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Biaxially stretchable silver nanowire transparent conductors

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Biaxially stretchable silver nanowire transparent conductors are demonstrated. The silver nanowire film retains its electrical conductivity up to 10% applied strain. We examine the factors limiting stretchability and compare the mechanics of biaxially and uniaxially stretchable systems, which will be useful for exploring biaxially stretchable systems in future. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4789795]

INTRODUCTION

Stretchable electronics integrates electronic devices on arbitrary substrates, eliminating the constraints of conventional stiff surfaces. The emergence of stretchable electronics has opened up vast opportunities in novel applications such as wearable electronics,1–3 conformable displays and sensors,4,5 artificial muscles,6,7 and electronic biointerfaces.8–10 Sophisticated prototypes such as epidermal electronics, which can monitor heart, brain, and skeletal muscles activities1 and stretchable light emitting diode display,4 have been demonstrated. An integral part of stretchable circuits is the stretchable conductor, which maintains its high electrical conductivity upon stretching.

Stretchable conductors based on thin metal films11–13 or metal nanoparticles14 have been widely studied. Thin metal films are deposited on a prestrained polymeric substrate. Buckled metal films are formed after the prestrain is released. The buckled structures provide stretchability as they “flatten out” when a tensile force is applied.12 Meanwhile, Ahn et al. have demonstrated stretchable microelectrodes based on carefully tailored silver nanoparticle inks.14 Besides metal films and metal nanoparticles, various groups have examined other stretchable conductors based on optically transparent materials such as carbon nanotubes (CNT),15–25 graphene,26,27 poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS),28,29 and metal nanowires.30–35 Being optically transparent, these stretchable conductors can potentially be used in niche applications such as transparent wearable electronics and stretchable displays.

CNT-based stretchable transparent conductors can be fabricated by embedding CNTs in elastic polymers15–23 or creating buckled CNT structures on an elastic substrate.24,25 The former approach is limited in success because a high loading of CNTs is required for high electrical conductivity, which increases the stiffness of the composite and decreases its stretchability. The transparency of the stretchable conductor is also compromised. Although the latter approach is capable of less than 5% increase in resistance when the sample is stretched by 100%,35 a high concentration of CNTs necessary for high electrical conductivity yields low optical transparency. Graphene26,27 and PEDOT:PSS28,29 films also face a similar challenge of attaining high electrical conductivity without compromising optical transparency.

A promising candidate for stretchable transparent conductor is one based on metal nanowires such as silver.30–36 Silver (Ag) nanowire films possess high electrical conductivity (9–70 \( \Omega \) sq) while maintaining high optical transparency (90–96%).30 Ag is also highly ductile.37–39 Lee et al. have demonstrated a uniaxially stretchable transparent electrode based on Ag nanowire film. The electrical conductivity of the stretchable transparent electrode remains constant up to an applied strain of 100%.30

Besides reports on uniaxially stretchable transparent conductors based on Ag nanowire films,30,36 there has been no study performed on biaxially stretchable nanowire films. Two dimensional stretchability is however desired for practical applications. This paper demonstrates exactly that. The factors limiting stretchability are examined and the mechanics of biaxially and uniaxially stretchable systems are also compared.

RESULTS AND DISCUSSION

1 wt. % of Ag nanowires dispersed in ethanol from Nanotron Corporation was used. The length and diameter of the Ag nanowires were 10–100 \( \mu \)m and 100 ± 20 nm, respectively. 2 mm thick PDMS substrates were prepared using Sylgard 184 Silicone Elastomer (Dow Corning) with a mixing ratio of 10 “base” to 1 “curing agent.” The mixture was thoroughly mixed in a vacuum mixer for 1 min to remove air bubbles before curing at 70 °C for 3 h. Figure 1(a) presents a schematic of the steps for creating two dimensionally stretchable Ag nanowire film. The PDMS was mechanically stretched by 10% in both planar axes on a stretch stage. A Ag nanowire film, which was prepared by collecting Ag nanowires on a Whatman Nanodisc membrane filter via vacuum filtration, was transferred from the membrane filter to the mechanically stretched PDMS, as shown in the digital camera image at the bottom of Figure 1(a). As adhesion of the nanowire film to PDMS is better than adhesion to the membrane filter, complete transfer can be consistently performed. When the mechanical prestrain was released, the Ag nanowire film buckled on the PDMS substrate. Parts (b) and (c) of Figure 1 provide close-up scanning electron microscopy (SEM) images of the biaxially stretchable Ag nanowire transparent conductor, which show that the Ag nanowires form buckled patterns on the substrate. The buckled patterns...
form because the nanowires with high aspect ratio (~3 orders of magnitude) are very flexible.\textsuperscript{40}

The optical transparency of such a stretchable transparent conductor was measured using a UV-visible-NIR spectrometer (Shimadzu UV-3101PC) and is demonstrated in Figure 1(d). The optical transmittance spectrum of a transparent conductor that uses 180 mg/m\textsuperscript{2} Ag nanowire film, with background subtraction to exclude the effect of substrate, shows a transmittance of >80\% between the wavelength of 400 and 1000 nm. The transmittance is very uniform in this range of wavelength. The inset in Figure 1(d) shows a camera image of the Ag nanowire transparent conductor. The sheet resistance of the transparent conductor that uses 180 mg/m\textsuperscript{2} Ag nanowire film was measured using Keithley 2612 A sourcemeters and found to be 14 ± 2 Ω/sq.

The sheet resistance and optical transparency of stretchable transparent conductors can be easily controlled by adjusting the density of Ag nanowires deposited on the PDMS. Supplementary Figure 1 compares the sheet resistance and optical transparency of two Ag nanowire films with different density.\textsuperscript{41} The film with a higher density of Ag nanowires (270 mg/m\textsuperscript{2}) has a lower sheet resistance but lower optical transparency than one with a lower density of Ag nanowires (180 mg/m\textsuperscript{2}).

Next, we examine the effect of prestrain on the stretchability of the Ag nanowire film. Figure 2(a) compares the normalized resistance (R/R\textsubscript{0}) of 180 mg/m\textsuperscript{2} biaxially stretchable, uniaxially stretchable, and unstrained Ag nanowire films with applied strain. R\textsubscript{0} and R are the resistances before and after stretching respectively. Prestrain in the stretchable films is 10\%. Strain is applied in the axis parallel to the prestrain in the uniaxially stretchable Ag nanowire film (named x-axis). Figure 2(b) shows a similar set of comparison except that the strain is applied in the axis perpendicular to the prestrain in the uniaxially stretchable Ag nanowire film (named y-axis).

The Ag nanowire film that is transferred to an unstrained PDMS does not display good stretchability. When a 3\% and 5\% strain are applied, the normalized resistances increase to 1.2 and 1.4, respectively. This is observed regardless of whether the strain is applied in the x- or y-axis. It is in stark contrast to the films that are transferred to prestrained PDMS. When 3\%, 5\%, 8\%, and 10\% strain are applied to the film that is transferred to a uniaxially prestrained PDMS in the axis parallel to the prestrain, the normalized resistances are 1, 1, 1.1, and 1.3, respectively. Resistance remains unchanged up to an applied strain of 5\% as the buckled Ag nanowires “flatten out” with strain. However, when the applied strain is 10\% (similar to the prestrain), an increase in resistance is observed. This can be attributed to an increase in junction resistance between the nanowires as they slide and no longer form good contacts between themselves.\textsuperscript{42} When 3\% and 5\% strain are applied to the film that is transferred to a uniaxially prestrained PDMS in the axis perpendicular to the prestrain, the normalized resistances are 1.2 and 1.5, respectively. The normalized resistances observed are similar to those observed for the film that is transferred to unstrained PDMS. This is expected as stretchability should only be observed in the axis parallel to the prestrain.

Stretchability is observed in both axes of a plane when a Ag nanowire film transferred to a biaxially prestrained PDMS is stretched. In both axes, the resistance remains constant after a 5\% strain is applied. Increase in resistance is observed only beyond 5\% applied strain, similar to the case when a film, transferred to a uniaxially prestrained PDMS, is stretched in the axis parallel to the prestrain. Hence, we have demonstrated two dimensionally stretchable Ag nanowire films, which are both highly transparent and electrically conductive.

In all cases, the electrical resistance of these films is recovered when the applied strain is released. In other words, no permanent deformation results from the applied strain and a continuous conducting nanowire network remains. We also investigate the stability of the electrical resistance of the
biaxially stretchable film after 50 stretching cycles. The electrical resistance remains unchanged up to 50 cycles of 10% applied strain, as shown in Figure 2(c).

The stretchability observed in our films is lower than that reported by Lee et al.\textsuperscript{30} This can be attributed to the higher prestrain they applied to the PDMS and the longer lengths of Ag nanowires they used (over 500 μm). The lengths of Ag nanowires used in our study range from 10 to 100 μm. Effect of length of Ag nanowires on stretchability of film can be explained using percolation theory. The critical number density of nanowires ($N_c$), of a given length ($L$), required for percolation in the nanowire film is given by $N_c L^2 = 5.71$.\textsuperscript{43} Hence, a higher critical density for percolation is required for shorter nanowires. The relationship between the sheet conductance of the nanowire film ($\sigma$) and the number density (N) and critical number density of nanowires ($N_c$) can be expressed as $\sigma \propto (N - N_c)^t$,\textsuperscript{43} where t is the conductivity exponent. Hence, a film with short nanowires with high critical number density requires a high density of nanowires for a given electrical conductance. The stretchability decreases when the nanowire density is increased because a film becomes less flexible as its thickness increases.\textsuperscript{44} This explains partially why the observed stretchability of our film (with a shorter average nanowire length) is lower than that reported in Ref. 30.

Another factor that plays an important role in the stretchability of the film is the prestrain applied to the PDMS substrate. In Figure 3, we compare the stretchability of two films transferred to PDMS substrates with different amount of prestrain applied. The film transferred to 20% prestrained PDMS shows higher stretchability than the one transferred to 10% prestrained PDMS. An obvious way to improve the stretchability will be to increase the prestrain applied to PDMS substrate. However, biaxial stretching/prestrain is more challenging than uniaxial stretching/prestrain as shown in Supplementary Figure 2.\textsuperscript{41} The PDMS substrate can be easily stretched up to 20% uniaxially. However, when 20% strain is approached biaxially, the stress built up is so high that the stretch stage fails to hold on to the PDMS, as shown in Supplementary Figure 2(d).\textsuperscript{41}

This can be easily understood when we compare the normal stresses built up during uniaxial stretching compared to biaxial stretching. The normal stress in a uniaxially stretched sample is expressed as\textsuperscript{45}

$$\sigma_1 = E \varepsilon_1,$$

$$\sigma_2 = 0,$$

where $\sigma_1$ and $\varepsilon_1$ is the stress and strain along the uniaxial stretch axis, respectively, and $E$ is the Young’s modulus. $\sigma_2$
is the stress perpendicular to the uniaxial stretch axis. In the case of biaxially stretched sample, it is

\[
\sigma_1 = \frac{E(e_1 + \nu e_2)}{1 - \nu^2}, \\
\sigma_2 = \frac{E(e_2 + \nu e_1)}{1 - \nu^2},
\]

where \(\sigma_1\) and \(\sigma_2\) are the stresses in 2 perpendicular axes, \(e_1\) and \(e_2\) are the corresponding strains in the 2 perpendicular axes. \(E\) and \(\nu\) are the Young’s modulus and Poisson’s ratio of the sample material. In our case, we have stretched the sample in both perpendicular axes by the same amount: \(\varepsilon = e_1 = e_2\). Hence, the stress in the biaxially stretched sample can be expressed as

\[
\sigma_1 = \sigma_2 = \frac{E\varepsilon(1 + \nu)}{1 - \nu^2}.
\]

The Poisson’s ratio of PDMS is \(\sim 0.5\). Hence, the maximum normal stresses are \(\sigma_1 = \sigma_2 = 2E\varepsilon\). Thus, the stress developed in a biaxially stretched sample is two times that of a uniaxially stretched sample. Hence, it is intrinsically more challenging to fabricate biaxially prestrained samples compared to uniaxially prestrained samples.

Nonetheless, an improved stage design would yield higher prestrains and better stretchability in our biaxially stretchable samples in future. It is important to note that the home-made stage has been designed to stretch a sample in two perpendicular axes by clamping the four sides of the square shaped sample and then stretching it. When the sample is stretched in both axes, only the square area of the sample that was initially surrounded by the stage clamps before stretching will be truly stretched in two axes. The area outside of it is not stretched completely in both axes. This is evident in parts (c) and (d) of Supplementary Figure 2.

Finally, we also test the viability of the stretchable Ag nanowire film as a stretchable transparent conductor by integrating the film into a LED circuit. Figure 4 shows camera images of an illuminated LED, which circuit is completed by a Ag nanowire film. When the film is bent to a large degree or twisted, the LED remains illuminated, manifesting the flexibility/stretchability of the transparent conductor.

The demonstrated stretchable Ag nanowire film has displayed promising properties. Nonetheless, more study on the adhesion of the Ag nanowire film to PDMS is essential as a scotch tape can easily remove the film from the PDMS substrate. Further investigation is underway to study means to improve the adhesion between the nanowire film and PDMS.

CONCLUSION

We demonstrate biaxially stretchable transparent conductor that uses silver nanowire films. Buckled silver nanowire films are formed after transfer onto a biaxially prestrained polydimethylsiloxane (PDMS) substrate. The buckled film “flattens out” when the sample is stretched. Hence, the silver nanowire film retains its superior electrical conductivity up to 10% applied strain. Longer nanowires and a larger magnitude of prestrain can potentially increase the stretchability of the transparent conductor. However, mechanical studies of uniaxially and biaxially stretchable systems show that it is intrinsically more challenging to prestrain a biaxially stretched system compared to a uniaxially stretched one. Such insights will be helpful in future development of biaxially stretchable transparent conductors.

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41See supplementary material at http://dx.doi.org/10.1063/1.4789795 for figures of Ag nanowire films and stretched substrates.