

Fabrication and Characterization of Thin Films of Single-Walled Carbon Nanotube Bundles on Flexible Plastic Substrates

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We describe an extremely simple method by which one can obtain thin, strongly adherent films of single-walled nanotube (SWNT) bundles on flexible, transparent plastic substrates such as poly(ethylene terephthalate) (PET: “overhead transparency”). These films show low sheet resistance, >80% optical transparency and robust flexibility, e.g., they can be bent and folded to a crease while retaining full electrical connection across the crease.¹ We believe this could open new opportunities in the design and development of next-generation transparent optoelectronic devices.

Carbon nanotubes (CNTs) are attractive materials for use in chemical and biological sensors,² although considerable challenges remain in being able to process them into films that can be tailored to a specific end use. For example, CNT “electrodes” can be made directly as free-standing films (CNT paper),² by casting CNT-sulfuric acid dispersions on glassy carbon surface,³ or by physically mixing Teflon with CNT.⁴ These electrode designs are, in principle, not immediately suited for the construction of flexible electronic devices. We believe the present study addresses some of these challenges and describes a method for obtaining any desired pattern of films of SWNT bundles on flexible insulating surfaces which may then be used for a variety of device applications, e.g., field-effect transistors (FET), sensors, etc.

Our results also suggest that these films show potential as viable alternatives to commercial transparent conductors. Transparent (inorganic) oxide semiconductors (TOSs) are employed in a variety of device architectures in optoelectronic applications⁵ where the optically transparent and highly conductive indium tin oxide (ITO), has enjoyed widespread use. Films of ITO can be readily obtained on glass and plastics, although even on plastics, the inherent brittleness of ITO severely limits film flexibility (see below). Alternatively, thin films of metals such as Ag, Au, etc., on flexible plastic substrates suffer from loss of optical transparency.^{6,7} Conducting coatings of doped electronic polymers, e.g. poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic) acid (PEDOT·PSS) show promise,⁸ although most organic electronic polymers are not stable above ~200 °C in air.⁹

Using the previously described Line Patterning method,¹⁰ films of SWNT bundles on PET (SWNT/PET) can be deposited in a wide variety of patterns. We observed that best results were obtained using chemically purified mixture of metallic and semiconducting SWNT bundles obtained by pulsed-laser ablation (laser-SWNT)¹¹ dispersed in an aqueous solution of Triton-X 100.² Aqueous dispersions of SWNT bundles made from charged surfactants such as sodium or lithium dodecyl sulfate (SDS, LDS) or cetyl trimethylammonium bromide (CTAB) do not yield highly conducting and/or strongly adhering films on PET.

In a typical procedure, a PET film (with or without a pattern) is immersed in a beaker containing the SWNT dispersion for ~0.5 min, removed, and air-dried at room temperature for ~5 min. Bath sonication in toluene for ~10 s removes any toner lines (in patterned

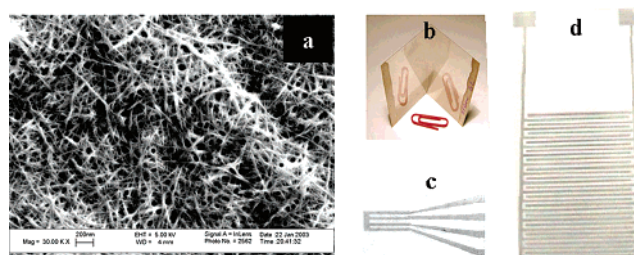


Figure 1. (a) SEM of SWNT bundles on PET. (b) Creased carbon nanotube provided by Eikos, Inc. (c) “4-Probe pattern”. (d) Interdigitated “finger pattern”.

samples) and also any residual Triton-X 100 surfactant.¹¹ This process can be repeated to obtain thicker films.

We observed that while bath sonication removed the toner lines cleanly, the film of SWNT bundles remained strongly adherent to the PET surface, passing a laboratory Scotch-tape test.¹² The reasons for the strong adhesion of the SWNT bundles to the PET surface are not clear, although the surface morphology of the PET appears to be playing a key role, e.g., PET whose surface had been modified (e.g. “overhead transparency” with special coatings for color printing, etc.) yield poorly adhering films. The resolution of the lines is limited solely by the resolution of the printer. By using a standard office laser printer we have been able to readily obtain films of SWNT with lines ~50 μm apart.

The SEM image of a film of laser-SWNT/PET reveals a dense cluster of randomly distributed fiber bundles of average diameter 20–30 nm (Figure 1). Depending on the end-use, any desired pattern may be readily obtained, e.g. the “channel pattern” for fabricating plastic FET-type devices, the interdigitated “finger pattern” for liquid crystal displays,¹⁰ and the “4-probe pattern” for gas and analyte sensors (Figure 1). Using the “channel pattern” we have recently observed transistor characteristics in an all-organic FET-type device where both the channel and gate electrodes were composed entirely of laser-SWNT bundles on PET.

The elemental compositions of the various types of SWNT bundles used in this study are as follows: *Purified laser-SWNT*: C: 84.43; H: 1.26; N: 0.20; O: 9.61; Co: 1.49; Ni: 1.40; Total: 98.39. *HiPco-SWNT*: C: 61.05; Fe: 37.98; Total: 99.03. *Purified HiPco-SWNT*: C: 86.77; H: 1.16; N: 0.50; O: 4.62; Fe: 5.78; Total: 98.83. A significant amount of metallic catalyst residues are found in all samples. In addition, oxygen impurity levels are high in all “purified” samples, presumably from carboxylate groups introduced during treatment with highly oxidizing acids.¹² It is, however, to be pointed out that chemically purified SWNT bundles adhere more strongly to the PET surface compared to “as synthesized” samples. It is possible that the adhesion of the SWNT bundles to the PET surface could be related to interaction between Triton-X 100 and the oxygen-containing species introduced during the purification step.

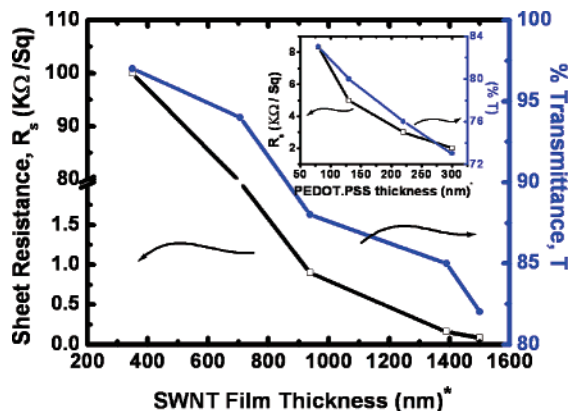


Figure 2. Comparison of sheet resistance and optical transparency between films of laser-SWNT/PET, PEDOT·PSS/PET. *Film thickness measured using atomic force microscopy (AFM).

The room-temperature four-probe DC conductivity of films of laser-SWNT/PET ($\sigma \approx 50$ S/cm) was approximately the same order of magnitude as films of PEDOT·PSS/PET, albeit lower than those of ITO/PET ($\sigma \approx 1500$ S/cm).¹³ Films of laser-SWNT/PET were significantly *more optically transparent* than films of both PEDOT·PSS/PET and ITO/PET (Figure 2) at the same sheet resistance. For example, the optical transparency (% T) of ~ 300 -nm thick films of both PEDOT·PSS/PET and ITO/PET was ~ 70 , while those of laser-SWNT/PET, ~ 95 .

The higher optical transparency of films of laser-SWNT/PET permits one to compensate for their lower conductivity by using thicker films, e.g. an ~ 1500 -nm thick film of laser-SWNT/PET afforded a sheet resistance (R_s) of ~ 80 Ω /sq and % T of ~ 80 . Similar values are observed for commercial ITO/PET films ($R_s \approx 60$ – 90 Ω /sq, % $T \approx 80$, film ~ 300 -nm thick). In contrast, in the best commercial films of PEDOT·PSS/PET sheet resistance was ~ 350 Ω /sq, and optical transparency $\sim 80\%$.⁸

As many commercial optoelectronic applications require a sheet resistance of <100 Ω /sq, the results obtained for films of laser-SWNT/PET are quite encouraging. It is to be pointed out that the laser-SWNT bundles themselves are mixtures of metallic and semiconducting tubes, and as methods to separate the two become available, we believe one can readily Line Pattern carbon nanotube films with significantly lower sheet resistance.¹⁴

In addition to displaying high optical transparency and low sheet resistance, films of laser-SWNT/PET are also significantly more flexible than commercial films of ITO/PET. Surprisingly, they can be bent all the way and creased with a thumb nail without a significant change in resistance (Figure 3). In contrast, films of ITO coated on PET (Mylar) become essentially insulating upon similar bending and creasing.¹⁵ We believe this leads to opportunities in the simple and rapid construction of flexible electronic circuits and devices.

In conclusion, we present for the first time, a convenient method to obtain patterns of films of carbon nanotubes on plastics using Line Patterning. Electronically conductive films of laser-SWNT bundles on PET are optically *more transparent* than commercial

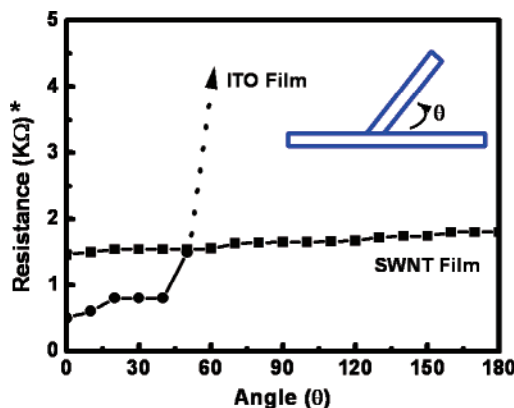


Figure 3. Flexibility of an ~ 1200 -nm thick film of laser-SWNT/PET vs ITO/PET.¹³ *Two-probe resistance.

films of both ITO and PEDOT·PSS on PET. In addition, these films show robust flexibility and *do not crack/break upon bending and creasing*. The ease with which these films may be obtained permits one to fabricate, simply and rapidly, transparent electronic devices such as FETs and sensors. The combination of high thermal stability (>1000 $^\circ\text{C}$), good adhesion, high optical transparency ($>80\%$), low sheet resistance (<100 Ω /sq), and robust flexibility of films of laser-SWNT could lead to important advances in the design and development of flexible optoelectronic devices in general and to their use as alternatives to commercial ITO films in particular.

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References

- (1) Nomura, K.; Ohta, H.; Ueda, K.; Kamiya, T.; Hirano, M.; Hosono, H. *Science* **2003**, *300*, 1269–1272.
- (2) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787–792.
- (3) Zhao, Q.; Gan, Z.; Zhuang, Q. *Electroanalysis* **2002**, *14*, 1609–1613.
- (4) Wang, J.; Musameh, M. *Anal. Chem.* **2003**, *75*, 2075–2079.
- (5) Romeo, N.; Bosio, A.; Canevari, V.; Terheggen, M.; Vaillant Roca, L. *Thin Solid Films* **2003**, *431*, 364–368.
- (6) Henry, A. C.; McCarley, R. L. *J. Phys. Chem. B* **2001**, *105*, 8755–8761.
- (7) Abate, K. *Chemist* **2001**, *78*, 9–13.
- (8) Louwet, F.; Groenendaal, L.; Dhaen, J.; Manca, J.; Van Luppen, J.; Verdonck, E.; Leenders, L. *Synth. Met.* **2003**, *135–136*, 115–117.
- (9) Kudoh, Y.; Akami, K.; Matsuya, Y. *Synth. Met.* **1998**, *98*, 65–70.
- (10) Hohnholz, D.; MacDiarmid, A. G. *Synth. Met.* **2001**, *121*, 1327–1328.
- (11) Lu, J.; Pinto, N. J.; MacDiarmid, A. G. *J. Appl. Phys.* **2002**, *92*, 6033–6038.
- (12) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C. B.; Rodriguez-Macias, F. J.; Boul, P. J.; Lu, A. H.; Heymann, D.; Colbert, D. T.; Lee, R. S.; Fischer, J. E.; Rao, A. M.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A* **1998**, *A67*, 29–37. Cinke, M.; Li, J.; Chen, B.; Cassell, A.; Delzeit, A.; Han, J.; Meyyappan, M. *Chem. Phys. Lett.* **2002**, *365*, 69–74.
- (13) Al-Dahoudi, N.; Aegerter, M. A. *J. Sol.-Gel Sci. Technol.* **2003**, *26*, 693–697.
- (14) Alternatively, even lower sheet resistance might be observed with coatings made using highly metallic multiwalled carbon nanotubes.
- (15) The limit of flexibility, in diameter, for films of ITO/PET is ~ 13 nm (Bekaert Specialty Films NV-CT-70-ST504-5).

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