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A method of printing carbon nanotube thin films

Yangxin Zhou, Liangbing Hu, and George Grüner^{a)}

Department of Physics and Astronomy, University of California at Los Angeles, Los Angeles, California 90095

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This paper describes a fabrication method for carbon nanotube thin films on various substrates including PET (polyethylene terephthalate), glass, polymethyl-methacrylate (PMMA), and silicon. The method combines a polydimethylsiloxane (PDMS) based transfer-printing technique with vacuum filtration, and allows controlled deposition—and patterning if needed—of large area highly conducting carbon nanotube films with high homogeneity. In the visible and infrared range, the performance characteristics of fabricated films are comparable to that of indium tin oxide (ITO) on flexible substrates. © 2006 American Institute of Physics. [DOI: 10.1063/1.2187945]

Recently there has been growing interest in using carbon nanotube thin films as flexible, transparent, and conducting coatings for applications in optoelectronics.^{1–5} However, controlled deposition of large area highly conducting carbon nanotube films with high homogeneity required for applications remains elusive. Direct deposition using spin coating, spraying, or incubation produces films with conductivity much lower than that of commercially used indium tin oxide (ITO).^{4–7} Deposition by vacuum filtration^{1,2,8} is limited by filters and requires consistent transfer to flat substrates for further applications.

We have developed a fabrication method that allows controlled deposition of large area highly conducting carbon nanotube films with high homogeneity on various substrates, including polyethylene terephthalate (PET), glass, polymethyl-methacrylate (PMMA), and silicon. This method combines a transfer-printing technique based on polydimethylsiloxane (PDMS) stamps⁶ with vacuum filtration.^{1,2,8} In the visible and infrared range, the performance characteristics of fabricated films compare favorably with ITO on flexible plastic substrates. Films can also be printed in patterned fashions for use as building blocks in electronic devices.

To prepare carbon nanotube films, we use commercially available purified arc discharge nanotubes with purity of 70%–90% (Carbon Solutions, Inc.). Powders of carbon nanotubes are dissolved in 1% solution of sodium dodecyl sulfate (SDS) surfactant. Then the solution is bath-sonicated for 16 h and centrifuged for 30 min. Alumina filters (Whatman, Inc.) are used in vacuum filtration.^{1,2,8} After the filtration, the filtered film is rinsed by deionized water to remove SDS surfactant for several minutes until no bubble is seen. The inset of Fig. 1 shows a photo image of a homogeneous nanotube film on a filter with 2 in. diam. The film homogeneity is guaranteed by the filtration because the accumulation of nanotubes on the filters can adjust the filtration rate. To measure the sheet resistance R_s ,¹ we deposit silver paint as contact pads. As shown in Fig. 1, R_s can be varied over a wide range by controlling the used amount of nanotubes. For nanotube films just above the percolation threshold, R_s reduces dramatically with the increase of nanotube amount,¹ while in the region far from the threshold, R_s decreases in-

versely with nanotube amount, as expected for constant conductivity.

PDMS stamps for transfer printing are fabricated by using SYLGARD 184 silicone elastomer kit (Dow Corning, Inc.) with silicon substrates as masters.^{6,9} Patterning of PDMS stamps illustrated in Fig. 2(a), is created by standard optical lithography^{6,9} using SU-8-25 resist (MicroChem, Inc.). To remove nanotube films from the filter, we first make conformal contact between the stamp and the films [Fig. 2(b)]. As soon as the wetting due to the conformal contact is seen, the stamp is raised from the filter and patterned films are transferred onto the stamp [Fig. 2(c)]. Transfer of nanotube films from one surface to another surface is guided by surface energies of the two surfaces.¹⁰ Since nanotube films loosely sit on alumina filters, they can be fully transferred onto the PDMS surface even though PDMS has a low surface energy of 19.8 mJ/m². Even for films with a low sheet resistance of 100 Ω , the leftover on the filter has a resistance larger than 100 M Ω . We note that the same filter can be reused for another film fabrication.

The availability of patterned nanotube films on PDMS stamps [Fig. 2(d)] readily allows them to be printed onto various flat substrates with a higher surface energy, such as PET (44.6 mJ/m²), glass (47 mJ/m²), and PMMA (41 mJ/m²).¹⁰ The surface energy of silicon substrates can

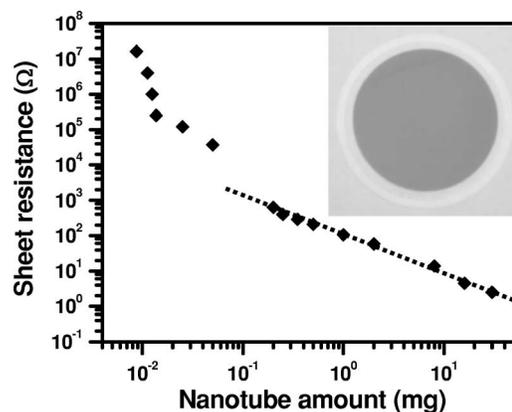


FIG. 1. Sheet resistance R_s of carbon nanotube thin films controlled by the amount of nanotubes. In the region far from the percolation threshold,¹ R_s decreases inversely with the amount of nanotubes as indicated by the dotted line. The inset shows a photo image of a uniform two-in. diameter carbon nanotube film (dark region) on a filter.

^{a)}Electronic mail: ggruner@ucla.edu

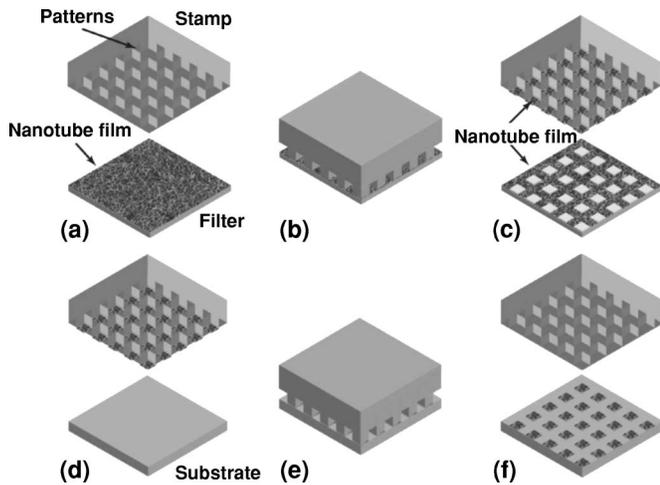


FIG. 2. (a) Illustration of a patterned PDMS stamp and carbon nanotube films made by vacuum filtration. (b) Conformal contact between PDMS stamp and nanotube films on the filter. (c) After the conformal contact, the PDMS stamp is removed from the filter. Patterns of nanotube films are transferred onto the PDMS stamp without any damage. (d) PDMS stamp with patterned nanotube films and a flat receiving substrate. (e) Conformal contact between PDMS stamp and the substrate. (f) PDMS stamp is removed from the substrate after mild heating. All patterned nanotube films on the stamp are fully transferred onto the substrate.

be increased by oxygen plasma cleaning and vapor silanization using 3-(aminopropyl)triethoxysilane (Aldrich, Inc.). To start the transfer, we first contact the PDMS stamp with nanotube films onto the receiving substrate [Fig. 2(e)]. After 10 min of mild heating at 80 °C, all nanotube films on the stamp are transferred onto the receiving substrate by simply removing the stamp from the substrate [Fig. 2(f)]. The PDMS stamp can also be recycled for another film transfer. Figure 3(a) shows a photo image of 1 mm square pattern arrays of nanotube films on a flexible PET substrate. The

smallest pattern size achieved is 20 μm , limited by the SU-8-25 resist used in optical lithography to pattern stamps. Usage of PDMS stamps with smaller feature sizes^{6,9} may lead to patterns of nanotube films with higher resolution.

Figure 3(b) shows a photo image of a transparent and homogeneous film with a 2 in. diam on a flexible PET substrate. Films transferred onto PET, glass slide, and PMMA cannot be removed from substrates by using Scotch Magic tapes. The sheet resistances of transferred films are similar to that of original films on the filters. Figure 3(c) shows an atomic force microscope (AFM) image of a nanotube film with $R_s=200\ \Omega$ on a glass slide. The root-mean-square roughness is 8 nm as estimated from the AFM image. Examining the film edge, we obtain the film thickness of 25 nm, which leads to a conductivity of 2000 S/cm. Similar evaluations of other films lead to conductivities of 1600–2000 S/cm for tested PET, glass, and PMMA substrates. This value exceeds the conductivity of ITO films on PET substrates that is 1500 S/cm,¹¹ while films deposited directly onto various surfaces^{4–7} do not exceed the conductivity value of 500 S/cm. The difference between our results and the results by Rinzler *et al.*² may lie in the fact that our films contain undoped nanotubes. We have, in fact, seen increases by a factor of 3 when doping our films with electron withdrawing species such as NO_2 .¹²

The transfer printing process also allows transfer of submonolayer films onto flat substrates. Figure 3(d) shows an AFM image of a submonolayer thin film with $R_s=100\ \text{k}\Omega$. From the section analysis [Fig. 3(e)] along the black line in the AFM image, the nanotube bundle size is 3–6 nm, which is smaller than the 20 nm bundle size in our early work where the conductivity is only 200 S/cm.¹ A possible reason for the bundle size dependency is that the current flows at the surface of the bundles with little contribution from nanotubes

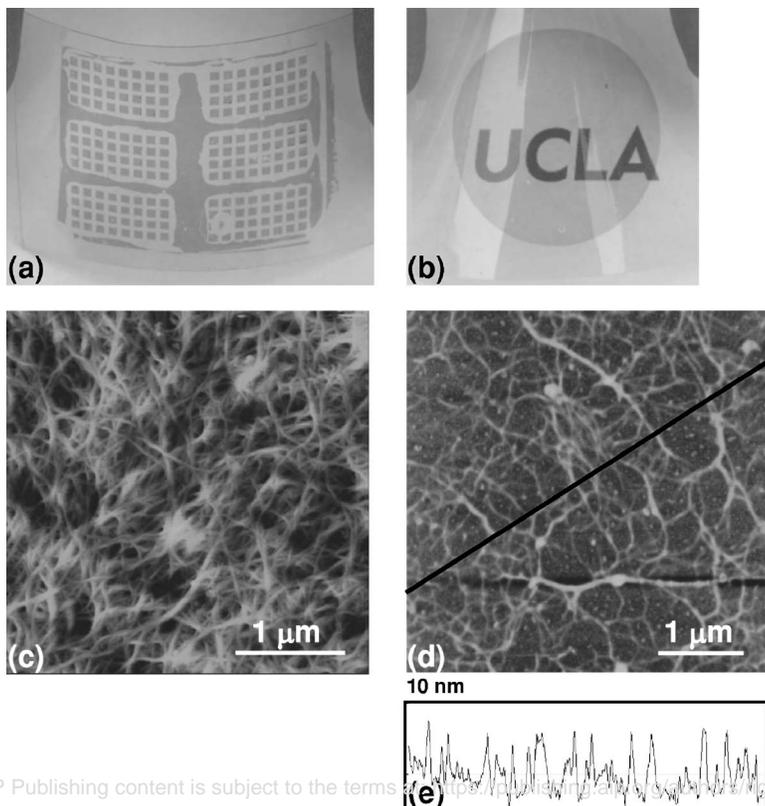


FIG. 3. (a) Photo image of patterned nanotube films on a PET substrate. The small gray square patterns have a size of 1 mm². (b) Photo image of a transparent and homogeneous film with 2 in. diam on a flexible PET substrate. (c) AFM image of a nanotube film with $R_s=200\ \Omega$ on a glass slide. The clean film has a roughness of approximately 8 nm. (d) AFM image of a submonolayer nanotube film with $R_s=100\ \text{k}\Omega$ on a glass slide. (e) Section analysis of the AFM image in (d) across the black line. The nanotube bundle size is 3–6 nm.

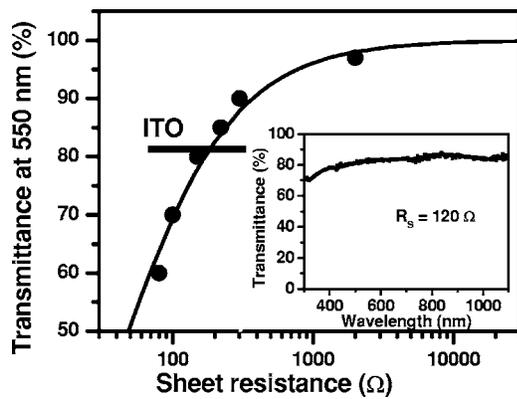


FIG. 4. Optical transmittance at 550 nm vs sheet resistance for nanotube films with different thickness on PET substrates. The bold line shows the performance of commercially available ITO films on PET substrates (CP-Films, Inc.). The fit to Eq. (1) gives $\sigma_{op}=175$ S/cm. The inset shows transmittance of a nanotube film with $R_s=120$ Ω at wavelengths in the visible and infrared ranges.

in the interior. The 8 nm roughness may also be related to this bundle size.

In order to examine the quality of fabricated films further and explore their application potential as transparent conducting coatings, we performed optical transmittance measurements in the visible and infrared spectral range, using a Beckman coulter DU 640 spectrophotometer.¹ The inset in Fig. 4 shows the transmittance (T) of a nanotube film with $R_s=120$ Ω on a PET substrate at different wavelengths in the visible and infrared regions. A bare PET substrate is used as the background.

Film thickness of 10–40 nm is significantly less than wavelengths in the visible and infrared regions. Under such conditions, optical conductivity, σ_{op} , and dc conductivity, σ_{dc} , determines the relation between T and R_s :^{1,13}

$$T = \left(1 + \frac{1}{2R_s} \sqrt{\frac{\mu_0 \sigma_{op}}{\epsilon_0 \sigma_{dc}}} \right)^{-2} = \left(1 + \frac{188(\Omega) \sigma_{op}}{R_s \sigma_{dc}} \right)^{-2}, \quad (1)$$

where the free space permeability $\mu_0=4\pi \times 10^{-7}$ s²/F m and permittivity $\epsilon_0=8.8542 \times 10^{-12}$ F/m. Figure 4 shows T measured at 550 nm for films with different sheet resistances. A fit to our data, together with the measured average $\sigma_{dc}=1600$ S/cm leads to $\sigma_{op}=175$ S/cm at 550 nm. This value is close to $\sigma_{op}=200$ S/cm obtained on bucky papers.¹⁴ The performance characteristics of nanotube films are comparable to that of commercially available ITO films on plastic substrates as shown by the bold line (CPFilms, Inc.), meet or surpass the requirements for applications in areas where flexible coatings are required, such as transparent EM shielding, electrochromic devices (ECDs), touch screen displays, solar cells, organic light emitting diodes (OLEDs), and flat panel displays. Demonstrations of ECDs,¹⁵ OLEDs,¹⁶ and solar

cells¹⁷ using fabricated films as transparent electrodes will be reported separately.

In conclusion, we have described a process that leads to homogeneous and highly conducting carbon nanotube films on various substrates (including PET, glass slide, PMMA, and silicon) by using vacuum filtration and PDMS based transfer printing, and have shown that the optical performance characteristics are comparable to that of commercially available ITO films on plastic substrates. The ultimate usefulness of the method may also lie in material and process cost. For a film with 80% transmittance, based on our current purchase price of \$400/g for purified nanotubes, the material cost is about \$64/m² based on starting material, a figure comparable to the current price of ITO films (CPFilms, Inc.). Recyclable use of filters and stamps may allow utilization of high cost large area filters and PDMS stamps at the industrial scale without significantly increasing fabrication cost of thin films. By considering all the attributes discussed above, we believe that carbon nanotube films fabricated by this printing method will find their application in a variety of areas that require flexible, transparent, and conducting coatings in a patterned or nonpatterned form.

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