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Highly stretchable, conductive, and transparent nanotube thin films

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We have studied the electrical and optical properties of transparent and conductive nanotube thin films subjected to extremely large strains, both isotropic and anisotropic. The films maintain electrical conductivity for strains up to 700% and the eventual loss of conductivity is due primarily to the buildup of cracks in the nanotube films. We also measured the change in optical transmittance and explain the observed haziness of the films by considering the micrometer sized cluster. This study of transparent nanotube films as stretchable electrodes is crucial for many applications, in particular, for medical implantation of electronic devices. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3114463]

A major roadblock faced in the development of electronic implants is the disparity between living tissue and materials used in microelectronics. Most tissues are supple, while the semiconductors and metals used in electronics are brittle and stiff. One key material parameter of consideration in the medical integration of electronic implants is the ability of the material to stretch. Indeed, the key failure mechanism is the isolation of the conductive pathways caused by the generation of cracks in the electrodes during stretching. For example, the transparent conductor indium tin oxide catastrophically fails under strains of less than 5%.[1] Many methods to bridge the material difference have been explored, such as using gold on elastomeric substrates to improve the biocompatibility and conformability of the electrobiological interface, or using organic polymers on plastic substrates for device integration.[2–4] However, the best stretchable metal electrode on an elastomeric substrate fails at less than 10%–20% strain,[1] while the necessary strain varies from minimal value of 5% for applications such as retinal prostheses that require conformal contact to 60% for large strain dielectric elastomer actuator based devices.[4]

An obvious method to avoid failure due to the buildup of cracks under stretching is to use conductive objects with large aspect ratio, which can bridge the cracked regions to remain conductive while subject to large strains. Thin films of randomly distributed carbon nanotubes (CNTs) have been actively explored as transparent electrodes for optoelectronic device applications. In particular, such films have already shown promising mechanical performance such as extreme flexibility, up to 5 mm bending curvature, which is crucial for medical implantation.[5] Recent studies have also found that CNTs do not exhibit any toxicity in mice which will help pave the way toward the future application of nanotubes in medical device applications.[6] Stretchable loudspeakers incorporating CNT thin films have also been studied, and devices do not show breakdown for strains up to 200%.[7] In this study, we examine the electrical and optical properties of CNT thin films under extremely high strain. We perform isotropic and anisotropic stretch tests on CNT films deposited on 3M VHB 4905 substrates for strains up to 700%. We explain the observed changes in performance with increasing strain based on the formation of microclusters during stretching. This study could benefit the further exploration of CNT thin film electrodes for medical implantations.

Arc-discharge single walled CNTs from Carbon Solutions Inc. were dispersed in water at a concentration of 2 mg/ml. The CNT thin films were deposited on 3M VHB 4905 films using a spraying method through shadow masks.[8] As a substrate, the 3M VHB 4905 films are highly viscoelastic; therefore we can truly investigate the stretching properties of the nanotube thin film. We used two methods for stretching the CNT thin films: unidirectional mechanical stretching which can lead to as much strain as needed and isotropic electrically induced stretching with a multilayer device setup. For the unidirectional stretch tests, a CNT thin film was sprayed through showdown mask in a $2\times5\ \mathrm{mm}^2$ area onto a 3M VHB 4905 substrate. The resistance was measured under constant strain conditions using a two-probe resistance meter. The distance between the probes was kept constant for the entire test and the same pressure was applied to the two probes to maintain consistency in the resistance measurements. Force was exerted to the two ends of the film to stretch the film slowly, which allows the films to maintain the internal stress. Figure 1(a) shows the change in resistance with strain. The film resistance increases superlinearly with strain. This indicates that, as the film is stretched, the increase in resistance cannot entirely be attributed to the decrease in areal density of the electrode material. The superlinearity of the curve points to some other phenomena in addition to film thinning that will be explored in the future. More importantly, the results show that the film remains conductive for linear strains up to 700%. To the best of our knowledge, this is the largest strain under which a conductor has remained conductive.

The second stretching method is detailed in our previous work.[9] Briefly, conductive nanotube thin films are coated on both sides of the 3M 4905 films prestrained biaxially to 300%. Upon voltage application, the film expands due to electrostatic force. During expansion, another rigid and adhesive substrate was attached to one side of the strained film in order to maintain the electrically induced strain after the voltage was turned off. The surface conductance was mea-

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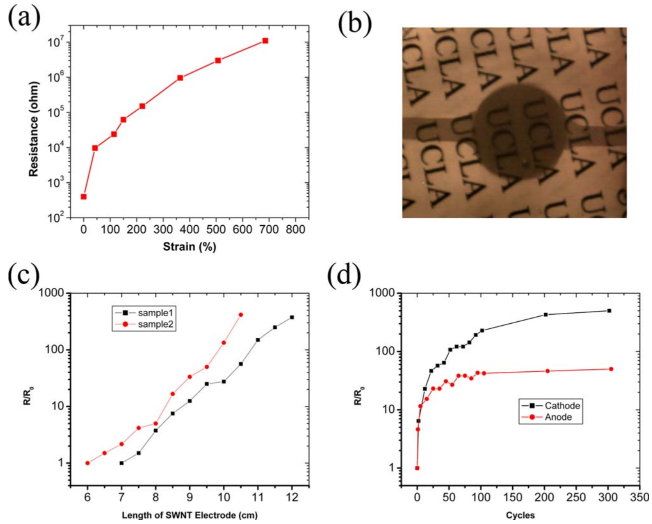

FIG. 1. (Color online) (a) Resistance as a function of strain under unidirectional stretching. (b) Set up for isotropically stretching of CNT thin film with layered structures. The circular area is where the cathode and anode CNT films overlap. (c) Resistance change as a function of strain for isotropically stretched CNT films in setup (b). (d) CNT film resistance change after cyclically actuating the films between 0% and 100% strain multiple times.

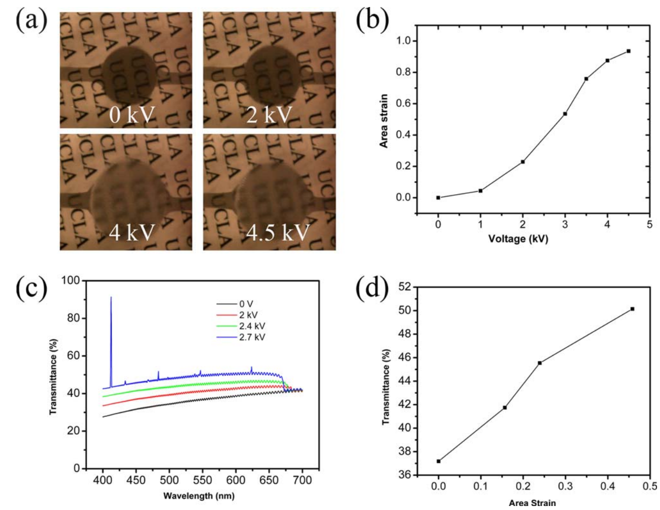

FIG. 2. (Color online) (a) Isotropically stretched CNT films under different applied voltages showing the increase in strain. (b) Area strain as a function of applied voltage, as shown in (a). (c) Spectra of stretched CNT films in visible range. As the CNT film was stretched, the transmittance increased due to the thinning of the nanotube film. (d) Transmittance at 550 nm as a function of area strain.

sured through parallel silver paste electrodes applied onto the free side of the strained nanotube film. Figure 1(b) shows the set up for the measurement. Both electrodes, anode and cathode, were made of conductive nanotube thin films. The two electrodes were deposited such that they overlap each other and a high voltage ranging from 1 up to 4.5 kV was applied. Figure 1(c) shows the percent change in resistance as a function of strain. Similar to the other tests, the resistance was observed to increase superlinearly. For applications as stretchable electrode, the ability for CNT films to maintain conductivity after a number of stretching cycles is very important. We cyclically actuated the electrode from 0 to 2.7 kV, with a corresponding strain change from 0% to 100% in area. We monitored the resistance after the nanotube thin film was released back to the original position. For both the anode and the cathode, the films resistance increased after a certain number of stretch cycles, 4 and 400 times, respectively [Fig. 1(d)]. The increased resistance of the CNT thin films, after breakdown due to stretching, can be attributed to the modification of the microstructure, even though as a whole it remains conductive. This is especially true where the nanotube-nanotube contact is separated, which results in large charge transfer barriers. For both cathode and anode, the resistance reached an equilibrium value after around 100 cycles of stretching.

CNT thin films with thicknesses in the range of 10–100 nm have been developed as a replacement for traditional transparent and conductive electrodes, such as indium tin oxide, with several advantages including a much greater mechanical flexibility. Here we have demonstrated the additional advantage of remaining conductive under large strain. We further investigate the optical transmittance change at different strains by monitoring the optical transmittance spectra. Figure 2(a) shows an image of an isotropically stretched nanotube thin film on a VHB 4905 substrate at different applied voltages. The ability to read the lettering underneath the films shows that they are transparent in the visible range. Figure 2(b) shows the strain increase as a function of applied voltage. As the strain increases, the letters become less clear which is due to increased scattering by the thin film electrodes and will be discussed later. As the strain increases, the films are uniformly stretched as shown in the figure due to the choice of the substrate and good adhesion of the nanotube thin films to the substrate. The loss of transmittance of nanotube thin films is mainly due to absorption thanks to their high absorption coefficient.[10] As the electrode increases in area, the density of nanotubes decreases, which results in a decrease in absorption and increase in transmittance. Figure 2(c) shows the spectra of a stretched film at different voltages. The overall structure of the curve remains unchanged; however, as the strain increases and the film transmittance increases, the lettering under the transparent and stretched CNT film appears hazier. As we will show in the SEM image, this is mainly due to the scattering of light as the domain structure reaches the length scale of visible light. Note that the peaks in the spectra are due to the breakdown and self-cleaning of nanotube films during the transmittance measurement under high applied voltages.

An extensive study of the stretched film morphology was carried out with scanning electron microscopy (SEM) on films at different levels of strain. The images were taken without the deposition of gold since the stretched films remain conductive at large strains. Figure 3(a) shows the films without any strain; the spraying method leads to uniform coating of CNT thin films. The nanotubes are packed with high density. Occasional impurities were found in SEM images of the films. In Figs. 3(b) and 3(c), the stretched films show large white areas indicative of a loss of conductivity. The cluster structures formed at high strains are mainly due to the uneven stress buildup in the nanotube network. As mentioned previously, the 3M VHB 4905 substrate in this study does not form cracks even under large strain. The nanotube films formed by the spraying methods, even though they appear uniform, form clusters and certain boundaries exists in the nanotube networks. Large strain causes the clusters to break up. However, since the nanotubes have a high aspect ratio, they maintain contact with neighboring clusters

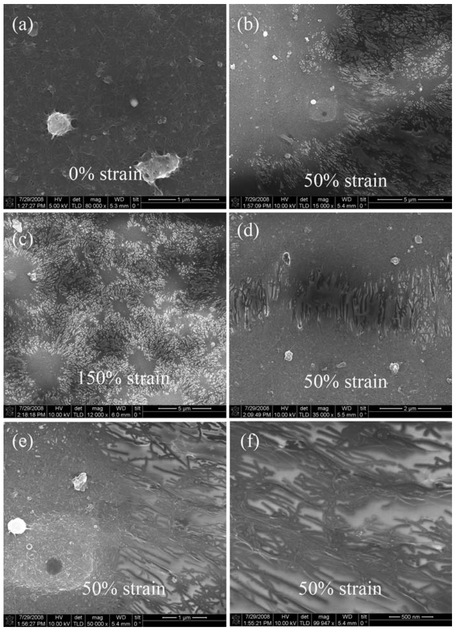

FIG. 3. (a) SEM of sprayed CNT film on 3M VHB 4905 substrate. (b) SEM of CNT film under 50% strain. (c) SEM of CNT film under 150% strain. (d) Enlarged view of the CNT film under 50% strain to show the cracks built up during stretching. (e) Enlarged view of the CNT film under 50% strain to show the boundary between high conductive area and low conductive area separation. (f) Enlarged view of the CNT film under 50% strain.

and link the conduction paths together. Increased strain results in an increased density of low-conductivity areas, which contributes to higher resistance. One can view such types of networks as highly conductive domains linked by highly resistive areas due to the decreased density of the nanotubes. A study on the temperature and voltage dependence of such type of network will be interesting and can provide deeper insight into its transport properties. Figures 3(d) and 3(e) show the boundary between the higher and lower density area, with a few tubes emerging out of the higher density area. Figure 3(f) shows the tubes in the lower density area. These tubes are preferentially aligned in the stretching direction. The aligned nanotubes are useful in anisotropic conductors and infrared filter applications. Improved coating methods or top coating with polymers to form better interpenetrated network could leads to CNT films which would have less cracks under the same area strain. As the strain increases, the area with a high density of CNTs will eventually reach below the percolation threshold and the film will lose conductivity entirely. The size of the high conductivity areas, which appear as black islands, is around $1-2\ \mu$m. Theoretical calculations show the required surface coverage to maintain conductivity for such a two dimensional case is 68%,[11] which means that largest area strain for a two dimensional film to remain conductive is $1/68\%-1=47\%$. It is clear that this is not the case for our CNT thin film. The films under this study remain conductive at strains greater than 700%. This can be explained as follows: as the strain increases, the surface coverage of the higher conductivity regions decreases and that of the low-conductivity regions increases. The situation becomes a percolation problem of high conductivity regions. Ideally, if no cracks buildup during the process, the films will remain conductive at 20 000% strain if the starting film thickness is 10 nm since the surface coverage required to reach the percolation threshold for nanotube films to be conductive is only 5% by area.[12] The morphology of the stretched CNT thin films explains the optical properties as well. Since nanotube films are highly absorptive rather than reflective, the loss of the transmission is mainly due to the absorption.[11] As the films are stretched and the nanotube surface density decreases, the absorption decreases and the transmission increases. Also, the change in morphology of the film to a more cracked structure results in an increase in light scattering with a concomitant increase in translucency, as indicated by the hazy UCLA letters.

We studied transparent and conductive nanotube films on 3M VHB 4905 substrates as stretchable electrodes that remain highly conductive up to 700% strain. We also investigated the change in film morphology under large strains and found that a percolationlike domain structure formed. The nanotube electrode remained conductive under much larger strain than any other material since the tubes cross over between the conductive clusters. With the development of more uniform coatings of nanotubes and better distributed internal stress release under strain, or by top coating nanotube network to fill the holes of the tubes to release the stress, the nanotube films can remain conductive even at much larger strains. Further development will be required prior to the use of transparent nanotube films as stretchable electrodes to bridge the gap of flexible and stretchable implantable electronics in biorelated applications.

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