Elastomer-Infiltrated Vertically Aligned Carbon Nanotube Film-Based Wavy-Configured Stretchable Conductors

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Supporting Information

ABSTRACT: Elastomer-infiltrated vertically aligned carbon nanotube (VACNT) forests are good candidates for use as stretchable conductors that can retain the electrical properties under relatively large stretching. The electrical performance can be further enhanced in terms of high stretchability and small change in the electrical resistance by using a wavy configuration. In this work, we present a wavy-structured high-performance stretchable conductor prepared by a simple prestraining approach based on polydimethylsiloxane (PDMS)-infiltrated VACNT films. Prior to the infiltration process, the VACNT forests can also be easily micropatterned by a PDMS stamp-assisted contact transfer printing technique. The conductive VACNT forest patterns are fully infiltrated with highly elastic PDMS, and the PDMS/VACNT film is conformal and strongly bonded to the prestrained PDMS substrate with the help of an intermediate thin PDMS layer, resulting in mechanical robustness of the whole device. The fabricated wavy VACNT conductor shows a small resistance change ratio of less than 6% with a tensile strain of up to 100% (prestrained level) and a high reversibility under multiple stretching/releasing cycles with a maximum strain of 100%.

KEYWORDS: vertically aligned carbon nanotube film, contact transfer printing, elastomer infiltration, prestraining, wavy stretchable conductor

1. INTRODUCTION

Recently, stretchable conductors that can retain electrical performance under large elastic deformations have been needed for the realization of stretchable electronic systems, including stretchable circuits, artificial smart skins, and skin-like soft sensors.1−8 Many different concepts of stretchable conductors have been developed by employing a wide range of fabrication techniques.9−11 Of the various attempts, prestraining methods have received considerable attention in recent years due to the simplicity of fabrication and the straightforward working principle of the resultant stretchable conductors. In this strategy, electrically conducting thin films or ribbons are first formed on a prestrained elastomeric substrate, followed by subsequent release of tensile force applied to the substrate, resulting in a spontaneous formation of wavy-configured or buckled structures. This simple method can open new possibilities for creating high-performance stretchable conductors. First, the wavy geometries make it possible for inherently non-stretchable materials to be employed as electrodes and interconnects that can withstand stretching without appreciable degradation in electrical performance.12−16 Second, the electrical performance of stretchable conductors with wavy geometries can be enhanced significantly at a similar level of stretching, as compared to flat platforms.17−22

During stretching, the wavelength of the wavy-structured conductors is increased while the amplitude is decreased, leading to minimal change in the electrical resistance. To date, wavy or buckled stretchable conductors have been developed by two main strategies: (1) the direct deposition of conducting materials12−17 and (2) layer transfer of conducting films.18−23 In the deposition approaches, conducting materials are formed by directly depositing them onto the prestrained elastomeric substrates by various deposition techniques including electrodeposition,12 metal electroless deposition,13 vacuum evaporation,14,15 inkjet printing,16 and dip coating.17 In the transfer approaches, wavy or buckled structures are formed by releasing the prestrained substrates with upper layers of conducting thin films such as patterned silicon films,18 silver nanowire (AgNW) networks,19,20 carbon nanotube (CNT) macrofilms,21 CNT ribbons,22 and CNT fibers23 after transferring them. In particular, Lee and co-workers have clearly showed the usefulness of the prestraining approach for the fabrication of high-performance stretchable conductors by demonstrating very long AgNW percolation network electrodes ensuring low

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sheet resistance even under extremely high strain above 460%. However, some critical issues in terms of device performance and stability can arise from the conventional prestraining approaches. In some cases, the preparation of conducting layers is quite cumbersome or time-consuming, resulting in fabrication complexity. In addition, most wavy stretchable conductors based on metallic thin films may suffer from crack formation in the direction perpendicular to the prestraining direction due to the Poisson effect. In several approaches, weak adhesion between the conducting layers and elastomeric substrates would be one of the most serious problems in their practical use. In particular, it has been reported that metallic layers suffer from poor adhesion to polydimethylsiloxane (PDMS) due to weak interaction between them.

Here, we report an efficient way of demonstrating highly reliable wavy stretchable conductors based on elastic polymer-infiltrated vertically aligned carbon nanotube (VACNT) films. In the present work, the VACNT forests were employed as conducting materials mainly due to the two advantageous aspects as follows: (1) VACNT forests can be easily patterned by a facile PDMS stamp-assisted contact transfer printing technique, and (2) unique architectures of conductive CNTs interconnected three-dimensionally in the forests can retain the electrical performance under stretching deformations. The conductive elastomeric films were prepared by simply infiltrating liquid PDMS into micropatterned VACNT forests and transferred onto prestrained PDMS substrate with an adhesive PDMS intermediate layer. This simple method makes it possible to fabricate crack-free wavy stretchable conductors while ensuring mechanical robustness and strong bonding with the substrate. The resultant wavy stretchable conductor shows excellent electrical performance with small resistance change as low as 6% with the application of 100% tensile strain while ensuring good reversibility.

2. EXPERIMENTAL DETAILS

Synthesis of VACNT Forest. VACNT forests were synthesized using a thermal chemical vapor deposition (CVD) process. In general, the three steps are known as a CNT growth mechanism. At first, the hydrocarbon gas is decomposed under hot temperature, and a carbon atom is diffused through the bulk and surface of the catalytic island. Finally, the carbon atoms are deposited between the catalytic island and the diffusion barrier. Because the carbon nanotubes are supporting each other by van der Waals attraction called the crowding effect, the VACNTs from being damaged due to a sudden change in temperature. With these process conditions, the height of the VACNT forests was determined by controlling the growth time.

Fabrication of VACNT-Based Wavy Stretchable Conductors. The proposed VACNT-based wavy stretchable conductors were fabricated by a prestraining method based on PDMS-infiltrated VACNT film (PDMS/VACNT film). First, the prepared VACNT forest was patterned by a PDMS stamp-assisted contact transfer printing technique. For this, a PDMS stamp was first prepared by a soft-lithography process. In detail, a ~70-μm-thick negative-tone photomask (PR, JSR-THB-151N) mold was patterned by a standard photolithography process. After that, a liquid PDMS solution mixed with a curing agent at a weight ratio of 20:1 was poured onto the polymeric mold and slightly cured in a convection oven at 70 °C for ~20 min by just imposing shorter curing time as compared to that of complete curing (1 h in the present work) while maintaining the same other conditions such as a curing temperature and a mixing ratio of the base polymer and curing agent. This soft curing step is greatly helpful for the site-selective removal of unnecessary portions of VACNT forest by making the surface of the PDMS stamp more sticky.

The PDMS stamp was then brought into slight contact with the prepared VACNT forest facing the ~70-μm-thick protruding parts of the PDMS stamp toward the VACNTs. After removing unnecessary VACNT portions with the PDMS stamp, a VACNT strip pattern was defined on the catalyst-deposited silicon substrate. The strip-patterned VACNTs were then infiltrated with liquid PDMS (with a mixing ratio of the base polymer to the curing agent of 20:1 by weight) to fabricate a conductive elastomeric film. The liquid PDMS solution was diluted with volatile toluene at a weight ratio of 10:1 to facilitate conformal permeation into the VACNTs by decreasing viscosity.

Thin PDMS/VACNT film was finally prepared by peeling from the silicon substrate after heat treatment at 70 °C for 1 h to fully evaporate the solvent components and solidify the PDMS at the same time. In particular, the patterned VACNT forests were entirely transferred to the PDMS films without any remaining residues on the catalyst-deposited substrates even on several times trials, indicating fairly good process repeatability. The prepared PDMS/VACNT film was then bonded to a prestrained (100%) PDMS substrate with an initial thickness of ~1 mm after aligning along the prestrained direction. The PDMS/VACNT film was maintained for the conductive side (VACNT forest side) to be exposed for electrical connections. Prior to bonding between the PDMS/VACNT film and PDMS substrate, thin liquid PDMS (mixing ratio of 20:1) was spin-coated onto the prestrained PDMS substrate to ensure strong and conformal interfacial bonding between the two plates. The assembled sample was then fully cured at 70 °C for 1 h. After the prestrained PDMS substrate was released, periodic wavy structures were spontaneously formed due to the different mechanical properties of the two plates. For comparison, a VACNT stretchable conductor without wavy geometries (flat VACNT conductor) was also prepared through the aforementioned fabrication procedures except that the prestrain was not imposed on the PDMS substrate.

Characterization. The VACNTs and wavy stretchable conductors were examined using field-emission scanning electron microscopy (FESEM; S4700, Hitachi) and optical microscopy (BX60M, Olympus). Up to 10 tape tests were performed on the fabricated VACNT stretchable conductor to evaluate its mechanical robustness by monitoring the change in the electrical resistance by a two-probe technique with a digital multimeter (U1253, Agilent Technologies) capable of measuring the electrical resistance of up to 500 MΩ with an accuracy of ±3%. The electrical performance of the fabricated VACNT stretchable conductors was evaluated by measuring the resistance changes with the application of tensile strain of up to 100% after electrically wiring with silver paste. The experimental setup for electrical characterizations of the devices with application of tensile strain is shown in Figure S1 (see the Supporting Information). The tensile strain was applied to the VACNT stretchable conductors using an automatic test stand (JSV-H1000, JISC) equipped with a push–pull force gauge (H-10, JISC). The electrical resistance in response to the applied tensile strains was measured and recorded in real time using a digital multimeter interfaced with a computer through an RS-232 data cable.
3. RESULTS AND DISCUSSION

Figure 1a shows a digital image of the VACNT forests grown on a 4-in. wafer by the stabilized thermal CVD process. The image clearly demonstrates the potential for large-scale production for VACNT-based applications. The height and sheet resistance of the as-grown VACNT forests were $\sim 25 \mu m$ and $\sim 554 \Omega/\square$, respectively. A cross-sectional SEM image of the synthesized VACNT forest is shown in Figure 1b, which shows the unique architecture with three-dimensionally interconnected CNTs. The densely entangled morphology of the conductive CNTs in the forest enables them to be employed as robust stretchable conductors after infiltrating highly elastic polymer.

The fabrication process of the VACNT stretchable conductors with wavy structures is illustrated schematically in Figure 2. It was found that the sheet resistance of the patterned VACNT forest was maintained with a minor change of $\sim 3.9\%$ even after infiltrating PDMS. This suggests that the vertically aligned morphology of the CNTs in the PDMS/VACNT film is fairly kept even after experiencing the process. The wavy-configured conductors can be easily fabricated by bonding patternable PDMS/VACNT films to prestrained PDMS substrates with a thin layer of uncured PDMS. In particular, the use of a thin intermediate PDMS layer can prevent the PDMS/VACNT film from slipping or exfoliating, resulting in mechanical robustness. The PDMS stamp-assisted contact transfer printing is highly desirable for the preparation of PDMS/VACNT films with various shapes of the VACNT patterns in a simple and precise manner.

In addition to superior electrical performance, good adhesion between the conducting layers and elastomeric substrates is also one of the strongest requirements for practical stretchable electronics. To investigate the mechanical stability, tape tests have been performed on the fabricated flat VACNT stretchable conductor. Figure 3 shows the normalized electrical resistance due to the mechanical tape tests. The electrical resistance of the device was almost retained with a small deviation as low as 1.5% with respect to the initial state, even after 10 tests. In addition, the inset in Figure 3 clearly suggests that the CNTs were not peeled off by the tape test. This mechanically stable behavior mainly originated from the fact that the VACNTs were completely embedded in the PDMS slab while only revealing their conducting ends. Moreover, this allows the VACNT
stretchable conductors to be stably operated without any top protection layers.

Figure 4a shows the surface morphology of the wavy VACNT stretchable conductor prepared on a 100% prestrained PDMS substrate, which represents that uniform, periodic wavy structures were formed by the compressive force induced upon releasing the PDMS substrate. The wavy structures of the VACNT conductor were further validated by the cross-sectional SEM image shown in Figure 4b. The SEM image showed that the PDMS/VACNT film was well established on top of the device along the wavy patterns and firmly integrated on the PDMS substrate without any structural uncertainty such as delamination and voids thanks to the PDMS bonding layer between the conducting film and substrate. Although the wavy patterns with a wavelength of \( \sim 220 \mu m \) and an amplitude of \( \sim 65 \mu m \) were achieved by imposing 100% prestrain in the present study, one can easily expect that the wavelength and amplitude of the waves and resultant electrical performance can also be easily controlled by changing the amount of prestrain and dimensions of the devices.$$^{20,26}$$

Figure 4c shows the top-view optical microscopy images of the fabricated wavy VACNT stretchable conductor under various strain levels of up to 100%, implying a key operational principle of the devices. With increasing tensile strain applied to the conductor along the prestrained direction, the wavelength of the wavy patterns was gradually increased with the applied strain levels. When 100% strain was reached, the wavy-structured surface mostly flattened out, as shown in Figure 4c. The stretched conductor fully returned to its original configuration with wavy geometries without any irreversible structural deformations when the tensile force was entirely removed.

Figure 5a shows the resistance change ratio \( (\Delta R/R_0) \) of the wavy VACNT stretchable conductor as a function of the applied tensile strains of up to 100% with a constant loading speed of 2 mm/min, where \( R_0 \) is the initial resistance of the conductor in an unstretched state after some preconditioning cycles. The sheet resistance of the tested wavy VACNT conductor was \( \sim 650 \Omega/\square \) in the initial unstrained state. For comparison, the resistance changes of the flat VACNT conductor are also plotted in Figure 5a. For the flat VACNT conductor, it can be seen that the resistance was increased in response to the increased tensile strain, indicating a maximum resistance change ratio of \( \sim 43\% \) for up to 100% strain.

The conducting CNTs in the PDMS matrix are three-dimensionally interconnected to each other with many contact junctions that facilitate the conduction of electrons. The CNTs in the PDMS matrix can slide across one another while

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**Figure 3.** Normalized electrical resistance of the fabricated VACNT conductor as a function of the number of tape test (inset: digital image of the VACNT conductor when taking off the tape).

**Figure 4.** Fabrication results of the wavy VACNT stretchable conductor. (a) Top-view optical microscopy image, (b) cross-sectional SEM image (the back of the PDMS/VACNT film is a carbon tape for mounting samples; inset: magnified SEM image of PDMS/VACNT part in the film), and (c) top-view images with application of different tensile strains of up to 100%.
maintaining electrical contacts up to certain levels of tensile strains.8,27 However, the application of higher tensile strain would give rise to the loss of several contact junctions by locally separating the entangled CNTs, leading to an increase in electrical resistance of the flat VACNT conductor. In contrast to the flat conductor, the wavy VACNT conductor exhibited much smaller resistance changes of less than 6% for up to 100% strain, as shown in Figure 5a. This significant improvement of the electrical performance of the wavy VACNT conductor as compared to its flat counterpart was achieved by its straightforward “wavy-to-flattening” operational principle. The wavy structures of the conductor were simply flattened in response to the applied tensile strains of up to the prestrained level (100%) without any severe deformations of the CNTs in the PDMS matrix, as shown in Figure 4c.

Figure 5b shows the resistance changes of the flat and wavy VACNT conductors at each cycle under repetitive stretching-releasing cycles with a maximum strain of 100%. For the flat VACNT conductor, the resistance change ratio was found to be robust against the deformations, revealing minimal resistance changes of ~2.2% under bending of up to a minimum bending radius of ~2 mm and ~1% under twisting of up to ~180°, as shown in Figure 6. This suggests that the unique morphology of the VACNT forests in the PDMS matrix can be maintained without appreciable distortions even under various deformations.

These experimental observations clearly reveal that the wavy VACNT stretchable conductor can feasibly be employed as stretchable electrodes and interconnects in various applications due to their superior electrical performance, reversibility, and mechanical robustness even under various deformations such as stretching, bending, and twisting.

4. CONCLUSION

In summary, we have fabricated VACNT-strip-based stretchable conductors by a simple prestraining method based on PDMS-infiltrated VACNT films. Embedding the VACNTs into PDMS matrix enables them to be employed as stretchable conductors that are robust against mechanical deformations. This process can also prevent the conducting CNTs in the PDMS matrix from being detached. In addition, a thin layer of PDMS between the PDMS/VACNT film and PDMS substrate facilitated wave formation by enabling the conformal contact between the two plates. Furthermore, the intermediate PDMS layer can ensure strong interfacial bonding between the two plates, resulting in enhancement of the mechanical robustness of the whole devices. The resultant wavy-configured VACNT conductor can accommodate a relatively large strain of up to 100% (identical to the prestrain applied to the PDMS substrate) while maintaining a small resistance change ratio as low as 6% after some preconditioning. Moreover, the response characteristics were found to be highly stable and reversible even under multiple stretching/releasing cycles. On the basis of the several advantages including superior electrical performance, mechanical robustness, and patternability, the wavy VACNT stretchable conductors developed in this work will be able to find diverse applications in stretchable electronics.
REFERENCES

■ ASSOCIATED CONTENT

■ SUPPORTING INFORMATION

Experimental setup for electrical characterizations of the devices with application of tensile strain. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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