Transparent conductive carbon-nanotube films directly coated onto flexible and rigid polycarbonate

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Abstract — Carbon nanotubes have quickly emerged over the last several years as a potential candidate material to replace metal oxides in devices which require transparent and conductive electrodes. Typically, these materials are coated onto substrates such as PET and PEN for flexible electrodes and glass for rigid electrodes. Recently, there has been interest in more durable and lightweight substrates to replace glass, one such substrate being polycarbonate. Sputter coating of indium tin oxide onto polycarbonate leads to low conductivity and inconsistent results, due to out-gassing and materials mismatch issues. In this work, it is shown that direct coating of carbon nanotubes onto polycarbonate leads to high-performance films with facile manufacturing.

Keywords — Carbon-nanotube films, transparent conducting polycarbonate, touch screen.
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1 Introduction

Over the past 5 years, thin films of carbon nanotubes (CNTs) have quickly emerged1 as a potential transparent and conductive material to replace conventional sputtered metal oxides such as indium tin oxide (ITO) for many applications2. These applications include touch panels,3 solid-state lighting,4 photovoltaics,5 LCDs,6 transparent heaters,7 and e-paper, all of which require one or more transparent conductive layers. The push to find a replacement for ITO stems from several key challenges. First, ITO is a brittle ceramic material that is prone to cracking upon flexing or straining.8 These cracks, once initiated, will propagate, causing eventual electrical failure of the device. This limits device operating lifetimes, especially in devices which require flexibility, as well as lowers manufacturing yields. Second, ITO consists mainly of indium, which is a rare and expensive metal that is in short supply.9 Price fluctuations of indium have caused ITO sputtered film prices to change over an order of magnitude during the previous decade, and continued strong demand for LCD televisions coupled with rising demand for CIGS solar cells should continue to drive indium pricing higher. CNT films solve both of these major issues, as the web-like topology allows unimpeded electrical conductivity even at high strains10 and the low materials cost and abundance of carbon will allow a large supply of inexpensive starting materials.

Many applications requiring a transparent and conductive coating are moving from glass and polyethylene terephthalate (PET) substrates to polycarbonate (PC) for many reasons. In particular, PC can be made both flexible and rigid, has an optical transmission higher than that of PET, and has a glass-transition temperature of 150°C, substantially higher than that of PET. Also, PC is more lightweight and durable than glass and has greater impact resistance. This is important for applications where devices could be dropped which could lead to catastrophic failure in a glass-based display. However, ITO films have proven difficult to sputter coat onto PC, often leading to discontinuous films with higher sheet resistance at a given transmission than an ITO film sputtered onto glass11. Though various techniques are currently being developed for coating of ITO on PC substrates (often requiring them to be coated with special adhesion layers), the resulting films typically have lower performance in terms of sheet resistance and optical transmission as the same films deposited onto glass or PET.12

In this paper, we demonstrate a PC substrate coated with a transparent and conductive CNT film. The coating is applied using standard wet-coating techniques from an aqueous-based ink (see experimental section below).

The films exhibit optical transmission and sheet resistance similar to that observed for CNT coatings on glass and PET. Other characteristics such as environmental and chemical stability, film uniformity, color, and electromechanical properties are also reported and discussed. These properties will enable CNT-coated rigid PC to replace glass as the bottom electrode for resistive touch panels.

2 Experimental details

2.1 Sample preparation

CNTs were grown via chemical vapor deposition and purified via air oxidation and acid washing. The CNTs were processed into a surfactant-stabilized water-based ink using previously discussed dispersion methods13 and spray coated at room temperature onto either rigid or flexible PC that

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was heated to 100°C, followed by an aqueous washing step to remove residual surfactant in the film. Film densities were made to be at least 10 times the percolation threshold to ensure electrical uniformity. Finally, the films were blown dry with clean air and allowed to sit for 1 hour before characterization.

2.2 Electro-optical characterization

Sheet-resistance measurements were made using a four-point probe set-up (Keithley 2400), and optical transmission measurements were made using a Jasco V-670 with an integrating sphere (optical transmission values are weighted over the visible spectrum from 380 to 780 nm according to ASTM 1003).

2.3 Stress/corrosion measurements

Monotonic and cyclic mechanical testing was conducted using an Instron 4410 mechanical tester. “Dog-bone” specimens were used with a 25-mm gauge length and a 5-mm width. The crosshead speed was set equal to 0.5 mm/min.

CNT-coated PC samples were also immersed in 0.1 M acrylic acid (50 ml) in order to monitor the corrosion resistance of the CNT films. A total surface area of 250 mm² was exposed. The electrical resistance of the samples was monitored using a data logger (Agilent 349708 Data Acquisition/Switch Unit).

3 Results and discussion

3.1 Film imaging

CNT films were coated onto both rigid and flexible PC. The resulting films are both visually and electrically uniform. Figure 1(a) shows an image of a 1-mm-thick PC substrate coated with a layer of CNTs. Notice that this relatively thick substrate can be bent without damage to the substrate or to the CNT conductive coating. This extreme flexibility can impart added impact resistance in applications with ITO-coated glass. Figure 1(b) depicts an SEM image of the CNT coating on PC showing a uniform film of CNTs coating the surface. No residual surfactant is observed under SEM, indicating that the washing step is effective (slight charging observed due to beam damage from SEM).

3.2 Film patterning

For many applications such as both four-wire resistive and projected-capacitive touch panels, the CNT film needs to be patterned. One effective patterning method is to use a laser to ablate the CNT film from the surface. Laser-ablation patterning has many benefits including elimination of acid waste products and reduction in the number of processing steps. Laser-ablation patterning of ITO can lead to cracking in the ceramic film, a problem which is not observed for laser patterning of CNT films. Figure 2 shows the result of laser-ablation patterning of the CNT coating on PC. Complete isolation was achieved (>10 MΩ) between conductive regions, with sharp and well-defined edges (edges are smooth on the length scale of 100 µm, which is typically adequate for resistive touch-panel applications).

3.3 Opto-electronic properties

CNT films were coated onto PC substrates at various coating thicknesses (between 5 and 20 nm dry thickness), and the sheet resistance and optical transmission (weighted from 380 to 780 nm using ASTM D1003) were measured. Figure 3 shows the results of these measurements, with both the CNT-only transmission (left axis) and the CNT/PC substrate transmission (right axis). These values are within 10% of what is measured when coating the same inks on either a PET, PEN, or glass substrate, showing that CNT coating processes are fully compatible with a PC substrate; this is not surprising considering that the process is done at ambient pressures and temperatures are kept below the glass-transition temperature of PC which is about 150°C. After coating/drying, films are washed to remove unwanted residual surfactant. After washing, the sheet resistance val-
ues decrease by an order of magnitude, likely due to the removal of insulating material from between the tube connections. The electro-optical values obtained (650 Ω and 86% transmission) are comparable to what is obtained using ITO sputtered onto PC or conductive polymer coatings and are already low enough to replace the ITO/glass bottom electrode in many touch-panel applications. The values obtained for sheet resistance \( (R_s) \) and optical transmission \( (T) \) can be used to calculate the film DC conductivity as shown previously, via Eq. (1):

\[
T = \left( 1 + \frac{1}{2R_s} \sqrt{\frac{\mu_0 \sigma_{op}}{\varepsilon_0 \sigma_{dc}}} \right)^{-2} = \left( 1 + \frac{188 \Omega \cdot 200 \text{ S/cm}}{R_s \cdot \sigma_{dc}} \right)^{-2}.
\]

The data lead to a DC/optical conductivity ratio of about 12, and a DC conductivity of 2400 S/cm. These values compare favorably to similar films of CNT on glass or PET.

### 3.4 Optical spectra/color

Another interesting feature of CNT coatings is that they have a very flat transmission spectrum over optical frequencies, leading to neutral “gray”-colored films. Figure 4(a) shows the transmission spectrum for a CNT film at 700 Ω coated onto PC versus air (bottom curve) and versus bare PC (top curve). The CNT film upper curve is featureless over the wavelength range probed, with the undulations observed due to interference patterns from the PC substrate hardcoat. The \( L^*, a^*, \) and \( b^* \) color coordinates can be calculated from the transmission spectrum, and the result is shown in Fig. 4(b). The black square near \((0,1)\) represents the \((a^*, b^*)\) coordinates for a CNT film on PC substrate (including the substrate contribution). A reading of \((0,0)\) would indicate the point of color neutrality. Also shown are color coordinate readings on various commercially available ITO/PET films from 250 to 500 Ω (ITO/PC films were not available), and a conductive polymer film at 500 Ω coated onto PC from a commercially available PEDOT:PSS-based ink. Notice that the ITO films tend to be towards the “yellow” side of the color chart (positive \( b^* \)) and the conductive polymer film is on the “blue” side of the color chart (negative \( b^* \)). The near 0 values for \( a^* \) and \( b^* \) are a major benefit for display applications such as LCD, electroluminescent lighting, electrochromics, and electrophoretics, where color displays will be viewed through the CNT conductive film.

### 3.5 Tensile testing

A major benefit of CNT transparent conductive films, especially when compared to metal oxide films, is their extreme mechanical robustness and durability. Various mechanical tests were performed on CNT films coated onto 127-µm PC. Figure 5(a) shows the monotonic electromechanical response of a CNT-coated PC sample. The abrupt increase in resistance at 8.5% nominal strain is due to complete PC substrate failure. Up to this strain, very little electrical resistance increase is measured (about 4.5%), indicating excellent mechanical behavior of the CNT coating. The low rate of increase of resistance is attributed to geometrical changes of the sample and minor initial deformation of the individual CNTs. Although a similar ITO on flexible PC coating was
not directly tested, ITO on PET typically fails at tensile strains around 2% due to crack initiation in the ceramic ITO material; these cracks propagate in a direction perpendicular to the tensile direction, eventually leading to catastrophic electrical failure.\textsuperscript{10}

A simple model based on geometrical changes was presented recently.\textsuperscript{10} The CNT-based film is approximated as an isotropic solid with an electrical resistance $R$, a resistivity $\rho$, and a length $L$. The fractional change in resistance due to uniaxial tensile stress is given by the Eq. (2):

$$\frac{\Delta R}{R_o} = \left(\frac{l_o + \Delta l}{l_o}\right) \left[1 - \nu \ln\left(1 + \left(1 + \frac{\Delta l}{l_o}\right)\right)^2\right] - 1,$$

where $\nu$ is Poisson's ratio, $l_o$ is initial specimen length, and $\Delta l$ is the change in length due to uniaxial stressing. An effective Poisson's ratio of 0.22 is consistent with the data and with typical values reported in the literature.\textsuperscript{18}

Figure 5(b) plots the results of cyclic testing. The nominal strain range employed was from 0 to 5% since the substrate fails at 8.5%. The applied uniaxial tensile load reached a maximum at 57 MPa. A total of 138 cycles were conducted before PC substrate failure. Similar to the previous experiment, the functionality of the CNT coating is limited by the mechanical behavior of the substrate. In particular, after an initial electrical resistance increase of 6% during the first 50 cycles, a plateau is reached until substrate failure occurs at 138 cycles. During each individual loading–unloading cycle, a slight variation in electrical resistance is observed as shown in the inset of Fig. 5(b). The resistance increases by 1.5% during loading and decreases by 1.5% during unloading. This indicates complete recovery. This behavior can be attributed to dimensional changes in the sample during loading and unloading. The ability of CNT films to maintain electrical conductivity even at relatively high strain values gives the CNT-coated PC added durability for applications which involve flexing or stretching of the film, such as resistive touch panels and flexible displays. It will also be an advantage in manufacturing where roll-to-roll processing and handling of the film during manufacturing can lead to significant film damage and device yield loss. The robustness of CNT films to mechanical strain may also open up new applications, such as truly flexible displays.

### 3.6 Corrosion

The chemical compatibility/durability of the transparent electrode with acid-containing layers, such as PEDOT-PSS, will be paramount in the design of future flexible devices. Figure 6 shows the electrical resistance of ITO-coated PET

#### FIGURE 5
(a) Typical monotonic electromechanical response of a CNT-coated PC samples. (b) Typical cyclic electromechanical response of a CNT-coated PC sample. Inset: change in electrical resistance during loading–unloading of CNT-coated PC transparent electrodes.

#### FIGURE 6
Electrical resistance versus time for CNT/PC film immersed in 0.1 M acrylic acid. Also shown in the inset is similar data for ITO/PET films (for comparison).
and CNT-coated PC samples when they are immersed in acrylic acid solution. This is an accelerated test which aims to determine the corrosion resistance of such electrodes. It is observed that the ITO electrical resistance abruptly increases after 60 minutes of immersion in 0.1 M acrylic acid. This increase in electrical resistance is associated with initiation of ITO corrosion and leaching of the indium into the acid. On the other hand, the electrical resistance of the CNT-coated PC sample does not change significantly over 180 minutes of immersion. This finding is very important since chemical-resistant transparent electrodes are needed for future flexible-device applications. Even today, devices such as touch panels are assembled using pressure-sensitive adhesive (PSA) materials that are largely acrylic based. Trace amounts of acrylic acid in the PSA can lead to early device failure due to electrical failure of the ITO layer, especially under hot and humid conditions. To solve this problem, manufacturers use special acrylic-acid-free PSAs that are up to seven times more expensive than conventional acrylic-acid-based adhesives. Using a CNT/PC film instead of an ITO/PC film can improve the chemical compatibility and lower the cost of current devices.

3.7 Accelerated aging

Accelerated tests are regularly conducted to assess the reliability of ceramic-based brittle films. Accelerated aging tests were performed on CNT films on PC at 60°C and 90% relative humidity. Resistance degradation was monitored as a function of time and plotted in Fig. 7. Films were exposed to 250 hours at 60°C and 90% relative humidity. Resistance degradation was monitored as a function of time and plotted in Fig. 7. Films were exposed to 250 hours at 60°C and 90% relative humidity and allowed to dry in air for 1 day. A 20% increase in sheet resistance was observed. This is attributed to a residual layer of moisture acting as an n-dopant in CNTs. The same samples were baked in air at 150°C for 1 hour. Sheet resistance shows a recovery of approximately 6% after bake. This is attributed to conformational changes in the network due to thermal stress to the underlying substrate as well as loss of oxygen dopant. The stability of the CNT/PC film to high temperature is important because many manufacturing processes involve curing steps over similar temperature/time ranges.

4 Conclusion

In conclusion, both flexible (5 mil) and rigid (1 mm) PC substrates were coated with transparent, conductive CNT films using a wet-coating process. Films exhibit excellent sheet resistance and optical transmission comparable to what is obtained for similar CNT films on PET. The films are color neutral, stable to heat and humidity, corrosion resistant, have superior electro-mechanical robustness at elevated strains, and can be readily patterned using laser-ablation methods. CNT films on PC meet the requirements to replace ITO on glass as the bottom electrode for some resistive touch panels. As the electro-optic properties of the CNT film continue to improve, additional applications in capacitive touch panels and displays are expected to emerge.

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