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Carbon nanotubes-semiconductor networks for organic electronics: The pickup stick transistor

X.-Z. Bo
DuPont, Central Research and Development, Wilmington, Delaware 19880 and Department of Chemistry and Columbia University Nanocenter, Columbia University, New York, New York 10027

C. Y. Lee and M. S. Strano
Department of Chemistry, University of Illinois at Urbana Champaign, Urbana, Illinois 61801

M. Goldfinger
DuPont, Central Research and Development, Wilmington, Delaware 19880

C. Nuckolls
Department of Chemistry and Columbia University Nanocenter, Columbia University, New York, New York 10027

Graciela B. Blanchet[a)]
DuPont, Central Research and Development, Wilmington, Delaware 19880

We demonstrate an alternative path for achieving high transconductance organic transistors in spite of relatively large source to drain distances. The improvement of the electronic characteristic of such a scheme is equivalent to a 60-fold increase in mobility of the underlying organic semiconductor. The method is based on percolating networks, which we create from a dispersion of individual single-wall carbon nanotubes and narrow ropes within an organic semiconducting host. The majority of current paths between source and drain follow the metallic nanotubes but require a short, switchable semiconducting link to complete the circuit. With these nanotube-semiconducting composites we achieve effectively a $60\times$ reduction in source to drain distance, which is equivalent to a 60-fold increase of the "effective" mobility of the starting semiconducting material with a minor decrease of the on/off current ratio. These field-induced percolating networks allow for the fabrication of high-transconductance transistors having relatively large source to drain distances that can be manufactured inexpensively by commercially available printing techniques. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1906316]

The primary goal for research on organic electronics is the desire to ultimately manufacture large-area inexpensive devices for use in displays, RF ID tags, and possibly, storage applications.[1–4] Reaching such goals requires the fabrication of transistors with sufficiently large transconductance and on/off ratios. Towards this end, the research community has been searching for organic semiconductors that show sufficiently high carrier mobility.[5] In organic thin-film transistors (OTFTs) extrinsic effects, such as contact resistance, grain boundaries, and interface properties, rather than intrinsic material properties, often limit the mobility.

Much of the research on OTFTs focuses on improving performance by increasing the effective mobility. However, the ultimate figure of merit is the transconductance of the transistor, provided that a sufficiently high on/off ratio and a sufficiently low leakage current can be maintained. Although, the transconductance increases linearly with mobility, it also increases inversely with source to drain distance providing another parameter to be tuned for optimum device performance. Yet, plastic electronics require inexpensive manufacturing techniques with inherently lower resolution than photolithography. Accordingly, source to drain distances are unlikely to reach into the submicron scale. State-of-the-art field-effective mobilities in organic thin films coupled with the restrictions in pattern resolution yield transconductances that are at best marginal for many applications.

Rather than improving mobilities or reducing the feature size of commercial engines, we have exploited the physics of percolation to achieve an effective reduction in channel length, thus increasing transconductance. The carriers flowing from source to drain take advantage of the highly conducting rods within the semiconducting matrix, flowing partially within the semiconductor and partially through the rods. Traveling only a fraction of the distance within the semiconductor leads to an effective channel length reduction. The effective channel length reaches vanishing distances as the network of rods approaches three-dimensional (3D) percolation. Being implicitly a geometrical modification of the source to drain current path, our approach can be applied to a wide range of starting organics. It should be able to improve the effective mobility of any such material by the same factor. With such a jump in transistor performance, relatively inexpensive patterning techniques should become viable for the fabrication of low-cost, large-area organic electronics.

This work exploits the extraordinary properties of carbon nanotubes.[6] It has been previously demonstrated that random arrays of nanotubes can form semiconducting[7,8] and conducting[9,10] networks, although semiconducting networks suffer degradation during removal of the metallic tubes. Taking advantage of our prior experience,[10–12] we used single-wall carbon nanotubes (SWNTs) as the conducting rods and

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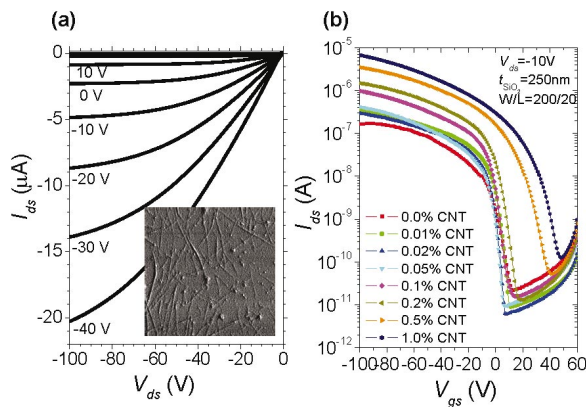[a)]Electronic mail: graciela.b.blanchet@usa.dupont.com

FIG. 1. (a) I_{ds}-V_{ds} curves of a PTH/0.2% SWNT composite device with V_{gs} ranging from 0 to −40 V. W and L are 200 and 20 μm, respectively. Inset: 2.5×2.5 μm AFM image of PTH/5% SWNT composite illustrating network formation. (b) I_{ds}-V_{gs} curves at V_{ds}=−10 V for SWNT concentrations of 0%, 0.01%, 0.1%, 0.2%, 0.5%, and 1%. Devices were baked 2 h at 180 °C to eliminate residual ODCB.
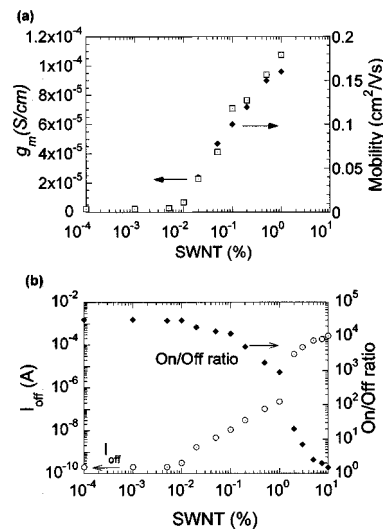

FIG. 2. (a) Linear-log plot of saturation mobility (diamonds) and transconductance (squares) at V_{ds}=−100 V as a function of SWNT. (b) Log-log plot of on/off ratio (filled diamonds) and I_{off} (empty circles) as a function of SWNT content, varied from 0% to 10%. The off current is defined as the minimum drain current when gate sweeping from +100 to −100 V at V_{ds}=−100 V. The TFT's channel length is 20 μm and width 200 μm.

polythiophene (P3HT) as the soluble semiconducting matrix. In order to form networks, the SWNT rods, an assortment of metallic and semiconductor tubes in a 1:2 ratio, were divided into individual tubes with the aid of surfactants.[13–15] The aqueous dispersion containing metallic and semiconducting tubes were filtered and the surfactant was removed. The individual tubes (and small diameter ropes) were dried and redispersed in ortho-dichloro benzene (ODCB) at ~0.02 mgr/ml concentration. The ability to redisperse individual tubes into organic solvents is key to this work, enabling soluble organic semiconductors as potential hosts.

Purified regio-regular P3HT was chosen as the semiconducting host. After a brief bath sonication, the SWNT dispersion was mixed into a 0.5% P3HT chloroform solution to form composites with SWNT concentration varying from 0.0001% to 10%. Thin films were spun onto a clean Si wafer with a 1500 Å thermally growth oxide and pre-patterned Au source and drains. This created the transport layer of a thin-film transistor with a bottom gate configuration.

The *IV* characteristics of composites at 0.2% SWNT loading are shown in Fig. 1(a). The atomic force microscopy (AFM) picture in the inset illustrates the formation of a nanotube network between the Au source and drain contacts 2.5 μm apart. The particles are likely an amorphous carbon produced as a by-product of the HiPco process. Figure 1(b) shows the *IV* curves for P3HT and various PHT composites at various SWNT concentrations for V_{sd}=−10 and −100 V, respectively. The data shows that the off current and threshold voltage remain essentially unchanged in the 0%-0.2% SWNT regime while I_{sd} increases by an order of magnitude. Correspondingly, the effective mobility in the same SWNT regime increases by an order of magnitude while maintaining the large on/off ratio of the P3HT host and without increase in V_{off} or threshold voltage.

Figure 2(a) shows the transconductance and apparent mobility of P3HT/SWNT composites for SWNT concentrations ranging from 0% to 10% by weight. μ_{app} remains constant and close to that of the P3HT host below 0.01%. Between ~0.01% and ~1% the apparent mobility increases strongly, reaching a 60× increase relative to the P3HT host. The huge increase in transconductance by a factor of 60× represents the central finding of our work. Effective mobilities calculated from the linear regimes are slightly lower than

those obtained from the saturated regime, the functional dependence on SWNT content remaining unchanged.

Figure 2(b) shows the off current, I_{off}, and the on/off ratio as a function of SWNT concentration. I_{off} shows an onset at the same concentration as the transconductance, 0.015%. These films were baked at 120 °C after spinning. The on/off ratio remains fairly constant at 10^4 below 0.2%, rapidly decreasing thereafter. I_{off} changes by seven orders of magnitudes in the concentration range investigated, following a power law with an exponent of 1.39. The effect of SWNT surfactants and impurities on I_{off} is negligible as we demonstrated in a device fabricated from a P3HT/0.5% SWNT solution spun after removal of all SWNTs. In addition, the functional dependence of I_{off} on SWNT concentration is independent of the annealing procedure and ODCB content.

In developing a model to describe our data we have little guidance by present theory. Although much work has gone into understanding transport in heterogeneous systems, such as semiconducting polymers[16] and nanotubes,[17–20] it has focused on each separately rather than both combined. Nevertheless, we do believe that a simple model of a percolating metallic network with semiconducting links can explain many aspects of our data.

Our electrically active composite is made from three components: metallic nanotubes, semiconducting nanotubes (at a ratio of ~1:2), and semiconducting P3HT. The fact, that two kinds of nanotubes are present simply reflects our inability to separate them. Our model assumes that transport through the tubes is dominated by the metallic species and that the semiconducting tubes are somewhat inactive. We will discuss this assumption later in the text.

The dependence of I_{off} on SWNTs is the key to our model. Under such bias conditions, P3HT is practically insulating ($I_{off} < 10^{-11}$ A) and we are dealing with a network of nanotubes within an insulating host. Having dimensions of ~2 nm diam and ~1 μm length within an ~50 nm-thick film, our networks are close to two-dimensions and can be represented as slightly canted metallic rods within an insu-

lating matrix. As the concentration of tubes increases, the off current has an onset at ∼0.005%, equivalent to ∼2 μm spacing, and then follows a power law with a 1.39 exponent. This value, characteristic of two-dimensional (2D) percolating systems,[21] is consistent with the assumption that the rods are indeed largely planar.

While the onset of a measurable I_{off} points to the formation of a few conducting pathways between source and drain, many others remain interrupted by stretches of insulating P3HT. However, interrupted links that fall close to the interface to the dielectric are switchable and can be turned on and off via the gate, which creates a thin electron channel within the P3HT. It is this switchable network that becomes the active component between source and drain rather than it being any homogeneous material. Carriers move largely within the highly conducting metallic nanotubes from source to drain. Only occasionally and for distances short compared to the *s-d* length do they travel through the activated P3HT channel. This represents an effective shortening of the *s-d* distance, giving rise to an equivalent increase in the transconductance. This notion represents the central part of our model and is the reason for calling such a device the *pickup stick* transistor.

As the SWNT concentration increases, the number of switchable current path increases and the transconductance, g_m, rises (Fig. 2). Since mobility enters the transconductance linearly, μ_{app} tracks g_m. However, according to our model it would be more appropriate to think of the enhancement in g_m as an effective reduction of the channel length, $l_{eff} \propto 1/\mu_{app}$, while the P3HT mobility remains constant.

Semiconducting tubes being converted into conducting tubes via the gate cannot explain the high g_m of our device. Switching based on this notion would be simply equivalent to a concentration increase of conducting tubes by a factor of 3, given by the ratio of such tubes in the starting material. As can be deduced from Fig. 2(b) this would result in an increase of the current by a factor $3^{1.39} \cong 4.6$, which is very small compared to what is seen in the actual device.

While the transconductance rises by almost two orders of magnitude from ∼0.005% to ∼0.1% CNT concentration, the on/off ratio remains at about 10^4. The ability to increase mobilities without lowering the on/off ratios, key for device fabrication, cannot be achieved with random SWNT networks. On the other hand, I_{off} rises almost in proportion to the gain in transconductance and/or apparent mobility. This is easily understood within our model. As the concentration increases, the number of both truly conducting as well as switchable paths increases. While the former ones contribute to the rising I_{off} current, the latter, much greater in number, contributes to I_{on}.

This dependence of the I_{off} current persists to a SWNT content of ∼1%. Beyond this concentration, I_{off} suddenly increases, accompanied by a rapid decrease of the on/off ratio and vanishing transistor action. We surmise that at this point the nanotubes have become tightly stacked in the third dimension, limited by the ∼50 nm film thickness. Different from lower concentrations, where tubes had some degree of freedom to tilt and avoid each other, at this point they push onto each other thereby vastly increasing the number of contact points between them. At this stage the channel no longer affects the conduction through the network and transistor action has ceased. A ∼1% threshold value for this transition, equivalent to a ∼30 nm tube to tube spacing, is quite reasonable for the onset of such shortage.[11–22]

In conclusion, we have created a unique transistor through the exploitation of percolating metallic networks within a semiconducting host. This method raised the transconductance of our device by a factor of 60. The origin of this vast improvement relies on the reduction of the effective source drain distance via a network of metallic nanotubes. While the equivalent improvement in effective mobility remains insufficient for electronic applications, optimization of the semiconductor for increased starting mobility and reduced contact resistance to nanotubes may well allow reaching this goal.

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