au film.

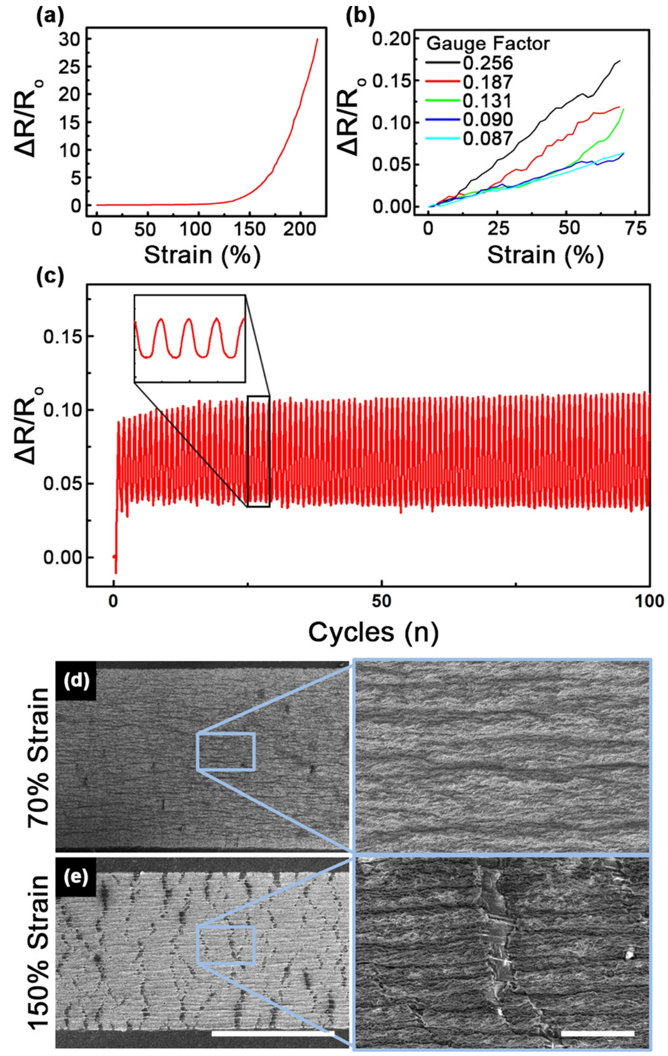

FIG. 3. (a) Metallic wrinkled wire strained to failure. (b) Calculated gauge factor of 5 different samples at approximately 70% strain. (c) Metallic wrinkled wire strained to 50% for 100 cycles. (d) Scanning electron microscope images of metallic wrinkled wire stretched to 70% and (e) 150% strain. Left hand column scale bar is 500 μm and the insets are 50 μm.

Samples were fixed to the apparatus at 0% strain and strained in a linear tensile fashion until failure. Figure 3(a) shows a plot of the strain-resistance behavior of the wrinkled thin film wires that were strained to failure in 0.3 mm increments. As seen in Figure 3(a), the metallic wrinkled wires were able to strain to a maximum of 200% with approximately 30% change in resistance at a 100% strain. Wrinkled wires show a significant improvement in withstanding large amounts of strain when compared to planar thin film wires which were only able to strain out to a maximum of 30% before failure as shown in supplementary Figure 1.[20]

Gauge factor is a measurement that defines the piezoresistive properties of a conductive film. The gauge factor represents the sensitivity of a metal film to mechanical strain and is measured by the normalized change in electrical resistance divided by the strain as shown by the following equation:

$$GF = \frac{\frac{\Delta R}{R_o}}{\varepsilon}, \quad (1)$$

where R_o, ΔR, and ε represent initial resistance, change in resistance, and strain, respectively. Therefore, materials with a high gauge factor are more sensitive to mechanical strain while the opposite is true for low gauge factor materials. Figure 3(b) lists the gauge factors of the wrinkled metallic wires at 70% strain. The gauge factor of the wires was as low as 0.087 showing very low sensitivity to strain. In comparison, other researchers have only been able to achieve a 22% change in resistance over 3% strain which is the equivalent of a 7.33 gauge factor.[14] Other researchers reported 10% change in resistance over 20% strain which is the equivalent of a 0.5 gauge factor.[21] However, the gauge factor of our wrinkled thin film wires increased sharply after 100% strain. This increase can be explained by the nucleation and elongation of fractures in the metal thin film, as expected of any thin film under high tensile strain.[15]

In addition to straining to failure, the mechanical robustness of the wrinkled thin film wire was tested. The metallic wrinkled wire was strained to 50% for 100 cycles as seen in Figure 3(c). In the first cycle, there was a large change in resistance. However, after several cycles, the variation in resistance between each cycle was stabilized. The large change in resistance in the first cycle is the conditioning phase in which the nucleation of nanofractures of the thin film wires occurs.[14] These nanofractures account for the initial increase

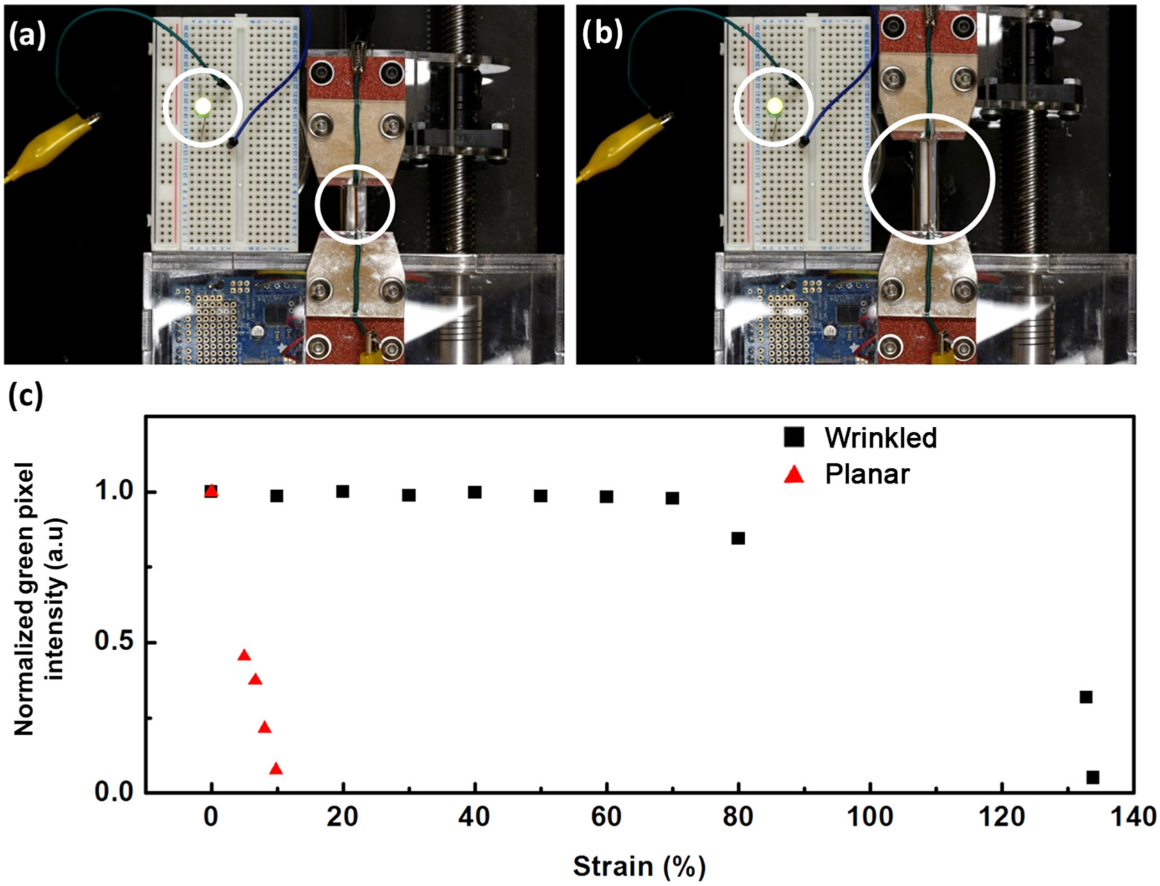

FIG. 4. (a) Top-down view of a metallic wrinkled wire at 0% and (b) 80% strain mounted to a custom made stretching apparatus and connected to a green LED. Circled is the green LED and metallic wrinkled wire. (c) Normalized pixel intensity plot of a metallic wrinkled wire and a planar wire.

in resistance when conditioned to a set dynamic strain. This can be seen by the stabilized change in resistance in the subsequent cycles and a marginally higher resistance at 0% strain when cycling is stopped (data not shown). The normalized change in electrical resistance over 100 cycles was approximately 7%. This corresponds well with Figure 3(b), which showed a resistance change of approximately 6% at 50% strain.

Supported by soft Ecoflex silicone elastomer, the wrinkles allowed the Au thin film to become more elastic compared with the planar thin film wire. As seen in Figure 3(d), the wrinkled Au film was able to withstand strains of up to 70% without any visible fracturing. This indicates that the wrinkling in the Au provides greater strain relief allowing the wrinkled thin film to strain further compared to its planar thin film counterpart. However, stretching out to 150% strain causes fracturing in the metallic film perpendicular to the tensile strain axis as seen in Figure 3(e).

To demonstrate that the metallic wrinkled wires can be used as electrical circuitry, the metallic wrinkled wire was connected to a green light emitting diode (LED) on a breadboard powered by a bench top power supply with limits set at 2.85 V and 0.020A. Images were taken under constant parameters to measure the output of the LED. To quantify the images, the Red Green Blue (RGB) values were calculated from a region of interest (ROI). The ROI was held constant in terms of size and location for both the metallic wrinkled and control (flat) wires. For analysis purposes, only the Green component of the RGB color model was measured. The summation of the green pixel intensity within the ROI was computed for each strain condition and compared to the zero-strain condition to determine relative change. This normalization accounted for intensity differences in ambient lighting conditions between the control and the wrinkled runs. As seen in Figure 4(c), the green LED pixel intensity did not diminish as the wire was strained up to 70%. Only after 80% does the green pixel intensity began to diminish, whereas the green pixel intensity in the control attenuated upon strain and diminished completely after 15% strain.

In conclusion, we have demonstrated a cost-effective method to fabricate flexible wrinkled metallic wires on stretchable substrates. We have shown that wrinkled metal thin films can be transferred onto soft stretchable substrates, while maintaining the self-similar micro- and nanostructures, and have improved sheet resistance over planar counterparts. While the sheet resistance demonstrated for the 25 nm gold thickness is still relatively high for some applications, other studies have shown that thicker wrinkled films (up to 200 nm) result in lower sheet resistances.[19] We have also shown that these wrinkled metallic structures provided a large amount of strain relief allowing otherwise brittle metallic films to stretch out to more than 200% with negligible changes in resistance of up to 100%. Even when compared to the more complex hybrid structures,[8] liquid metals,[10] and optimized geometries,[14] our simple wrinkled thin film wires are more robust to strain with significantly less change in resistance. Our fabrication methods are compatible with roll to roll manufacturing as previously demonstrated.[22] In combination with this scalable manufacturing platform, these wrinkled thin film wires have the potential to be very low-cost. Further optimization may be made to improve the performance of the metallic wrinkled wires. Some design changes including geometrical serpentine designs as well as encapsulation may further improve the range of tolerable strain. Because these wrinkled metallic wires are conformable, scalable, and low cost with a facile fabrication process, they are an attractive alternative to conventional wires for wearable technology.

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