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Extreme bendability of single-walled carbon nanotube networks transferred from high-temperature growth substrates to plastic and their use in thin-film transistors

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In this paper we describe printing methods for transferring single-walled carbon nanotubes (SWNTs) from high-temperature growth substrates to flexible, low-cost plastic supports. Thin-film transistors (TFTs) built with networks of transferred SWNTs grown by chemical vapor deposition show good performance—mobilities and on/off current ratios similar to those of devices fabricated on the growth substrates for a wide range of channel lengths. Bending tests on these TFTs show that their output current varies only in a narrow (±5%) range, even for bend radii that induce surface strains larger than 1%. Similar structures evaluated under sharp folding, with strains larger than 20%, show that the SWNT networks are operational even under extreme bending conditions. This level of mechanical robustness, the good electrical performance, and optical transparency make transferred SWNT networks an attractive type of electronic material for applications in macroelectronics, sensors, and other systems that require wide area coverage and unusual substrates. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1947380]

New materials and patterning techniques enable classes of mechanically flexible circuits that might be interesting consumer electronics applications such as flexible paperlike displays and wearable computers. Networks[1,2] and arrays[3] of SWNTs are particularly interesting as effective semiconductors for TFTs because the tubes (i) have exceptionally high mobilities, as inferred from single tube device studies,[4] (ii) can be deposited from solution onto a range of low-temperature plastics, and (iii) have good mechanical properties—elongation strains at a break of ~30% and threshold strains for intratube electronic scattering of 5%–10%.[5] The SWNTs are also, due to their small size, effectively transparent, which makes them interesting for certain classes of electronic devices. Devices can be built on plastic substrates using SWNTs cast from solution (surfactant stabilized and synthesized by laser ablation or high-pressure carbon monoxide procedures).[6] These devices, however, show poor electrical properties compared to those of tubes synthesized by chemical vapor deposition (CVD) and evaluated on their growth substrates. Unfortunately, the type of substrates needed for CVD growth must be compatible with high temperatures, which makes them unsuitable for flexible electronics and many other applications that could use SWNTs. In this paper we introduce dry printing-type methods for transferring, with high efficiency, CVD tubes from their growth substrates to arbitrary device substrates, including low-temperature plastics. We use networks of SWNTs transferred onto flexible plastic substrates to form high performance TFTs. Electrical and mechanical tests reveal that the SWNT networks have an extreme level of bendability, that exceeds, to our knowledge, that of any other class of semiconductor material that can be used in TFTs. These results indicate that this type of device could be important for sensing large area electronics and other areas.

Figure 1 schematically illustrates the steps for transfer

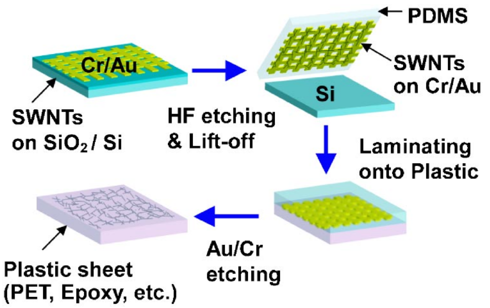

FIG. 1. (Color online) Schematic illustration of the physical transfer of CVD grown SWNTs to plastic substrates. The first step involves evaporating a layer of Cr(2 nm)/Au(20 nm) onto the SWNTs and then patterning it by photolithography or microcontact printing. Exposing the resulting substrate to HF removes the SiO_2 layer underneath the SWNTs. A flat piece of PDMS can remove the metal/SWNT layer and transfer it to a plastic substrate. Etching away the metal leaves a layer of SWNTs on the plastic.

[a)] Author to whom correspondence should be addressed; electronic mail: jrogers@uiuc.edu printing of CVD SWNTs from their growth substrate (SiO_2/Si in this case) to a plastic substrate. Random submonolayer networks of SWNTs were first grown on SiO_2(100nm)/Si wafers using established chemical vapor deposition (CVD) techniques.[7] By controlling the growth conditions, we could control the density of the network from ~1 tube/μm^2 to ~30 tubes/μm^2. Blanket electron beam evaporation (3×10^{-6} Torr; Temescal BJD1800) formed thin layers of Cr (2 nm) and then Au (20 nm) on the SWNTs. Photolithography and lift-off or microcontact printing (μCP) and etching patterned this metal layer to expose the SWNTs in certain regions. The regions where metal was removed provided chemical access of a concentrated hydrofluoric acid etchant to attack the SiO_2 layer underneath the SWNTs. Undercutting of the etchant enabled the SiO_2 to be completely removed in ~5 min for the geometries investigated here. The substrates were then blown dry with nitrogen. Contacting a flat elastomeric stamp poly(dimethylsiloxane) (PDMS) against the substrate, and then peeling the stamp away quickly transferred the metal pattern, with the embedded SWNT, to the stamp. This transfer was possible because of the very poor adhesion of the metal pattern to the underlying Si substrate. Contacting this "inked" stamp to a plastic substrate (i.e. epoxy, PET, Polyimide) for 30 min at 80 °C and then slowing peeling it back led to the transfer of the metal/SWNT structure to the plastic. Removing the metals with suitable wet etchants (Au—TFA, Transene Co.; Cr—CR-7, Cyantek Co.) left the CVD derived SWNT on the plastic substrate, and completed the transfer process.[8]

Figure 2 shows scanning electron and atomic force microscope images (SEM and AFM, respectively) collected at different stages of the fabrication sequence illustrated in Fig. 1. Figure 2(a) shows a metal pattern on SWNT/Si after HF etching; the left half of this image corresponds to parts of the metal that have been removed with the PDMS stamp. Metal patterns with sufficiently high density of openings could be undercut etched over large areas, and successfully transferred to the PDMS; areas of up to 1 cm × 1 cm were possible, as shown in the inset of Fig. 2(a). Figure 2(b) shows a region of the Si substrate where the metal was induced to lift up on its own; the SWNTs are clearly visible on the underside of the metal ribbon. Figure 2(c) shows metal patterns after transfer printing onto a layer of cured epoxy (1.7 μm SU 8, Microchem) on ITO (100 nm)/PET(180 μm). After etching away the metal, mesh or line patterns of networks of SWNTs were clearly observed, as shown in Figs. 2(d) and 2(e). High-resolution SEM and AFM images show that the tube density on epoxy is ~15 tubes/μm^2, which is comparable to the density measured on the growth substrates. It is notable that the metal etchants do not tend to wash away the tubes. The van der Waals forces between the tubes and the substrate provide sufficient adhesion for them to remain on the substrate. SWNTs transferred onto other plastic substrates such as PET (Mylar, Dupont) and polyimide (KAPTON, Dupont) exhibited a similar behavior.

We used these techniques to build TFTs by transferring SWNTs onto plastic substrates of PET coated with indium tin oxide (ITO; 100 nm, gate electrode) and epoxy (SU8; 1.7 μm, gate dielectric).[9] Source and drain electrodes of Ti(2 nm)/Au(20 nm) were formed either by photolithography and liftoff (Shipley 1805) or by nanotransfer printing.[8] Figure 3(a) shows bent array devices and a SEM image of the channel region (inset). Reactive ion etching of the SWNTs through photolithographically defined patterns of resists created network stripes oriented along the transistor channels. These stripes are designed to prevent electrical cross-talk between devices.[2] Figure 3(b) shows transfer characteristics of a device whose channel length and channel width were 100 and 250 μm, respectively; the inset shows current-voltage measurements at various gate voltages. These devices showed unipolar *p*-channel behavior, similar to those made at the original SWNTs/SiO_2/Si substrates. As shown in Fig. 3(c), the transferred devices on plastic showed mobilities and on/off current ratios similar to those fabricated on the growth substrates for the entire range of channel lengths (L between 10 to 100 μm) investigated here.[10] The slight decrease in μ_{device} of transferred devices could be due to some incomplete transfer of tubes, particularly near the open areas in the metal films.

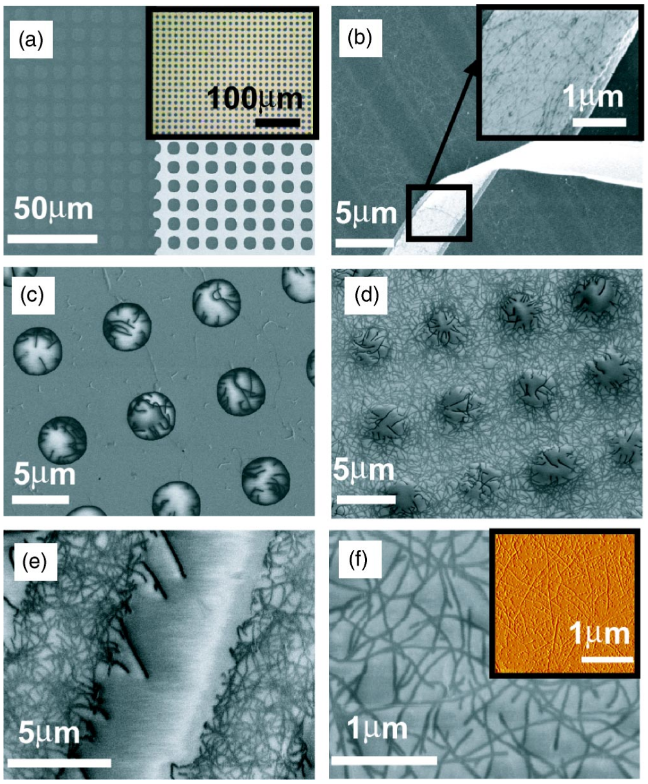

FIG. 2. (Color online) Scanning electron microscope image of (a) metal patterns on Si after HF etching and lifting off with PDMS; the inset shows an optical image of a metal pattern on PDMS; (b) SWNTs on a peeled backed region of a ribbon of Cr/Au after HF etching; (c) SWNT/metal patterns printed on a layer of epoxy; (d) SWNT patterns printed on a layer of epoxy after removing the Cr/Au by wet etching; (e) SWNT line patterns on epoxy after removing the Cr/Au by wet etching; (f) high-resolution SEM image of SWNTs on epoxy after Cr/Au etching; inset: AFM image of SWNTs on epoxy.

To investigate the mechanical flexibility of these devices, we performed systematic bending tests, with bending directions that induce either compressive or tensile strains. The details of the experimental setup can be found elsewhere.[9] Figure 4 shows the change of the on current, normalized by the value in the unbent state, $I_{0,\max}$, as a function of strain (or bending radius). Negative and positive strains correspond to tension and compression, respectively. For both compression and tension, the $I_{\max}$ varied only in a narrow (±5%) range. The current measured in the unbent state after testing was the same as that before testing. A fracture of the ITO gate electrode determined the limit of

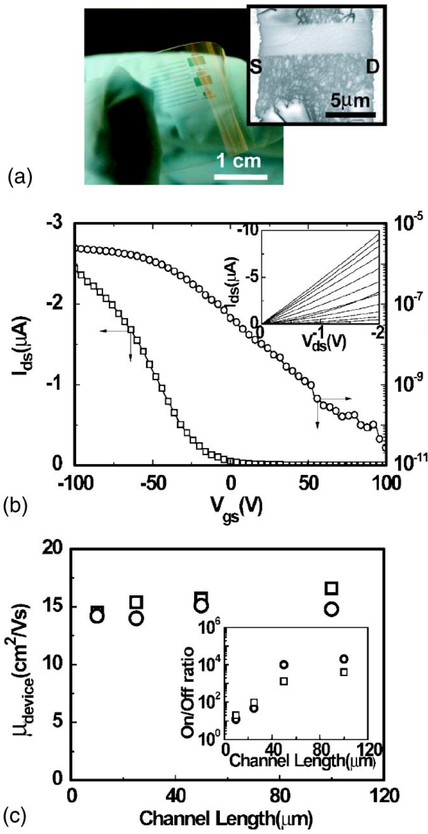

FIG. 3. (Color online) (a) Optical microscope image of an array of SWNT TFTs on plastic; inset: SEM image of channel; (b) transfer characteristics of a SWNT TFT. Channel length and channel width were 100 and 250 μm, respectively, and V_{ds} was −0.5 V; inset: output characteristics; V_{gs} varied from −100 to 0 V from the top with steps of −10 V; (c) a comparison of device mobilities on plastic (squares) and on the SiO_2/Si CVD growth substrate(circles); inset: on/off ratio. A 100 nm thick layer of SiO_2 formed the gate dielectric in the latter case; a 1.7 μm thick layer of epoxy formed the gate dielectric in the former case.

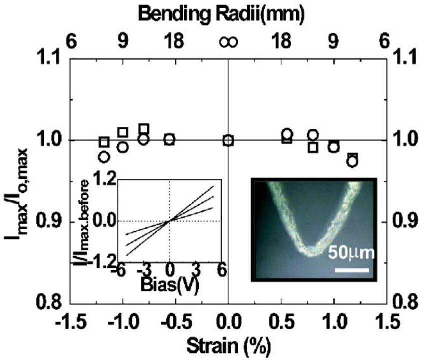

FIG. 4. (Color online) Change in current output of a SWNT TFT for various degrees of bending; channel lengths were 5 μm (squares) and 100 μm (circles). The thickness of the gate dielectric layer (epoxy) was 1 μm. Left inset: I-V curves before folding (top), in compression folding (middle), and in tension folding (bottom). The devices in this case used SWNTs transferred onto a 25 μm thick PET film with source/drain electrodes of Ti (2 nm)/Au(20 nm) formed by evaporation through a shadow mask to define a channel length and width of 500 μm and 1 mm, respectively. No gate electrode was used in this case. Right inset: Optical microscope image after sharp folding.

bendability in these devices. The SWNT networks themselves are extremely robust in bending. To illustrate this feature, we evaluated the source/drain current in a device without a gate electrode, bent in such a manner as to produce a sharp fold in the region between the channel region. The bending radius in these tests was as small as ~ 50 μm, corresponding to strain as much as ~25%, which is far beyond plastic deformation of the 25 μm thick PET substrate, as shown in the inset in Fig. 4.[11] The current only varied by only a few tens of percent, even at these high strains. This behavior, which illustrates the extreme bendability of SWNT networks, is similar to a recent report of sheet conductance in an electrode of a thick layer of SWNTs by Kaempgen *et al.*[12] These data suggest that the practical bendability of SWNT TFTs is not limited by the semiconductor (or potentially the gate and source/drain electrodes, if they are also formed by SWNTs) but rather the mechanical properties of the plastic substrates.

In summary, in this paper we demonstrate transfer printing-type methods to build a high performance SWNTs thin-film transistor on flexible substrates using CVD tubes. The methods used here and the good performance of the resulting devices suggest that SWNT might be useful as materials macroelectronics, sensors, OLED, solar cells, and other systems that require wide area coverage and unusual substrates. Bending and folding test results show that SWNTs might form one of the most mechanically robust type of material for semiconductors and conductors in flexible electronics.

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