

Flexible carbon nanotube transparent electrodes

by Chris Weeks

Chris Weeks is a senior engineer at Eikos Inc, working on device applications where transparent and conductive carbon nanotube inks are used as a wet-deposited alternative to indium tin oxide (ITO). Prior to Eikos, Chris spent five years in the semiconductor industry, designing modems and digital signal processors at Analog Devices. He holds both a BS and MS in Electrical Engineering from Brown University.



Display technologies require one or more transparent electrode layers for functionality. Indium tin oxide (ITO) has been the transparent conductor of choice due to its optoelectronic performance, but has serious drawbacks; it is costly to pattern and has a tendency to crack with use due to its brittle nature. Eikos, Inc. has conceived and developed technologies to deliver low cost flexible alternatives using single walled carbon nanotubes (CNT). This is a review of CNT coating properties versus those of existing transparent conductors such as ITO.

CNT technology offers a variety of beneficial properties allowing flexible display designers to create high performance, low cost devices with fully flexible form factors. Because CNTs are deposited at low temperature on any substrate, displays can be created using roll-to-roll manufacturing, thus reducing fabrication time, equipment cost, and reject rate.

- broad range of conductivity (10^{-10} to $10^7 \Omega/\square$)
- uniform and linear conductance
- excellent transparency
- low reflectivity
- neutral color tone
- wet processing
- good adhesion
- durability
- abrasion resistance
- good chemical resistance
- flexibility
- ease of patterning

Overview: Engineers at Eikos have developed transparent conductive films that form when carbon nanotube (CNT) dispersions are applied as thin coatings (<100 nm). After the CNT coating is applied, it is infiltrated with a polymer binder coat, which further enhances the optoelectronic performance and increases adhesion, abrasion resistance, and flexibility. Today, the highest quality Eikos Invisicon CNT films result in 90-99% visible light transmittance and 100-1000 Ω/\square , sheet resistance – very close to the optoelectronic performance of sputtered ITO, and suitable for many flexible display applications. These optoelectronic properties will improve further in the future with increased CNT purity and degree of dispersion.

Morphology: Carbon nanotubes are an allotrope of carbon formed in the presence of carbon, heat, and a metal catalyst. Pictured in *Figure 1*, these tubes are typically 1-2 nm in diameter, and several microns long. Carbon nanotubes have strong bonding to each other, and have a tendency to bundle or “rope” during production. Eikos uses a proprietary purification and dispersion process to produce high purity, high yield dispersions of carbon nanotubes. When a CNT dispersion is applied through spray, slot-die, gravure, screen print or other wet-processing techniques, the nanotubes intertwine to form a conductive 2-D network on the substrate. A scanning electron microscope (SEM) micrograph of the network is shown in *Figure 2* (next page).

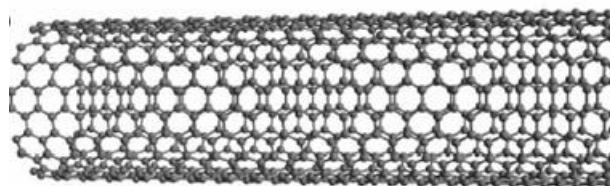


Figure 1: The high aspect ratio of carbon nanotubes makes them ideal wires

Optoelectronic performance: Three different transparent conductor materials were evaluated for optoelectronic performance: 1) ITO sputtered onto glass substrate and PET substrates; 2) Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT/PSS) wet-coated onto PET substrate; and 3) CNT spray coated onto glass and PET substrates. ITO was sputtered to $200\ \Omega/\square$, and an antireflective coating was used to optimize visible light transmittance. BAYTRON FHC PEDOT/PSS films were coated using a Meyer rod to $250\ \Omega/\square$. The CNT films were spray coated to a sheet resistance of 230 and $450\ \Omega/\square$ and contained a melamine/acrylic coat.

The visible light transmittance of ITO, PEDOT, and CNT films (with substrate effect removed) is shown in *Figure 3*. The CNT film displays high transparency across the complete visible light spectrum. In comparison, ITO has a maximum transparency in the range of 500-550 nm, at the expense of significantly lower transparency at other wavelengths. For the same level of conductivity, current CNT films show slightly lower transparency at 550 nm compared to the peak transmittance of ITO. However, CNT films exhibit significantly higher transparency across the whole visible light spectrum. CNT films are much more transparent than PEDOT. The gap between CNT and ITO will be minimized by further product optimization. As shown in *Figure 4*, optoelectronic performance of Invisicon coatings has been continuously improving over the last 4 years. An advantage of the CNT coatings is the ability to tailor the sheet resistance over a large resistive range from $10\ \Omega/\square$ to $107\ \Omega/\square$. Wet processing and the ability to control sheet resistance while maintaining high transparency make Invisicon® a preferred material for flexible transparent electrode manufacturing.

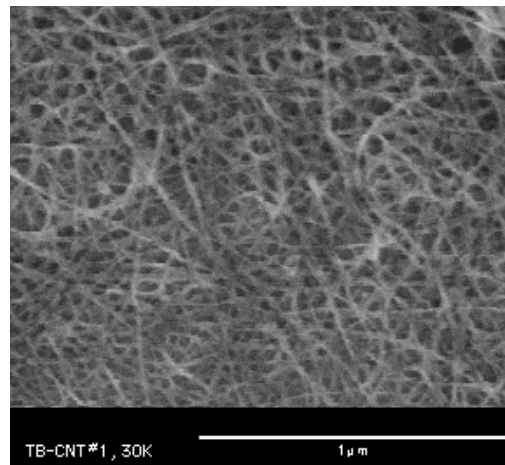


Figure 2: SEM Micrograph of CNT Film at $100\ \Omega/\square$

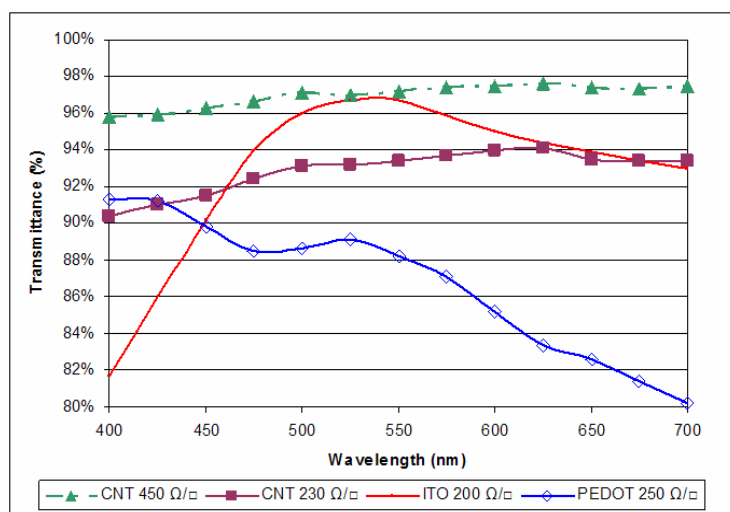


Figure 3: Optical performance: visible light transmittance of ITO, PEDOT and CNT films

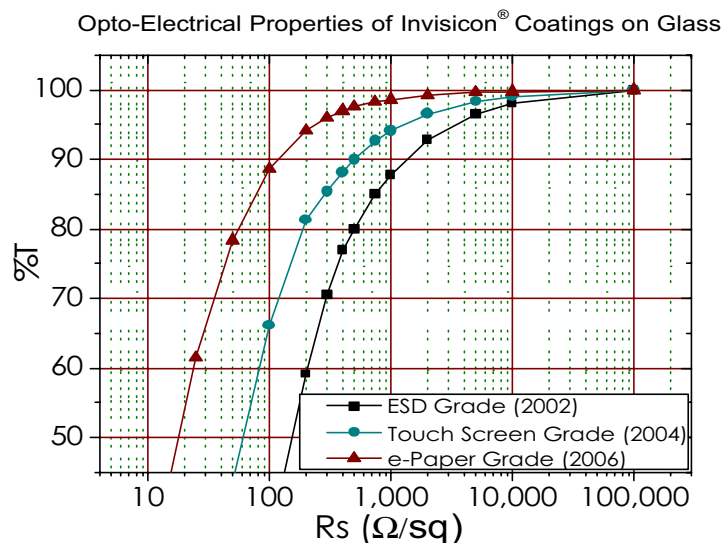


Figure 4: Optoelectronic performance of carbon nanotube transparent conductive coatings

For most flexible display applications, neutral color is desired. Color measurements using a MacBeth Colorimeter with a D65 illuminant and a 10° Observer confirm that CNT films are much closer to neutral color than both ITO and PEDOT, which show their characteristic yellow and blue hues respectively (*see Figure 5, next page*).

Mechanical and chemical durability: Carbon nanotubes are inherently flexible, strong, and chemically resistant. In fact, one of the main applications for carbon nanotubes is as a high strength fiber additive for composites. CNTs

can easily be bent without breaking and will spring back to their original shape with no degradation in properties. CNTs can withstand heat greater than 400°C in air and react only under special conditions.

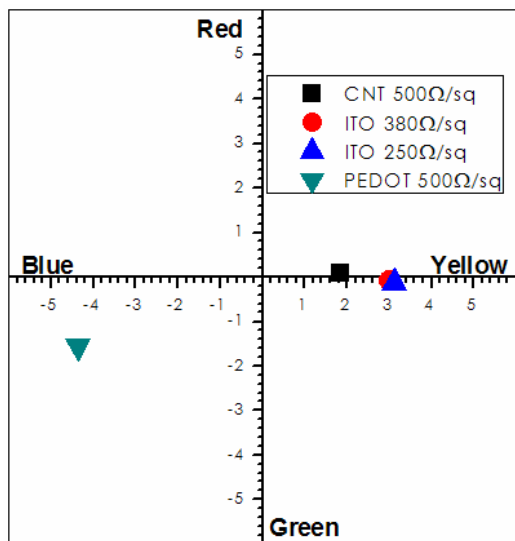


Figure 5: Color measurements: CNT films exhibit much closer to neutral color (closest to origin) than ITO and PEDOT

To quantitatively evaluate the mechanical and chemical durability of Invisicon CNT coatings, test specimens were made via spray coating a purified CNT dispersion onto heat stabilized PET film to shear resistance $\sim 650\Omega/\square$. Melamine/acrylic was applied by dip coating to bind the nanotubes to each other and to the substrate. Cyclic loading tests were conducted at Brown University using a “Roll Fatigue Tester” (mandrel diameter 19.1 mm). Testing was at 0.7% strain amplitude at 1.25 Hz and 25°C, and resistance was measured continuously throughout the experiment. As shown in Figure 6, Invisicon CNT coating showed < 0.5% change in resistance after 2,500 cycles, whereas ITO control samples showed > 2% change after only 1,000 cycles. The difference is even more dramatic when one compares rate of change in resistance. From 200 ~ 1,000 cycles, the slope of the ITO curve is more than 10x larger than the slope for the Invisicon coating throughout 2,500 cycles. The degradation in ITO conductivity during flex testing is attributed to cracking of the ITO film. As flex cycling continues, these cracks continue to grow, ultimately leading to catastrophic failure (open circuit). This failure mechanism is not observed for Invisicon CNT coatings.

The same Invisicon CNT coated PET samples were tested at 25°C in a Minimat tensile testing machine at 0.1 mm/min strain rate, in uniaxial tension, up to 18% strain. (see Figure 7). Samples were cut into traditional “dog bones”, and the resistance was measured in-situ using a digital multimeter. Between 1~5 % tensile strain, the Invisicon CNT coated PET film behaves elastically. Above 5% strain, the PET substrate plastically deformed, which dominates the electrical resistance response. However, even after 18% tensile strain, only 14% change in resistance was observed, which is a smaller change than would be expected for a plastically deforming metal. ITO coated PET has been extensively evaluated by Crawford et al. They report that the onset of cracks in the ITO film occurs at $\sim 2.5\%$ tensile strain, with ITO failing catastrophically before 5% tensile strain is reached (resistance change > 20,000%). CNT films are unique in that they maintain functional properties, despite irreversible deformation to the substrate.

To further evaluate the robustness of CNT films, we evaluated the change in transparent CNT electrode visible light transmittance after exposure to chemical and heat treatments commonly used in manufacturing. Overall, the CNT film performed quite well, except in the case of immersion for 30 minutes in 5% NaOH solution. This alkaline test is very challenging for many organic coatings. For investigation revealed that while the CNT films exhibited high resistance to alkaline attack, the CNT film delaminates from the glass when NaOH solution penetrates the CNT network and aggressively attacks the film/glass interface. The CNT film exhibited excellent resistance to strong acid, organic solvents, and high temperature exposure (250°C). This is consistent with the expected stability of CNT materials and summarized in Figure 8 (next page).

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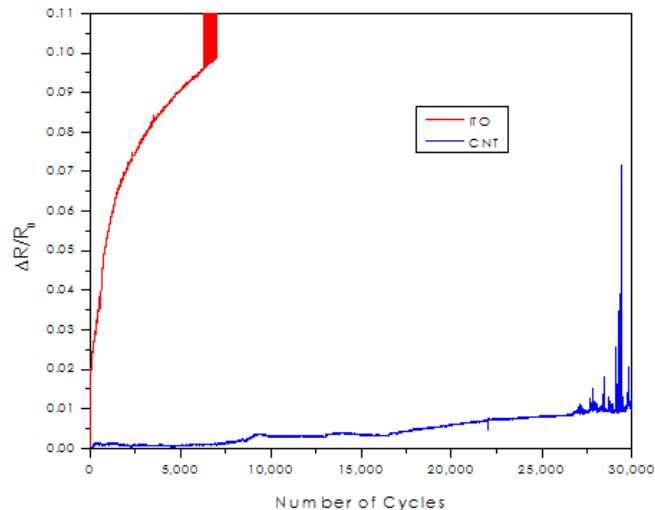


Figure 6: Cyclic testing of Invisicon CNT coating on 175 μm PET compared to ITO on PET

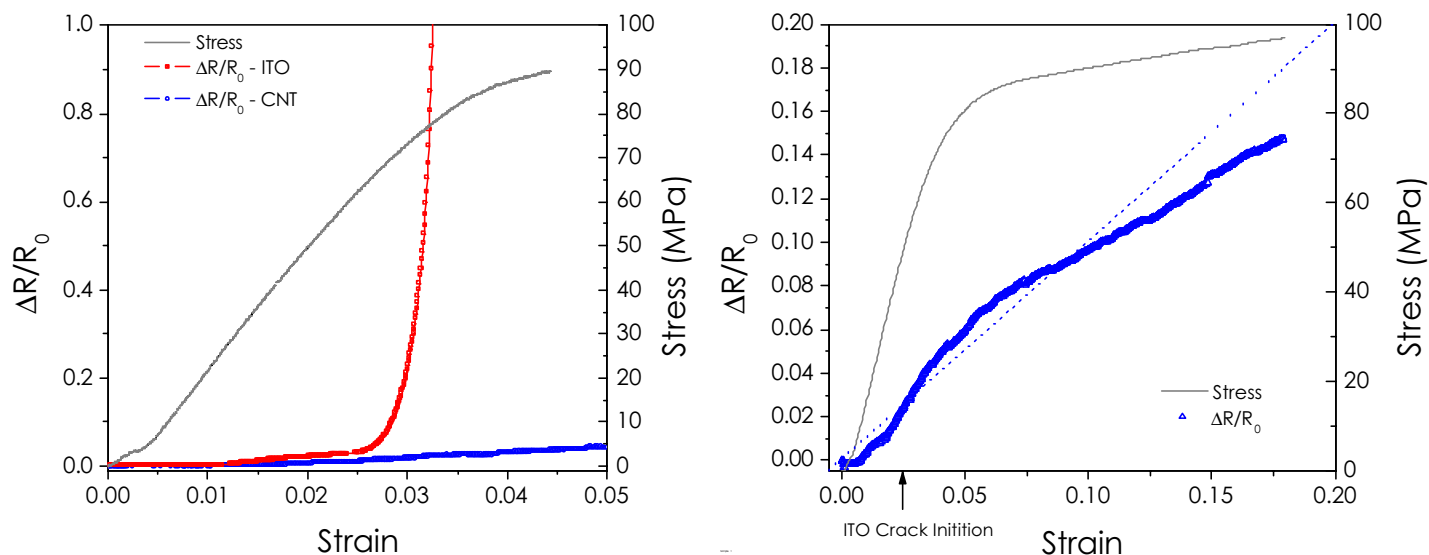


Figure 7: Minimat tensile testing machine at 0.1 mm/min strain rate, in uniaxial tension comparing CNT and ITO coated PET

Conclusion: The ideal transparent electrode for flexible displays is low cost, with tunable resistance, good transparency, flex durability, and compatibility with roll-to-roll processing. Invisicon has similar optoelectronic performance to ITO, and can be deposited at low cost and in-line with other coatings on flexible substrates, thereby enabling fully roll-coated displays. Invisicon is deposited at low temperature and can withstand high temperature and a variety of chemical environments, making it compatible with display processing. The ease of processing is a significant advantage; coatings can be easily deposited using slot die or gravure coating with greater than 95% transparency and $500\Omega/\square$. Since Invisicon does not undergo the catastrophic failure that ITO experiences, a higher manufacturing yield and lower device failure rate is possible with Invisicon transparent electrodes. Eikos transparent CNT electrodes are a viable alternative to ITO for flexible applications, offering superior durability and flexibility, ease of processing (wet coating and patterning), low reflectance, and neutral color.

Harsh Environment	Duration (minutes)	Appearance	Transparency (T%@550nm)		
			Before	After	$\Delta T\%$
5% H_2SO_4	30	○	93.91	94.3	0.39
5% NaOH	30	x	94.1	—	—
γ -Butyrolactone	30	○	93.46	94.44	0.98
NMP	30	○	94.48	94.57	0.09
250°C	60	○	93.99	93.66	-0.33

○ - no change; x - peel off

Figure 8: Compatibility with LCD CF Process: CNT films exhibit excellent chemical and heat resistance

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