Nanotubes on Display: How Carbon Nanotubes Can Be Integrated into Electronic Displays

Justin Opatkiewicz, Melburne C. LeMieux, and Zhenan Bao*

Stanford University, 381 North-South Mall, Stanford, California 94305

ABSTRACT Random networks of single-walled carbon nanotubes show promise for use in the field of flexible electronics. Nanotube networks have been difficult to utilize because of the mixture of electronic types synthesized when grown. A variety of separation techniques have been developed, but few can readily be scaled up. Despite this issue, when metallic percolation pathways can be separated out or etched away, these networks serve as high-quality thin-film transistors with impressive device characteristics. A new article in this issue illustrates this point and the promise of these materials. With more work, these devices can be implemented in transparent displays in the next generation of hand-held electronics.

In the age of hand-held portable electronics, the need for robust, lightweight materials becomes increasingly important. Of particular concern are conductive films that are optically transparent and yield adequate, reproducible, and uniform electronic properties for display applications. A variety of materials have been analyzed for such conductive films,[1−3] and single-walled carbon nanotube networks (SWNTnts) have shown the most promise. Although they can become slightly p-doped in air, single-walled carbon nanotubes (SWNTs) are stable in ambient conditions and can yield reproducible electronic characteristics. Devices composed of SWNTs can obtain extremely high mobilities and ON/OFF ratios, while network devices can yield characteristics that are competitive with amorphous Si.[4,5] Of critical importance is the ability of these nanotubes to operate at low voltages and have low threshold voltages (a major setback for most organic semiconducting materials).[5] Finally, the flexibility and strength of carbon nanotubes (CNTs) makes them the most logical candidate for use in flexible displays and electronics. CNTs have not yet been implemented in practical device architectures primarily because of the difficulty in device fabrication (uniformity over large areas) and processing. Despite the impressive properties of single-tube devices, they are difficult to fabricate and virtually impossible to scale up. In addition, as-grown nanotubes are typically a mixture of semiconducting and metallic types. Researchers have documented methods of preferentially growing one type *versus* the other, but no synthetic method yields 100% of one type and yield is relatively low.[6] Purification techniques such as density gradient ultracentrifugation,[7] polymer wrapping,[8] electrical breakdown of metallic tubes,[9] surface sorting,[10] and others[11−15] have been shown to be moderately successful, but most are difficult for scale up or some may drastically alter the electronic properties of the purified tubes. As Kim *et al.* show in their article in this issue, these problems can be readily solved by the use of nanotube networks where the range of electronic behaviors can be averaged out.[16] These networks lose the phenomenal electronic properties of individual nanotubes but can carry significantly higher currents and can readily be scaled up. The network enables multiple percolation pathways between source and drain, and hence, the greater the density of SWNTs, the higher the maximum current. This density reduces the mobility of the film due to the large number of tube−tube junctions, but the resulting devices can still have mobilities greater than 1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$, which is competitive with amorphous Si and, hence, usable in electronic displays. To maximize the current density of the network, the alignment (or randomness) of the SWNTs can be altered. As shown by Pimparkar *et al.*, the degree of alignment can dramatically influence the performance of the network device.[17] A similar trend was observed with spin-assembled SWNTnts.[18,19] Whereas alignment is important in reducing carrier path lengths and hence improving mobilities, perfect alignment reduces the number of percolating paths, requiring a significantly higher density of SWNTs in the network. The higher the density of the network, the higher the probability of a purely metallic percolation pathway, which would short the entire device.

Subsequently, the primary restriction with the use of as-grown random SWNTnts is the presence of these percolating metallic pathways. As noted above, electrical breakdown/burnoff of metallic single-walled carbon nanotubes (M-SWNTs) can

See the accompanying Article by Kim *et al.* on p 2994.

*Address correspondence to zbao@stanford.edu.

10.1021/nn101092d

> These networks lose the phenomenal electronic properties of individual nanotubes but can carry significantly higher currents and can readily be scaled up.

be used,[9] but the electrical fields required cannot realistically reach an industrial scale. A more practical method, as discussed by Pimparkar *et al.* and Ryu *et al.*[20] and utilized by Kim *et al.*,[16] is the striping technique, wherein the random SWNTnt is etched into individual stripes to cut off these metallic pathways. In the article by Kim *et al.*, strips of 5 μm width separated by spacings of 2 μm are fabricated by photoresist deposition and oxygen plasma exposure. The strip width is chosen based on percolation theory. Depending on the length distribution and density of the nanotube network, a metallic percolation pathway could develop that spans the channel length. Due to the random growth, this percolation path will likely span a certain amount of the channel width, as well. By etching the device channel into short strips, these conducting pathways are broken, leaving primarily semiconducting strips. The strip and gap widths are optimized to break all metallic pathways while still maximizing the semiconducting pathways to maximize current carrying capacity. Upon optimizing this process, Kim *et al.* were able to fabricate devices consistently with ON/OFF ratios $>10^3$ ON currents around -2.5 μA, mobility around 20 $cm^2\ V^{-1}\ s^{-1}$, and threshold voltage around -0.5 V. The authors claim that 90% of devices fabricated yielded similar results, deviating by roughly 10%. This shows some promise given that reproducibility has often been an issue for random SWNTnt devices.

To date, random networks of carbon nanotubes have been utilized in a variety of applications, most of which have simultaneously exploited their transparency and their conductivity as an electrode material. In these applications, the efforts to cut off metallic pathways are abandoned entirely in order to maximize the current density of the film. High densities of nanotubes (which can be multiwalled, single-walled, or bundled) are grown or deposited to allow for a large number of conductive percolation paths. The conductivity and optical transmittance are inversely related and must be balanced by tuning the nanotube film density and thickness. A thicker, higher density nanotube network produces a more conductive film but absorbs more light; sparse networks can yield extremely high transmittance but low conductivity, as shown in Figure 1. High conductivity and high transmittance are crucial for use in organic photovoltaic electrode material. Optical transparency allows photons to reach the active material, whereas high conductivity is necessary to collect the positive charge carriers fully and to increase solar cell efficiency. Film smoothness can be an issue in this case, as stray tubes penetrating the active material can short the cell.[22] Conducting nanotube films have also been implemented in organic light-emitting diode (OLED) displays, typically acting as the anode material. Such devices can obtain high transmittance, high flexibility, and high luminescence, as shown by Li *et al.*[23] and Sekitani *et al.*[24] (see Figure 2).

Most efforts in utilizing SWNTnts as transistor materials are carried out using solution processing—dispersing the nanotubes in solvents or polymers, followed by deposition on rigid or flexible substrates.[4,22,25] Similar to as-grown networks, the striping technique, as described above, can be used to improve the performance of high-density networks. Efforts to separate the nanotubes in solution typically leave the nanotubes dirty or defective, which can

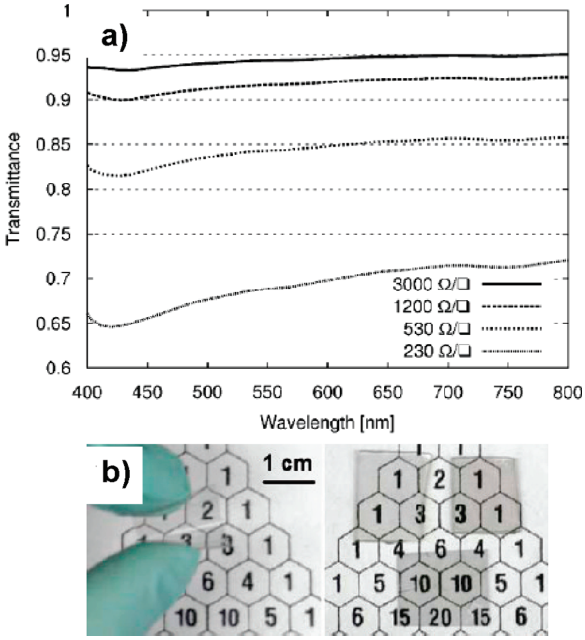

Figure 1. Transmittance *vs* conductivity. (a) Transmittance of spray-coated SWNTnt layers with different thicknesses. Note that increasing thickness reduces sheet resistance (increases conductivity) but reduces transmittance. Reproduced with permission from ref 4. Copyright 2007 Elsevier. (b) rr-P3HT:CNT composite films on PET (left) and glass (right). Reproduced with permission from ref 21. Copyright 2009 American Chemical Society.

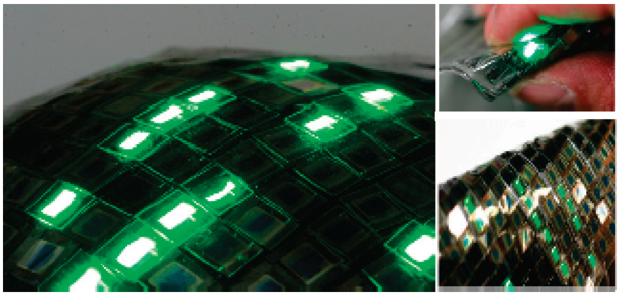

Figure 2. Ultimate goal: LED displays on a flexible substrate. Nanotubes are used as a conductive ink embedded in a conducting rubber in a two-organic transistor, one-capacitor (2TIC) driving cell. Reproduced with permission from ref 24. Copyright 2007 Nature Publishing Group.

dramatically limit the eventual transistor performance. Polymer dispersion/wrapping has promise in separating the nanotubes, but subsequent purification of this composite to obtain the separated nanotubes from the polymer can be extremely difficult.[8] Recent efforts to separate the SWNTs during deposition by exploiting molecular interactions with organic functional groups have shown some promise.[10,18,19,25] In this surface sorting technique, the SWNTnts are deposited and aligned from solution *via* spin assembly on amine-coated surfaces to produce moderately pure semiconducting networks (aromatic surfaces produce metallic networks). The process yields high-quality and reproducible network devices and can be readily applied to flexible substrates.

The plastic substrates to be used present a problem for most processing of these networks. These substrates cannot survive the temperatures required for the chemical vapor deposition growth of the SWNTnt or the oxygen plasma treatment in the striping technique. For this reason, most work with SWNTnts on flexible substrates requires the use of solution-processed nanotubes, which produces its own set of problems: choice of solvent,[26] purification from catalyst,[27] deposition technique,[10] separation,[12] and so on. Research is ongoing to solve each problem. Alternatively, transfer printing of these SWNTnt stripes from quartz to plastic could side step these problems even though it is more difficult to scale up. The transfer method has been shown to yield highly reproducible results with minimal to no damage to the original device network.[28−31] Despite their past difficulties, the hope of adequately integrating SWNTnts into modern devices seems to have come to fruition. High-quality active-matrix OLED thin-film transistor circuits can be fabricated and utilized in OLED pixels. Perhaps within the next decade, these nanotube networks will find themselves in the displays of the next generation of hand-held electronic devices.

Despite their past difficulties, the hope of adequately integrating SWNTnts into modern devices seems to have come to fruition.

Acknowledgment. Carbon nanotube research in the Bao group is supported by the National Science Foundation (NSF) ECCS 0901414, the Center for Advanced Molecular Photovoltaics (Award No. KUS-C1-015-21) made by King Abdullah University of Science and Technology (KAUST), Stanford Global Climate & Energy Program (GCEP), Samsung Advanced Research Institute, and Intel.

REFERENCES AND NOTES

1. Zhou, L.; Wanga, A.; Wu, S.-C.; Sun, J.; Park, S.; Jackson, T. N. All-Organic Active Matrix Flexible Display. *Appl. Phys. Lett.* **2006**, *88*, 083502.
2. Ju, S.; Facchetti, A.; Xuan, Y.; Liu, J.; Ishikawa, F.; Ye, P.; Zhou, C.; Marks, T. J.; Janes, D. B. Fabrication of Fully Transparent Nanowire Transistors for Transparent and Flexible Electronics. *Nat. Nanotechnol.* **2007**, *2*, 378–384.
3. Cao, Q.; Kim, H.; Pimparkar, N.; Kulkarni, J. P.; Wang, C.; Shim, M.; Roy, K.; Alam, M. A.; Rogers, J. A. Medium-Scale Carbon Nanotube Thin-Film Integrated Circuits on Flexible Plastic Substrates. *Nature* **2008**, *454*, 495–500.
4. Schindler, A.; Brill, J.; Fruehauf, N.; Novak, J. P.; Yaniv, Z. Solution-Deposited Carbon Nanotube Layers for Flexible Display Applications. *Physica E* **2007**, *37*, 119–123.
5. Snow, E. S.; Campbell, P. M.; Ancona, M. G.; Novak, J. P. High-Mobility Carbon-Nanotube Thin-Film Transistors on a Polymeric Substrate. *Appl. Phys. Lett.* **2005**, *86*, 33105.
6. Li, Y.; Mann, D.; Rolandi, M.; Kim, W.; Ural, A.; Hung, S.; Javey, A.; Cao, J.; Wang, D.; Yenilmez, E.; Wang, Q.; Gibbons, J. F.; Nishi, Y.; Dai, H. Preferential Growth of Semiconducting Single-Walled Carbon Nanotubes by a Plasma Enhanced CVD Method. *Nano Lett.* **2004**, *4*, 317–321.
7. Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. Sorting Carbon Nanotubes by Electronic Structure Using Density Differentiation. *Nat. Nanotechnol.* **2006**, *1*, 60–65.
8. Yi, W.; Malkovskiy, A.; Chu, Q.; Sokolov, A. P.; Colon, M. L.; Meador, M.; Pang, Y. Wrapping of Single-Walled Carbon Nanotubes by a π-Conjugated Polymer: The Role of Polymer Conformation-Controlled Size Selectivity. *J. Phys. Chem. B* **2008**, *112*, 12263–12269.
9. Collins, P. G.; Arnold, M. S.; Avouris, P. Engineering Carbon Nanotubes and Nanotube Circuits Using Electrical Breakdown. *Science* **2001**, *292*, 706–709.
10. LeMieux, M. C.; Roberts, M.; Barman, S.; Jin, Y. W.; Kim, J. M.; Bao, Z. Self-Sorted, Aligned Nanotube Networks for Thin-Film Transistors. *Science* **2008**, *321*, 101–104.
11. Kanungo, M.; Lu, H.; Malliaras, G. G.; Blanchet, G. B. Suppression of Metallic Conductivity by Single-Walled Carbon Nanotubes by Cycloaddition Reactions. *Science* **2009**, *323*, 234–237.
12. Chattophadhyay, D.; Galeska, I.; Papadimitrakopoulos, F. A Route for Bulk Separation of Semiconducting from Metallic Single-Wall Carbon Nanotubes. *J. Am. Chem. Soc.* **2003**, *125*, 3370–3375.
13. Zheng, M.; Jagota, A.; Semke, E. D.; Diner, B. A.; McLean, R. S.; Lustig, S. R.; Richardson, R. E.; Tassi, N. G.

DNA-Assisted Dispersion and Separation of Carbon Nanotubes. *Nat. Mater.* **2003**, *2*, 338–342.

14. Krupke, R.; Hennrich, F.; von Lohneysen, H.; Kappes, M. Separation of Metallic from Semiconducting Single-Walled Carbon Nanotubes. *Science* **2003**, *301*, 344–347.
15. Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization. *Science* **2003**, *301*, 1519–1522.
16. Kim, S.; Kim, S.; Park, J.; Ju, S.; Mohammadi, S. Fully Transparent Pixel Circuits Driven by Random Network Carbon Nanotube Transistor Circuitry. *ACS Nano* **2010**, *4*, 2994–2998.
17. Pimparkar, N.; Kumar, S.; Cao, Q.; Rogers, J. A.; Murthy, J. Y.; Alam, M. A. Limits of Performance Gain of Aligned CNT Over Randomized Network: Theoretical Predictions and Experimental Validation. *IEEE Electron Device Lett.* **2007**, *28*, 593–595.
18. LeMieux, M. C.; Sok, S.; Roberts, M. E.; Opatkiewicz, J. P.; Liu, D.; Barman, S. N.; Patil, N.; Mitra, S.; Bao, Z. Solution Assembly of Organized Carbon Nanotube Networks for Thin-Film Transistors. *ACS Nano* **2009**, *3*, 4089–4097.
19. Opatkiewicz, J. P.; LeMieux, M. C.; Bao, Z. Influence of Electrostatic Interactions on Spin-Assembled Single-Walled Carbon Nanotube Networks on Amine-Functionalized Surfaces. *ACS Nano* **2010**, *4*, 1167–1177.
20. Ryu, K.; Badmaev, A.; Wang, C.; Lin, A.; Patil, N.; Gomez, L.; Kumar, A.; Mitra, S.; Wong, H.-S. P.; Zhou, C. CMOS-Analogous Wafer-Scale Nanotube-on-Insulator Approach for Submicrometer Devices and Integrated Circuits Using Aligned Nanotubes. *Nano Lett.* **2009**, *9*, 189–197.
21. Hellstrom, S. L.; Lee, H. W.; Bao, Z. Polymer-Assisted Direct Deposition of Uniform Carbon Nanotube Bundle Networks for Networks for High Performance Transparent Electrodes. *ACS Nano* **2009**, *3*, 1423–1430.
22. Rowell, M. W.; Topinka, M. A.; McGehee, M. D.; Prall, H.-J.; Dennler, G.; Sariciftci, N. S.; Hu, L.; Gruner, G. Organic Solar Cells with Carbon Nanotube Network Electrodes. *Appl. Phys. Lett.* **2006**, *88*, 233506.
23. Li, J.; Hu, L.; Wang, L.; Zhou, Y.; Gruner, G.; Marks, T. J. Organic Light-Emitting Diodes Having Carbon Nanotube Anodes. *Nano Lett.* **2006**, *6*, 2472–2477.
24. Sekitani, T.; Nakajima, H.; Maeda, H.; Fukushima, T.; Aida, T.; Hata, K.; Someya, T. Stretchable Active-Matrix Organic Light-Emitting Diode Display Using Printable Elastic Conductors. *Nat. Mater.* **2009**, *8*, 494–499.
25. Roberts, M. E.; LeMieux, M. C.; Sokolov, A. N.; Bao., Z. Self-Sorted Nanotube Networks on Polymer Dielectrics for Low-Voltage Thin-Film Transistors. *Nano Lett.* **2009**, *9*, 2526–2531.
26. Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. Dissoltion of Small Diameter Single-Wall Carbon Nanotubes in Organic Solvents. *Chem. Commun.* **2001**, *2*, 193–194.
27. Shen, K.; Curran, S.; Xu, H.; Rogelj, S.; Jiang, Y.; Dewald, J.; Pietrass, T. Single-Walled Carbon Nanotube Purification, Pelletization, and Surfactant-Assisted Dispersion: A Combined TEM and Resonant Micro-Raman Spectroscopy Study. *J. Phys. Chem. B* **2005**, *109*, 4455–4463.
28. Ding, L.; Tselev, A.; Wang, J.; Yuan, D.; Chu, H.; McNicholas, T. P.; Li, Y.; Liu, J. Selective Growth of Well-Aligned Semiconducting Single-Walled Carbon Nanotubes. *Nano Lett.* **2009**, *9*, 800–805.
29. Kang, S. J.; Kocabas, C.; Kim, H.-S.; Cao, Q.; Meitl, M. A.; Khang, D.-Y.; Rogers, J. A. Printed Multilayer Superstructures of Aligned Single-Walled Carbon Nanotubes for Electronic Applications. *Nano Lett.* **2007**, *7*, 3343–3348.
30. Ishikawa, F. N.; Chang, H.-K.; Ryu, K.; Chen, P.-C.; Badmaev, A.; De Arco, L. G.; Shen, G.; Zhou, C. Transparent Electronics Based on Transfer Printed Aligned Carbon Nanotubes on Rigid and Flexible Substrates. *ACS Nano* **2009**, *3*, 73–79.
31. Vosgueritchian, M.; LeMieux, M. C.; Bao, Z. In preparation.