

Flexible Nanotube Electronics

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ABSTRACT

Nanotube network transistors have been transferred to polymer supports. The polymer-supported networks can be bent through at least 60° angles without changing their electronic properties. They operate as p-type field-effect transistors with mobilities of 12 cm²/V s, the highest reported values to date for flexible organic transistors. Finally, the networks can be modified chemically to produce n-type transistors. Taken together, these properties provide the basis for high-mobility flexible electronics.

Organic electronic components promise to have a wide variety of important applications because they are inexpensive, lightweight, and flexible.^{1–3} For example, organic light-emitting diodes have been incorporated into flexible displays and electronic papers.^{4,5} The development of other integrated devices has been hampered by the limitations of organic semiconductors. In particular, the low speed of organic transistors is determined by the low mobility of charge carriers in these materials³ (Table 1). The best crystalline organic semiconductors have room-temperature hole mobilities μ near 2 cm²/V s.⁶ Polymeric semiconductors such as poly(3-hexylthiophene) have lower mobilities, near 0.1 cm²/V s.⁶ N-type carrier mobilities are even lower. By contrast, common semiconductors have mobilities 3 orders of magnitude greater, such as 450 cm²/V s for holes in silicon and even higher for carbon nanotubes.⁷ Nanotubes also combine strength and flexibility, so they are excellent candidates for flexible electronic components. Traditionally, nanotubes have been incorporated in field-effect transistors as single nanotubes on rigid substrates. Recently, transistors have been fabricated from sparse networks of individual nanotubes with good mobility and an on–off ratio of at least 10⁴.^{8,9} In this report, we show how to transfer such nanotube network transistors to flexible polymeric substrates. These polymer-supported networks exhibit durability during bending and have mobilities of at least 12 cm²/V s.

Nanotube networks were grown by chemical vapor deposition on 200-nm silicon oxide films on silicon substrates⁸ (Figure 2, inset). These networks consist of randomly oriented individual nanotubes (as opposed to nanotubes in bundles). Metal contacts were patterned onto the nanotube networks (3.5-nm Ti followed by 50-nm Au; 200- μ m pads separated by 50- μ m gaps) using conventional lithography. With the gate field supplied by the conducting silicon

Table 1. Typical Mobility Values for a Selection of Semiconductors

	mobility (cm ² /Vs)	reference
carbon nanotube network on polyimide	12 ^a	this work
p-type semiconductors		
pentacene	1.5 ^a	14
α - <i>o</i> -dihexyl-quaterthiophene	0.1 ^a	15
Si	450 ^b	16
GaAs	400 ^b	16
polycrystalline silicon	69	17
n-type semiconductors		
NTCDI-8F	0.1 ^a	18
copper hexadecafluorophthalocyanine (F16CuPc)	0.03 ^a	19
GaAs	8500 ^b	16
Si	1500 ^b	16
polycrystalline silicon	80	17

^a Field-effect mobility. ^b Drift mobility.

substrate, the networks acted as field-effect transistors,^{8,9} with on/off ratios as high as 10⁴ (Figure 3). To make nanotube network electronic devices on flexible support material, the semiconducting networks were attached to flexible films and lifted off the silicon substrates, as follows (Figure 1). Polyimide films (HMD 2610, 500 rpm, 15- μ m thickness) were spin-coated onto the silicon substrates and cured at 200 °C for 30 min. The silicon substrates with polyimide coatings were immersed in 8% HF for 10 h, until the polyimide films detached from the substrates and floated freely in the solution. The films were rinsed and blown dry. Upon inspection, the patterned metal pads were found to be attached to the polyimide films. (Figure 2) Thus, the process transferred the contacts intact to the polymer support.

Now, if the nanotube networks are successfully transferred, then the flexible network devices can be expected to operate as field-effect transistors. The devices were characterized by

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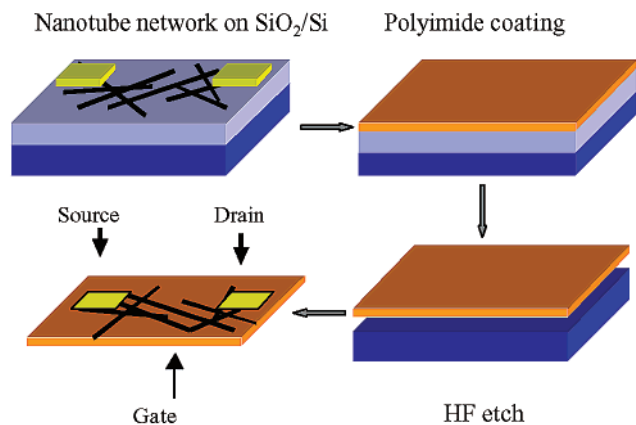


Figure 1. Schematic of the nanotube network transfer process. Networks are grown on oxide-coated silicon substrates, and metal contacts are deposited. Next, a polymer film is applied to the substrate. When the silicon oxide is etched away, the polymer film and the nanotube network lift off the substrate.

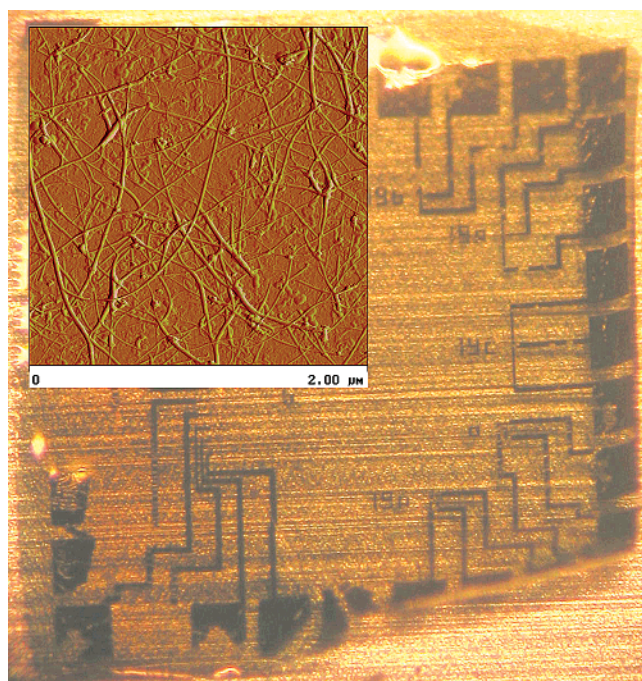


Figure 2. Photograph of a polymer-supported flexible nanotube network transistor. The patterned metal contacts are visible on the surface of the transparent polymer support. Inset: AFM image of a typical network of individual nanotubes, which provides conduction paths through multiple nanotube–nanotube junctions. The networks are sparse, so every conduction path contains semiconducting nanotubes.

placing the polyimide films on a metal chuck, which served as the gate electrode. The conductances of the polymer-supported networks were similar to their conductances measured on the rigid substrates. (Blank samples obtained using the same procedure but starting from substrates without nanotube networks did not conduct.) In addition, the resulting device-transfer characteristics (Figure 3) exhibited large modulations in conductance for voltages less than ± 100 V, confirming that the polymer-supported networks behave as field-effect transistors.¹⁰ For a dielectric film as thick as 15 μm , these switching voltages are remarkably low. We believe

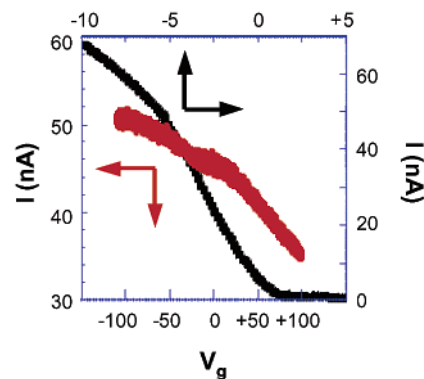


Figure 3. Current vs gate voltage for networks on a flexible polymer substrate (red) and on a rigid substrate (black), showing field-effect transistor operation in the two cases. The transistor on–off ratio of the latter is $\sim 10^4$.

that the low switching voltage is due to the high carrier mobility of the nanotube network, which is estimated as follows.

In a traditional field-effect transistor, the conductivity is expressed as $\sigma = n|e|\mu$, where e is the charge on an electron and n is the 2D carrier density. The effect of the field is to modulate the carrier density: $ne = C_g(V_{\text{th}} - V_g)/LW$ (here V_{th} is the threshold voltage, V_g is the gate voltage, C_g is the gate capacitance, W is the channel width, and L is the channel length). Because the conductance $G = \sigma W/L$, the mobility can be calculated from the slope of G versus V_g : $\mu = (L^2/C_g)(\Delta G/\Delta V_g)$. In our devices, the directly measured capacitance was $C_g = 0.35$ pF, and the pad separation was $L = 50$ μm . Using these parameters, together with typical device data of a 25- μS change over a 150-V change in gate voltage, we measured a mobility of 12 cm^2/Vs for the polymer-supported transistors.¹¹ This mobility is an order of magnitude larger than the best room-temperature mobilities of currently-used organic materials.⁶

In our system, the mobility is due to hole carriers; the devices are p-type transistors. To make stable n-type nanotube transistors, numerous methods are available¹² that involve noncovalent chemical functionalization of the nanotubes. To demonstrate that chemical doping is feasible, we tested the devices for sensitivity to ammonia, a common n-type dopant.¹³ The networks responded to ammonia (Figure 4) as rapidly as nanotubes on rigid substrates,¹³ indicating that the polyimide support does not inhibit functionalization.

Finally, to demonstrate the flexibility of the polyimide-supported networks, the devices were bent through 60° (0.5-mm radius of curvature). Bending produced a 12% decrease in conductance. The change in conductance was reversible, with unbent networks recovering their original conductances over all 12 cycles of bending that we performed. Thus, the flexible network devices are remarkably resilient, despite the presence of multiple nanotube–nanotube junctions.

In conclusion, polymer-supported network transistors exhibit electronic properties that are similar to those of more conventional, silicon-supported nanotube devices and are flexible and inexpensive. Furthermore, nanotube networks could be fabricated as metallic networks by increasing the

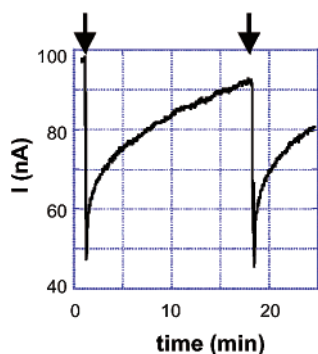


Figure 4. Response of a flexible network transistor to ammonia gas. Arrows indicate the timing of brief pulses of ammonia. The current changes with time as the ammonia modifies the transistor characteristics.

nanotube density. These could serve as cheap, solution-processed contacts and interconnects. Polymer-supported networks form the basis for complete flexible integrated circuits.

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- (10) (a) In principle, the on–off ratios of the polymer-supported networks are also quite large. However, gate voltages greater than 100 V induced a dielectric breakdown in the polymer substrate. (b) Of the devices in which the polymer integrity was retained, 100% could be modulated. However, this was obtained on a limited number of devices. This rate is given to the reader as an indication and should not be taken as the result of a statistical analysis.
- (11) This mobility is only a lower bound for the actual mobility. Because the geometry of the film permits conduction over areas that are not directly between the pads, the effective channel length is significantly longer than the pad separation used in the calculation.
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