Durable transparent carbon nanotube films for flexible device components

K.A. Sierrosa,⁎, D.S. Hechtb, D.A. Banerjeea, N.J. Morrisa, L. Hu b, G.C. Irvinb, R.S. Leeb, D.R. Cairnsa

a West Virginia University, Mechanical and Aerospace Engineering, Morgantown, WV, 26506, USA
b Unidym Inc., 1244 Reamwood Dr., Sunnyvale, CA, 94089, USA

ABSTRACT

This paper describes a durable carbon nanotube (CNT) film for flexible devices and its mechanical properties. Films as thin as 10 nm thick have properties approaching those of existing electrodes based on indium tin oxide (ITO) but with significantly improved mechanical properties. In uniaxial tension, strains as high as 25% are required for permanent damage and at lower strains resistance changes are slight and consistent with elastic deformation of the individual CNTs. A simple model confirms that changes in electrical resistance are described by a Poisson’s ratio of 0.22. These films are also durable to cyclic loading, and even at peak strains of 10%, no significant damage occurs after 250 cycles. The scratch resistance is also high as measured by nanoscratch, and for a 50 μm tip a load of 140 mN is required to cause initial failure. This is more than 5 times higher than is required to cause cracking in ITO. The robustness of the transparent conductive coating leads to significant improvement in device performance. In touch screen devices fabricated using CNT no failure occurs after a million actuations while for devices based on ITO electrodes 400,000 cycles are needed to cause failure. These durable electrodes hold the key to developing robust, large-area, lightweight, optoelectronic devices.

1. Introduction

There have been significant advances in flexible optoelectronic devices with organic functional layers in the last few years and they are beginning to become a commercial reality. Device flexibility is vital for roll-to-roll manufacturing processes required for the fabrication of large area devices which could be integrated onto virtually any surface. Durable transparent conducting films are a key component that must be developed to achieve these goals. The durability of flexible transparent electrode materials is currently the limiting factor in developing these devices.

The first generation of flexible electrodes is based on well-established techniques used to make transparent electrodes on glass but with much lower peak processing temperatures. On glass, transparent conducting oxides (TCOs) such as indium tin oxide (ITO), tin oxide, and zinc oxide (ZnO) are sputtered at elevated temperatures (300–600 °C). ITO combines excellent optical transparency (~90%) and low electrical resistivity (~10−4 Ω cm) [1,2]. To produce flexible electrodes, oxides are deposited at low temperature, on polymeric substrates [3].Polyester substrates such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) are often used because of the combination of low-cost and high optical transparency. The glass transition temperature of the substrate limits the peak temperature for deposition or post-processing and this reduces the electrical resistivity (~7.5 × 10⁻³ Ω cm) and decreases transmission (~85%). Utilization of polyester substrates promotes roll-to-roll processing of low-cost large-area flexible devices [4]. However, a common drawback of the first generation of flexible electrodes is their brittle nature which makes them susceptible to cracking with subsequent loss of functionality when they are mechanically deformed [5]. Despite these shortcomings the most commonly used flexible transparent electrode today is indium tin oxide (ITO) deposited on PET. There have been some preliminary efforts to replace TCOs with conductive polymer coatings such as poly(styrenesulfonate) doped poly (3,4-ethylenedioxythiophene) and they have shown some promising results in terms of conductivity and transparency. However, there are issues associated with the environmental and thermal stability of such conductive polymer films [6] which have yet to be overcome.

The electromechanical response of TCO coated polyester composites can compromise the performance of flexible optoelectronic devices during service [7]. When deformed under tension, TCO coated PET forms cracks in the conductive TCO layer perpendicular to the tensile direction starting at around 2% strain [8]. This has been observed for ITO on PET [7] and aluminum doped zinc oxide (Al:ZnO) films [9]. The onset of cracking results in an abrupt increase of the ITO electrical resistance and initiation of device degradation. In addition to catastrophic failure when a critical strain is reached, TCOs are also susceptible to damage accumulation during cyclic repetitive loading

⁎ Corresponding author.
E-mail address: kostas.sierros@mail.wvu.edu (K.A. Sierras)
at lower strains [10]. To characterize this damage accumulation cyclic mandrel bending of ITO coated PET samples has been performed and the resistance increase and progressive damage of the coating measured [10]. For applications that require flexibility, cyclic loading is important because the electrode component will be flexed, bent and deformed multiple times during its lifetime. Damage due to buckling of ITO coated PET is also important and can be even lower than 2% [11]. In all cases, a tensile strain of around 2% is the absolute maximum for flexible optoelectronics when ITO electrodes are used, although a more conservative value of 1% may be more appropriate. It is, therefore, of paramount importance to develop a second generation of transparent conducting electrodes which will exhibit significantly increased electromechanical reliability.

Carbon nanotube (CNT) films are emerging as a promising alternative to TCOs, with several advantages [12]. CNT films can be processed from solution at room-temperature, making them suitable for roll-to-roll manufacturing. Fig. 1. CNT films leverage the extensive existing research and machinery available for solution coating, enabling low cost deposition at throughputs up to 30 times faster than vacuum deposited TCOs. Materials cost is another advantage for CNT films. Applications requiring optical transparency of 80–95% (solar cells [13], organic light emitting displays [14], electronic paper, liquid crystal displays and touch panels [15]), require CNT films between 10 and 50 nm. Therefore, very little mass of CNT material is required to achieve the desired film thickness (5–25 mg/m²). Highly purified CNTs are still expensive on a per gram basis because they are produced only in small quantities; however, as production capacity increases, the cost of CNTs is expected to fall dramatically. Even at today’s material costs, CNT based transparent films have a comparable cost to ITO based films. CNT based films can also be fabricated to have comparable sheet resistance and transmission to ITO on PET for many applications. Further improvements in CNT materials should continue to increase the DC conductivity of CNT films [16]. Other advantages that CNT films offer over TCOs are reduced reflection (better index matching), more neutral color, resistance to acids, ease of laser patterning, ability to coat rough or curved surfaces, enhanced IR transmission [17], and greatly enhanced mechanical durability. It is this last property that will be discussed in this paper.

There is limited previous research on the mechanical durability of CNT-based flexible transparent electrodes. In a previous study it was found that even after heavy mechanical crumpling, CNT coated polyester films still remain conductive [18]. It has also been reported that ITO coated PET films reinforced with CNTs remain mechanically intact after monotonic bending experiments [19]. Furthermore, CNT coated PET films were found to exhibit superior mechanical integrity under cyclic mandrel bending (0.7% strain amplitude) and monotonic tensile testing when compared with ITO coated PET films [20]. In addition, Pei et al. conducted cyclic bending experiments on CNT coated PET films and reported almost no electrical resistance change after 10,000 cycles at a fixed bending radius of 5 mm [21]. Hu et al. reported that CNT based transparent electrodes 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 [22]. Finally, it has been reported that parylene-C encapsulated CNT networks are hysteresis-free for up to 100 tensile cycles [23]. These reports highlight the excellent mechanical durability of CNT based transparent conductive films. We have completed a broad study of the mechanical behavior of CNT flexible electrodes focused on behavior up to high strains; cyclic loading performance; and adhesion. We also incorporated CNT electrodes into 4-wire resistive touch panels to confirm the mechanical durability in a challenging real world device. In all cases a direct comparison with ITO coated PET films was made.

We report on the electromechanical behavior of CNT flexible electrode materials at relatively high tensile strains above the threshold of 2%. Tensile strains from 2% and up to 25% are considered in this work. CNT-based films deposited on PET substrates are tested under both monotonic and cyclic uniaxial tension. Progressive linear scratch testing is also conducted in order to assess the scratch resistance of the CNT based coating.

2. Experimental details

Carbon nanotubes (CNTs) were grown via chemical vapor deposition and subsequently purified via air oxidation followed by acid washing to remove residual metal catalyst and amorphous carbon. The purification method was proposed by Sen et al. [24]. The resulting CNTs consisted of largely single-walled and double-walled tubes. The CNTs were dispersed in a 1% aqueous solution of sodium dodecyl sulfate surfactant at 0.01 wt.% and spray coated onto a 175 μm thick PET sheet, of 600 cm² area, which was heated to 100 °C. The films were then rinsed in de-ionized water to remove residual surfactant. The resulting dry CNT film is approximately 10–20 nm thick as measured using atomic force microscopy. A polymethylmethacrylate (PMMA) layer was coated with a Mayer rod from a 0.5 wt% solution of PMMA in methyl ethyl ketone over the dry CNT film to enhance film adhesion to the PET and provide enhanced chemical/environmental resistance. The dry thickness of the binder layer is ~50 nm, thin enough such that it does not electrically insulate the surface of the CNT film. The polymer coating is not continuous and in some regions the CNT layer is exposed allowing a conducting path. The resulting film has a 4-point probe sheet resistance of approximately 600 Ω/sq and a total transmission (including the PET substrate, CNT, and polymer) of about 85% at 550 nm. The presence of a polymer binder layer does not affect the results shown in Figs. 2–4, which were repeated both with and without the polymer binder layer, with similar results. However, the polymer binding layer increases the film adherence to a standard “tape” test. The results of Figs. 5–7 were not performed without the polymer binder layer, and could be different.

ITO coated PET samples, 250 Ω/sq, were also tested for comparison purposes. ITO films with 250 Ω/sq were chosen because they are widely used in industry for display and touch-screen applications. They exhibit similar mechanical properties to other TCO films of various thicknesses (50 to 300 nm) which all crack at around 2% strain. The ITO is sputtered, at room temperature, on the PET (Melinex ST504, 125 μm thick) surface that is heat treated and biaxially oriented. The thickness of the ITO layer, as measured by contact-
mode stylus profilometry (Veeco Dektak 110), is 250 nm. The applied load of the stylus was 1 mg and the stylus radius was 12.5 μm.

Samples were tested under monotonic and cyclic uniaxial tension with in situ electrical resistance monitoring using a commercial mechanical testing machine (Instron 4410). ITO electrical resistance data were recorded during the tests using an Agilent 349708 data acquisition switch unit. Typical ‘dog-bone’ specimens with gauge length of 25 mm and width of 5 mm were used and the operating crosshead speed was 0.5 mm/min.

Nanoscratch testing was performed using a 50 μm radius spherical diamond indenter. Samples were adhered to glass slides for testing and the applied load was increasing linearly. Low-load scratching was performed using the high-resolution cantilever of the nano scratch tester (CSM Instruments). Critical loads for coating failure were determined using in-situ optical microscopy.

Sample surfaces were studied using a Leica optical microscope, magnifications 10, 20 and 50 times, equipped with a frame grabber (Guppy, Allied Visions Technology). More detailed imaging of the CNT network was conducted using a scanning electron microscope (SEM) (Hitachi S-4800) with a field emission gun. The acceleration voltage was 15 kV.

3. Results and discussion

Monotonic uniaxial tensile testing of the two transparent conductors highlights the enhanced mechanical properties of CNT based materials and their potential for use in application which require large deformations. As shown in Fig. 2, the electrical resistance of the ITO coated PET sample increases abruptly at around 2% nominal tensile strain. This is associated with ITO surface cracking perpendicular to the tensile direction. In contrast, the electromechanical behavior of the CNT based film follows a different trend. A linear increase in resistance is observed and reaches 38% at 25% nominal uniaxial tensile strain. This critical strain is 10 times larger than that observed in the ITO coated PET case. The linear increase in the resistance of the CNT-based electrode with strain could be due to changes in resistivity or geometrical changes. In previous studies by Li et al.[25] and Vemuru et al.[26] it was found that for strains of 0.1% and below CNT films exhibited a high sensitivity to applied strain that did not depend on geometry changes alone and that changes in resistivity dominated. For the very large scale deformations investigated in this study we have not isolated the relative contribution of geometry changes and resistivity increases, however, a simple model based on geometry changes alone does seem to give a good first approximation. A simple approximation of the CNT based film as an isotropic solid with a resistance given by $R = \rho L/A$ where $\rho$ is resistivity, $L$ is length and $A$ is cross-sectional area. As the length increases due to straining of the film, the resistance also increases and we can approximate the fractional change in resistance by:

$$\frac{\Delta R}{R_0} = \left(\frac{L_0 + \Delta l}{L_0}\right) \frac{1}{1 - \nu \ln \left(1 + \frac{\Delta l}{L_0}\right)^2} - 1$$

where $\nu$ is Poisson’s ratio, $L_0$ is the initial length and $\Delta l$ is the change in length. An effective Poisson’s ratio of 0.22 is consistent with the data. Typical values reported in the literature for carbon nanotubes are close to 0.2 [27] and it is reasonable that this simple model is within 10% of this. The CNT-based film’s electrical resistance did not increase in a more abrupt fashion until a nominal strain of 25%. At strains as high as 25%, a permanent deformation of the PET film has already been established. This is showing a remarkable mechanical durability of the CNT-based transparent conducting film and that the maximum strain to failure is actually limited by the substrate.

During the device’s operational lifetime, externally applied forces may cause cyclic deformation of the transparent conducting...
component. It is therefore important to investigate and compare the response of the CNT-based polymer film under a cyclic uniaxial tensile loading with the ceramic alternative. As shown in Fig. 3a, repeated tensile loading and unloading, from 0 to 5% strain, of the CNT-based electrode does not have an effect on its structural integrity. The electrical resistance does not significantly change after a total of 250 cycles. This notable stability of the electrical resistance suggests that the CNT film remains intact thus the absence of coating cohesive and/or substrate-coating adhesive failure mechanisms should be underlined.

On the other hand, the tensile cyclic response of the ITO based transparent component is inferior to the one observed in the previous case. The ITO electrical resistance increases abruptly, during the initial loading region. ITO resistance does not recover during the unloading part of the first cycle as shown in Fig. 3a. In contrast the CNT-based film’s electrical resistance slight change during loading is followed by total recovery during unloading as shown by the inset graph in Fig. 3a.

To further investigate the mechanical durability of the CNT-based transparent conductor, we conducted tensile cyclic experiments at a higher strain region, from 5 to 10% nominal tensile strain. This is a very high strain region for transparent conducting oxide films. However, the CNT-based film shows an excellent response, as shown in Fig. 3b. After an initial 10% increase in resistance, mostly associated with dimensional changes of the underlying polymer substrate, no further increase in resistance was observed. As noted in the previous case a slight increase in resistance during the loading portion, around 3%, is also observed in this case. This is depicted by the inset graph in Fig. 3b. Measurements were performed for 6 samples and no significant variation in the electromechanical properties was observed. The ‘dog-bone’ samples were cut from two sheets. Each sheet has an area of 600 cm². Figs. 2 and 3 show a typical behavior.

The structural integrity of the CNT-based conducting surface, after testing, is further confirmed when optical microscopy is used. As shown in Fig. 4a and b, there are no visible microscale coating cracks for both 0–5% and 5–10% nominal strain cases. This is consistent with the electromechanical measurements conducted since cohesive and adhesive failure is associated with significant electrical resistance increase.

Perpendicular to the tensile direction cohesive coating failure in the form of cracking is observed for the ITO coated PET sample in both cases, Fig. 4c and d. This is a typical response of a brittle thin coating bonded to a compliant polymer substrate and is in full agreement with the preceding electromechanical test results. Also worth noting is the increased number of cracks, as well as limited adhesive failure parallel to the loading direction, when the externally applied tensile strain is between 5 and 10%.

During the scratch test a diamond stylus is drawn across the surface of the coating, under a linearly increasing load, until some well-defined failure occurs at a specific load. This load is often termed the critical load. One or more failure mechanisms may be detected during a scratch test depending on the coating/substrate system under consideration. Scratch testing is important for characterizing the cohesive and adhesive failure mechanisms of thin coatings on relatively thick substrates at relatively low loads [28].

In this study, two failure modes are observed when scratching CNT on PET films. Both failures are dominated by the plastic deformation of the coating and the underlying polymer substrate. At first, coating delamination is initiated at around 140 mN applied normal load. As shown in Fig. 5a, a sudden increase in the penetration depth is associated with this failure. As the normal load is increasing, material accumulates in front of the indenter tip and spallation of the coating is observed at around 190 mN.

When ITO coated PET samples are tested two failure mechanisms are also observed (Fig. 5b). These failure mechanisms occur at significantly lower loads compared with those observed for the CNT based material. Since the ITO coating is brittle and the polymer

---

**Fig. 4.** (a) Optical image of a CNT-based film surface strained from 0 to 5% for 250 cycles. (b) Optical image of a CNT-based film surface strained from 5 to 10% for 250 cycles. (c) Optical image of an ITO film surface strained from 0 to 5% for 250 cycles. (d) Optical image of an ITO film surface strained from 5 to 10% for 250 cycles.
substrate is soft, through-thickness cracking of the coating occurs at about 28 mN loading. The second failure mechanism is coating detachment, which leads to complete coating delamination at 45 mN loading. As shown in Fig. 5c, the critical loads for CNT coating failure are considerably higher than those measured during the ITO coated PET testing. This is also confirmed when using optical microscopy. Fig. 5c includes error bars that represent the standard deviation.

Fig. 5. (a) Penetration depth versus applied normal load for CNT-based film on PET. Two distinctive coating failure modes are observed from the optical images. Scale bars in the optical images are 5 μm long. (b) Penetration depth versus applied normal load for ITO film on PET. Two distinctive coating failure modes are observed from the optical images. Scale bars in the optical images are 5 μm long. (c) Comparison of scratch critical loads for ITO and CNT-based films deposited on PET substrate.

Fig. 6. (a) Architecture of a four-wire touch-screen device tested in this study. (b) Equivalent electrical circuit for the four-wire touch-screen. (c) Normalized switch resistance versus number of actuations for ITO and CNT-based top electrodes.
Fig. 7. (a) SEM imaging of ITO contact area after touch-screen device testing. (b) SEM imaging of CNT contact area after touch-screen device testing.
deviation of the measured data. 5 scratch tests were conducted on two different sheets for each case.

One of the most demanding applications for flexible electrode materials is as the touch electrode for four-wire resistive touch panels. While ITO on PET is currently used, these films are much more subject to cracking and fracture damage that eventually leads to catastrophic electrical failure. This problem is amplified in a device such as a touch panel, especially for the top flexible electrode which undergoes repeated stress throughout device use. For today’s four-wire resistive touch panels, especially for small sized screens typical in cell phones and other portable devices, the fragility of the ITO electrode is exacerbated near the device edge, especially within approximately 2 mm from the optically clear adhesive joint. Here, touch actuations quickly damage the device and render it inoperable. For future devices that are flexible and incorporate touch sensitivity, this problem will become even more significant. Some preliminary work has been reported by Hecht et al. [15] considering touch activation at the center of a model device. We have extended this work by considering the activation near the device edge where degradation is most severe and we have disassembled these devices to investigate failure mechanisms using SEM.

To test the robustness of CNT vs. ITO films in 4-wire device operation, we performed touch actuation tests on two touch panels, one using an ITO/PET top electrode and one using a CNT/PET top electrode (both devices use an ITO/glass bottom electrode). Both touch panels were 4-wire resistive panels using standard spacer dot and silver bus bar configurations, and were about 3” x 4” in dimension. Fig. 6a shows a schematic diagram of the touch panel device set-up. Touch actuations were performed using a standard personal display assistant stylus actuating at 3 Hz and 260 g of force. A constant bias voltage of 3.3 V was applied between the top and bottom electrodes so that current was applied throughout device testing. Touch actuations were performed two mm from the device edge, where ITO based devices are especially prone to damage. After every thousand touch actuations, the switch resistance between the top electrode “x” bus bar and the bottom electrode “y” bus bar was measured. The current flows from the top bus bar, along the top electrode, through the contact point, along the bottom electrode, and out from the bottom bus bar. An equivalent circuit is shown in Fig. 6b. Fig. 6c shows the device performance as a function of touch actuation. The switch resistance of the ITO device clearly fails catastrophically around 400,000 touch actions, while the switch resistance of the CNT device gradually increases but is still within device limits even after 1 million touch actuations. The degradation in switch resistance is solely due to degradation in the touch resistance, that is, a sharp increase in the resistance at the contact point between the top and bottom electrodes. To investigate further the mechanism behind this degradation, SEM images were taken from the contact area after device testing was finished.

The touch panels used for the data in Fig. 6c were disassembled and the contact area was imaged with an SEM. Fig. 7 shows the contact area after device testing in the ITO (7a) and CNT (7b) top electrodes. The ITO device shows catastrophic electrical failure which seems to occur due to damage of the ITO layer. The brittle nature of the ITO makes it susceptible to delamination due to repetitive contact. The CNT layer also shows limited plastic deformation. However, the nature of the damage is different, as electrical conductivity never reaches ultimate failure. The damage that is observed is due to bending or deformation of the polyester substrate coupled with some fragmentation from the ITO/glass bottom electrode depositing on the surface of the top electrode. In Fig. 7b, ITO fragments can be observed in the CNT film, suggesting a significant transfer of ITO delaminated particles from the bottom ITO-based electrode to the top-sheet.

4. Conclusions

During this study a durable carbon nanotube film for flexible devices and its mechanical properties were described. The mechanical integrity of flexible electrodes becomes important when designing flexible optoelectronic devices. Under uniaxial tension the critical strain for 25% electrical resistance increase is 10 times higher for CNT films than for ITO films, and is ultimately limited by catastrophic substrate failure. Also, CNT based electrodes show excellent stability during repeated tensile loading and unloading. In particular between 0–5% and 5–10% applied strain, the electrical resistance of the CNT based electrode does not change significantly for 250 cycles. Optical microscopy observations confirm that the CNT-based electrode is less susceptible to cracking from repeated tensile loading. Also, CNT based electrodes exhibit improved resistance to scratching. The first failure mechanism for the CNT film is observed to occur at around 140 mN load whereas the first failure for ITO is observed at around 28 mN. Further, touch screen devices fabricated using CNT show no device failure after a million actuations, while for devices based on ITO electrodes, 400,000 cycles are needed to cause failure. CNT based electrodes could hold the key to developing large-area, lightweight, conformable and robust optoelectronic devices such as solid state lighting, electronic-paper, printable solar cells and displays. Such devices will lead towards producing inexpensive green energy, providing reliable solid-state lighting and significantly reducing our carbon footprint.

Acknowledgements

D. R. C, K. A. S. and D. A. B acknowledge the support of WVEPSCoR under award no. EPS08-01 and the Department of Energy under award no. DE-FC26-04NT42136.

References