

Thin films of carbon nanotubes form transparent circuits for flexible displays.

# the TWISTS of Carbon Nanotubes

ILLUSTRATION BY DON BISHOP

BY PAUL GLATKOWSKI, PHILLIP WALLIS,  
AND MICHAEL TROTTIER, EIKOS INC.

**T**ransparent conductors are essential components in many optoelectronic devices, including flat-panel displays, touch screens, electroluminescent lamps, solar panels, “smart” windows, and organic light-emitting diode (OLED) lighting systems. Transparent conducting oxides like indium tin oxide (ITO) have been the preferred choice for four decades.<sup>1</sup> ITO has some rather significant limitations, however. The films are brittle, which is a mechanical reliability concern for flexible display applications. ITO circuits are typically formed by vacuum sputtering followed by photolithographic etching; the fabrication cost for this formation process may be too high for high-volume or large-area applications.

Our group has recently discovered that carbon nanotube dispersions applied in very thin layers (less than 100 nm) form highly transparent conductive films. They can achieve performance comparable to most of today’s commercial sources of sputtered ITO on plastic film and are suitable for many display applications. The carbon nanotube films exhibit mechanical reliability that exceeds that of ITO and can be formed using

atmospheric, low-temperature, wet-coating/printing techniques, making them an attractive alternative for applications requiring low cost, large area, and flexibility.

## Carbon Nanotubes 101

Carbon nanotubes consist of helical tubes formed from single graphite sheets. Single-walled nanotubes are 1 to 2 nm in diameter and combine to form rope-like structures. The lengths of the ropes are difficult to determine but are approximately 1  $\mu\text{m}$  long, with diameters ranging from 10 to 30 nm. Carbon has different properties depending on its structure. Think of a sheet of paper wrapped in a cylinder. Depending on whether the tube is wrapped as a simple cylinder or a tighter helical form, the nanotube material can possess the properties of a semiconductor or a metallic material. Graphite, for example, is a 2-D conductor. When wrapped into a nanotube, it conducts current down the tube.

Carbon nanotubes are not found naturally as individual structures but always as an assembly of tubes that forms a

rope. This rope formation is the result of Van der Waals attractions between the sidewalls of each tube and leads to some unique structural configurations (see figure 1). The material can, for example, form a continuous network of carbon nanotube ropes; it is this network of conductive carbon nanotubes that conducts electricity across the coating.

Carbon nanotubes form whenever a source of carbon is heated in the presence of a metal catalyst like iron, nickel, and molybdenum; they are most commonly heated by chemical vapor deposition and electrical arc processes. Nanotubes form easily in nature but not in a useful form. Forming useful nanotubes requires processes regulated in time, temperature, and other normal process controls to achieve correct diameters and lengths for the application of choice. We produced the carbon nanotubes discussed in this article by arc discharge across a carbon rod containing a yttrium and nickel catalyst. The resulting raw product contained several other forms of non-tubular carbon that had to be removed.

Optoelectronic properties improve dramatically with increased carbon-nanotube purity. About 60% of the raw material produced during fabrication is other forms of carbon that have to be removed, although researchers have recently reported obtaining pure nanotubes straight from the reactor.<sup>2</sup> To remove the unwanted forms, we treated the material using chemical processes like acid reflux, filtration, and centrifugation, and repeated washes with solvents and water. The result was highly purified carbon nanotube material.

The highest quality carbon nanotube films we have developed achieve roughly 90% visible-light transmittance and about  $200 \Omega/\square$  sheet resistance  $R_S$  (see figure 2). The material can achieve optical transparency of better than 95% for sheet resistance values in excess of  $1000 \Omega/\square$ . A transparency that yields high-luminosity performance for sheet resistances in the  $10^3$  to  $10^5 \Omega/\square$  range is important for certain applications, such as touch screens and reflective displays.

Measures of optical transmittance versus wavelength for carbon nanotube films show reduced optical transmittance with decreasing sheet resistance (see figure 3). A useful attribute of the material is demonstrated in the flatness of the curves across the visible spectrum. In contrast, ITO shows stronger absorbance at shorter wavelengths in the visible range (hence, its characteristic yellow color). Carbon nanotube films exhibit neutral color, a big advantage for display applications.

The nanotubes also exhibit other useful properties such as electrical conductivities as high as  $100 \Omega^{-1}/\text{cm}^{-1}$ , plus high strength, thermal conductivity, and flexibility. To test their flexibility and response to strain, we made carbon nanotube test samples by spray coating heat-stabilized, 125- $\mu\text{m}$ -thick polyester (PET) film with purified carbon nanotube dispersion. We then dipped the film in a melamine/acrylic binder solution, air dried, and cured it. The nanotube/binder stack was about 75-nm thick, with sheet resistance of about  $650 \Omega/\square$  and visible-light transmittance of 90%. We subjected the samples to up to 18% strain at a 0.1 mm/min strain rate in uni-axial tension at 25°C. For comparison, we tested commercially available ITO films with sheet resistance of about

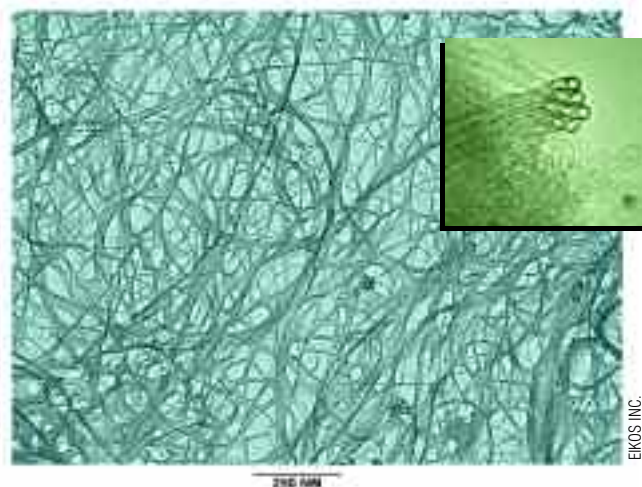
$250 \Omega/\square$  and PET films 125  $\mu\text{m}$  thick. The resultant plot of change in resistance ( $\Delta R/R_0$ ) versus strain ( $\Delta L/L_0$ ) shows the stability and robustness of carbon nanotubes compared to ITO.

In cycle testing, carbon nanotube films showed no signs of cracking until about 27,000 cycles, with failure observed at about 32,000 cycles. To put the carbon nanotube performance into perspective, 25,000 cycles is roughly equivalent to seven years of use for a roll-out flexible display device flexed every day, 10 times per day. In comparison, ITO films developed cracks that led to catastrophic failure (open circuit) at about 6000 cycles.

Based on scanning electron microscope images of the failed nanotube films, we attribute the ultimate failure to agglomerates in the film (point defects that act as stress concentrators). The melamine/acrylic binder is also more brittle than other binder resins we have used. We plan to do additional work to improve the quality of carbon nanotube dispersion and use more flexible/ductile binder resins.

## Circuitry and Displays

Conductive carbon nanotube structures can produce transparent circuits on display substrates, offering a method for fabricating flexible displays. We have tested three methods for fabricating transparent circuits and electrodes from carbon nanotubes. Each uses a two-step approach in which we form



**Figure 1** Graphite sheets can form carbon nanotubes (inset), which can combine, in turn, to form ropes. Applied as very thin films, they create a fabric of nanotube ropes that can conduct electricity in circuits (main image).

the carbon nanotube layer and then add a polymeric binder topcoat. This two-step approach yields improved optoelectronic properties for the carbon nanotube layer and enables some simple circuit fabrication methodologies.

In the first method, we feed the PET substrate into a standard laser jet printer to print a negative image of the desired circuit in styrene carbon-block ink (standard printer ink). The nanotubes are extremely durable; they deform but they

spring back. If a hole is punched in them, they reform. The carbon nanotube layer is deposited by a wet coating method. We use spray application with ultrasonic or airbrush methods, but other techniques like dipping or roll coating are compatible. Next we dip the carbon-nanotube-coated film in organic solvent (toluene) for 3 s to remove the negative image, leaving behind the patterned carbon nanotube layer. A polymeric topcoat applied over the top protects the carbon nanotube circuit.

In the second method, we deposit the carbon nanotube film over the entire substrate surface and pattern it with a polymer binder material like amorphous fluoropolymer or polyester. We can pattern the binder with screen printing, ink jet printing, or other methods. Rinsing the substrate with a water/surfactant solution removes the unprotected carbon nanotube regions.

In the third method, we print the carbon nanotube pattern directly on the substrate. Several different methods to print the carbon nanotube layer are currently being studied, includ-

ing ink jet printing, focused-beam spray, screen printing, and gravure roll printing. This third approach is very attractive because it results in the least waste and has the simplest manufacturing flow.

There is no inherent technological barrier limiting the use of carbon nanotube films for applications in which ITO is currently used. At this point in the development of the technology, however, specifically with regard to the resistance versus transmittance properties, there is further work to do to meet the needs of some display applications.

The material has been evaluated with very encouraging results in various electrophoretic or reflective display technologies for which higher resistance (1 K  $\Omega/\square$  to 100 K  $\Omega/\square$ ) is acceptable and for which the very high transmittance (better than 95% at 550 nm) of the material at these resistance values is especially important. Dozens of full-size reflective displays incorporating carbon nanotube circuitry are currently operating in various laboratories and long-term testing for brightness and durability is underway. Initial results are very promising. Brightness is improved by approximately 8 to 10% over ITO in most of these displays, with less change as the display ages.

In addition, these durable coatings are potentially important for touch screens; qualification tests are underway. These display technologies are expected to be early adopters. Other applications include LCD television circuitry.

OLED displays are also quite demanding from an  $R_s/\%T$  performance standpoint, since the conductors must have sheet resistance below 50  $\Omega/\square$  and transparency better than 90%T. An application of this technology to OLED displays will thus take several years longer than that of the other display types. This is also true for application to plasma television electrodes.

Much progress has been made with this technology but its full potential has only begun to be exploited. In the next year, research and development will continue to push the performance of the coatings toward meeting the most demanding applications, while focusing on commercial production and leveraging the existing level of technology. **oe**

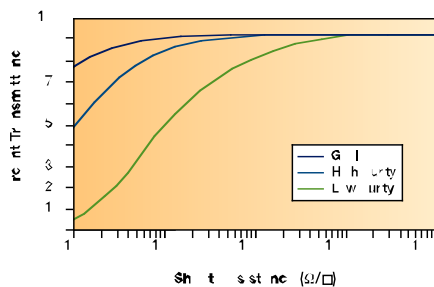
*Paul Glatkowski is vice president of engineering, Phillip Wallis is technical director, and Michael Trottier is senior engineer at Eikos Inc., Franklin, MA. For questions, contact Glatkowski at 508-528-0300; 508-528-0101 (fax); or pglatkowski@eikos.com.*

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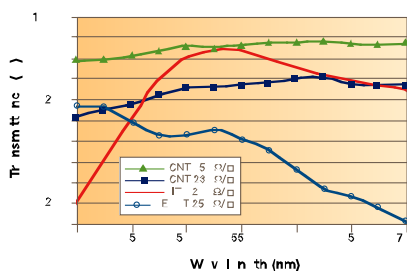
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**Figure 2** A plot of optical transmittance versus sheet resistance ( $\Omega/\square$ ) compares the performance of two different-quality carbon nanotube films with the goal performance. Optical measurements were made at  $\lambda = 550$  nm, using a Perkin Elmer Lambda 3B UV/VIS Spectrophotometer. Sheet resistance measurements were made using a Mitsubishi Chemical Loresta-GP MCP-T600 Low Resistivity Meter.



**Figure 3** Curves of optical transmittance versus wavelength for different grades of carbon nanotubes and ITO show relatively flat transmittance for nanotubes across the visible spectral region. All transmittance values refer to the transparent conductor layer only, with substrate effect removed.