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From the Editors of R&D Magazine

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Flexible transparent circuits from CNTs

By *Paul Glatkowski, Phillip Wallis,* and *Michael Trottier,* Eikos Inc.

Flexible, transparent circuits can be formed from CNT (carbon nanotube) dispersions that are combined with polymeric binders using atmospheric wet coating and printing techniques. The coatings can be produced at lower cost and exhibit greater flexural endurance and abrasion resistance than ITO (indium tin oxide).

Transparent conductors are a key component in many optoelectronic devices with transparent conducting oxides like ITO being the preferred choice. And, polymers like PEDOT (poly3,4-ethylenedioxythiophene) doped with PSS (polystyrenesulfonate) have found application in some niche markets. However, ITO has limitations: inherent brittleness; high cost associated with vacuum sputtering deposition and patterning by photolithographic etching; and a 10× recent cost increase for indium due to high demand and a dwindling supply.

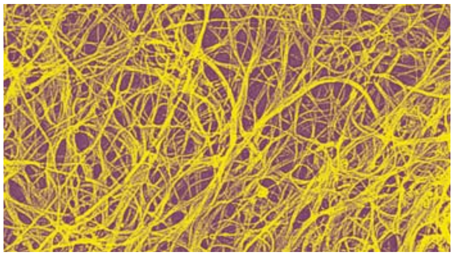

Fig. 1. Network of purified CNT ropes from prepared dispersion/ink. *Source for graphics: Eikos Inc., Franklin, Mass.*

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Nanotechnology

World's smallest nanobrush

Brushes with CNT (carbon nanotube) bristles grafted on fiber handles have been created by Anyuan Cao and colleagues at Rensselaer Polytechnic Institute in Troy, N.Y., and the Univ. of Hawaii, Manoa.

The brushes clean nanoparticles from narrow spaces, act as movable electromechanical brush contacts and switches, and perform other tasks. The bristles (Fig. 1) can also be chemically functionalized for selective removal of heavy metal ions. The brush's handle consists of a SiC fiber (16-µm dia) and its bristles are aligned MWNTs (multi-walled carbon nanotubes) grafted on the fibers' ends. The tubes (30-nm dia) are grown by selective CVD (chemical vapor deposition) with ferrocene and xylene as the precursors.

Various styles of brushes are obtained by designing an Au (gold) mask area on SiC fibers and varying growth conditions. A double-ended brush (different bristle geometries and spans on each end) is produced by masking Au on the middle portion of the fiber. Brushes with multiple bristles regularly distributed along the handle are fabricated by patterning a Au mask along the fiber.

The work is reported in the July 2005 issue of *Nature Materials.*

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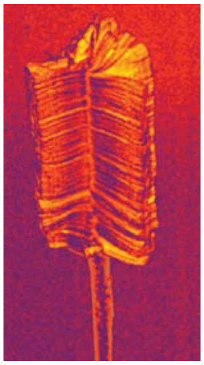

Fig. 1. Bristles' length: 60 µm; spans >300 µm along handle. *Source: Anyuan Cao, Rensselaer Polytechnic Institute, Troy, N.Y.*

BUSINESS NEWS

Japan-based **Sharp Corp.** (www.sharp-world.com) has developed a method to treat semiconductor plant wastewater that combines a micro-organism treatment with nanotech, reducing nitrogen content in chip plant wastewater by 90% without sludge.

NAPOLEON (www.ehu.es/napoleon), an international project launched by the European Commission with 21 teams from 8 countries and 9 companies, will transform polymer nanoparticles into coatings, adhesives, and cosmetics products.

HL Planartechnik (www.hlplanar.de), Germany, reports $15 million in annual revenues with ~50% of their business coming from inclination sensors.

The American Academy of Nanomedicine (www.nanomedacademy.org), an international society devoted to nanomedicine, has launched in Washington, D.C. Its First Annual Meeting will be at Johns Hopkins Univ., Baltimore, on Aug. 15-16, 2005.

The Intl. and North Coast Nanotechnology Business Idea Competitions (www.tiime.case.edu) is accepting submissions for its 2005 event, which awards winners $150,000 for business ideas that will commercialize nanotechnology research being done worldwide.

Flexible transparent circuits

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CNTs are an identified carbon allotrope, consisting of tubular single graphite sheets with a helical structure. They are not found in nature as individual tubes but as an assembly of tubes to form a rope, which only occurs for small diameter CNTs and is the result of Van der Waals attractions between the side walls of each tube. By controlling their rope assembly, a layer with a unique morphology can be formed and exploited to yield electrically conductive networks. CNTs exhibit extraordinary properties—high electrical and thermal conductivity and extreme strength and flexibility.

Researchers at Eikos Inc. in Franklin, Mass., discovered that highly transparent conductive films can be formed from thin CNT layers deposited from water-based dispersions. Their optoelectronic properties improve dramatically with increased CNT purity and proper control of rope morphology (Fig. 1, page 1).

The highest quality CNT films result in ~90% visible light transmittance and ~200 Ω/□ sheet resistance—comparable with commercial sources of sputtered ITO on plastic film. CNT-based films exhibit superior mechanical reliability vs ITO and are formed using atmospheric, low-temperature wet coating/printing techniques, making them an alternative to ITO for applications requiring low costs, large areas, and flexibility.

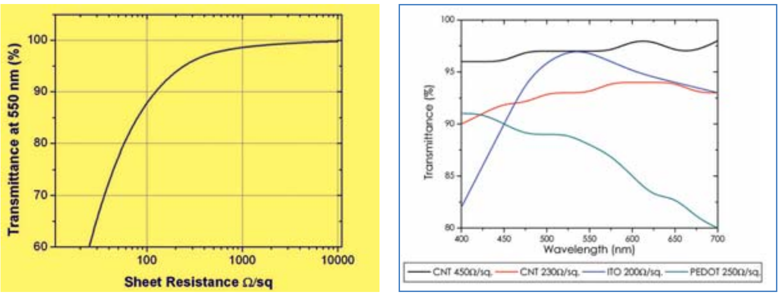

Fig. 2. ***A)*** Optoelectronic performance of CNT coatings. ***B)*** Optical transmittance vs wavelength for CNT, ITO, and PEDOT coating on PET film.

Optoelectronic properties

Fig. 2A (above) shows a plot of optical transmittance (%T) vs sheet resistance (Ω/□) for Invisicon CNT coatings. Optical measurements were made at λ=550 nm and sheet resistance measurements taken using a four-point probe with correction factors for geometry. The optical transparency of >95%T can be achieved for sheet resistance values >1,000 Ω/□. This high-transmission region of performance in the 10^3-10^5 Ω/□ range is important for applications like touch screens and reflective displays and is not possible using ITO or PEDOT/PSS coatings.

Fig. 2B shows visible light transmittance of ITO, PEDOT, and CNT films—transmittance values refer to the transparent conductor layer (substrate contribution removed). The curves for the CNT coatings in the visible light spectrum are flatter than ITO, which shows stronger absorbance at the shorter wavelengths (characteristic yellow color). The Invisicon CNT films have a neutral color, an advantage for display applications.

Mechanical reliability

One key difference between other transparent conductors and those fabricated from CNT are in the mechanical properties. The CNT layer can be formed by spraying CNT ink onto a substrate at room temperature. Once dried, a network of CNT ropes self-assemble on the substrate surface, resulting in a porous coating wherein the CNTs occupy ~50% of a layer's volume. This structure enables infiltration down to the substrate with a variety of materials selected to provide environmental, mechanical, or optical properties suited for the final application. For example, a CNT-coated PET film placed under uniaxial strain of up to 300% shows no signs of failure as measured by change in resistivity. However, when ITO-coated PET is strained, the onset of cracks in the film occurs at ~2.5% strain with ITO failing catastrophically well before 5% tensile strain is reached.

Cyclic loading tests were conducted at Brown Univ. in Providence, R.I., using a roll fatigue tester—a film sample is bent 300° around a 19-mm mandrel repeatedly while monitoring electrical resistivity. The commercial grades of ITO started to crack within the first 100 cycles. As flex cycling continued, the cracks grew, leading to catastrophic failure (open circuit) at ~6,000 cycles. The CNT films showed no signs of cracking until ~27,000 cycles with failure observed at >32,000 cycles. To put the CNT performance into perspective, 25,000 cycles are equivalent to ~7 yrs of use for a roll-out flexible display device used 10×/day. More impressive is the CNT film's ability to withstand a 180º folding to a crease while maintaining electrical resistance of the transparent circuit.

Most applications for transparent conductive coatings require some degree of abrasion resistance to survive handling during manufacturing and use. On plastic substrates, poor abrasion resistance leads to reduced optical and electrical performance. The poor abrasion resistance of ITO films is attributed to imperfections in the film initiating cracks, crack propagation, and delamination. This failure mechanism is not observed for the CNT-coated films, which exhibit high-abrasion resistance dominated by the binder properties, not the conductive layer. The binder or top coating can be selected to encapsulate the CNT layer or infiltrate the CNT network, leaving the surface electrically conductive. It is also known that conducting polymers suffer from poor abrasion resistance due to their low modulus and adhesion to substrates.

CNT circuit fabrication

Here, three methods for fabricating transparent circuits and electrodes from CNTs are described. In the approaches, a two-step coating method is deployed whereby the CNT layer forms first, followed by a polymeric binder topcoat. This results in superior optoelectronic properties and enables the use of simple subtractive methods for forming circuits. Additive processes are also possible using direct deposition of CNT by injection or printing technologies that form a pattern.

One of the simplest methods to form circuits is to feed PET (polyethylene terephtalate) film into an office laser jet printer, printing a negative image of a circuit. A CNT layer is deposited over this image by a wet coating method such as spraying, but other techniques can be used. The negative image is removed with organic solvents resolving a patterned CNT layer, and additionally the polymeric topcoat is applied to protect the CNT circuit.

In a second method, the CNT film is deposited over the entire substrate surface and then a binder is printed. The unprotected CNT regions are rinsed away in a water/surfactant solution. The two techniques that have been successful for printing binder are screen- and inkjet printing, but other methods are possible.

The third method directly prints the CNT coating. Currently, several methods are being studied—inkjet, focused beam spray, screen printing, gravure roll printing, and others. This approach has the least waste and the simplest manufacturing flow.

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Paul Glatkowski (pglatkowski@eikos.com), VP, is the inventor of Invisicon transparent conductive coatings and holds patents in this and related CNT technologies.

Philip Wallis (pwallis@eikos.com), technical director, is an inks expert and holds patents related to ink and ink flow control systems.

Michael Trottier (mtrottier@eikos.com), senior scientist, has contributed to numerous papers on the characterization of single-walled carbon nanotubes and piezoelectric composites.