Large Scale, Horizontally Aligned Arrays of Single Walled Carbon Nanotubes for Flexible Thin Film Transistors

NSF NIRT Grant 0403489
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Overview and Objectives: The objective of this research is to develop means for using large scale arrays of individual single walled carbon nanotubes as a effective 'thin film' semiconductor materials for unusual classes of electronic devices. Potential end applications include large area displays, steerable antennas and sensors, wearable computers and other systems that would be difficult or impossible to achieve with conventional electronics technology. This interdisciplinary scientific effort involves the chemistry and materials science of the tubes and means to chemically functionalize them, chemical engineering of their separation/patterning, physics of charge transport through the SWNT films, and electrical engineering aspects of thin film type transistors built with them. The approach includes the combined use of high resolution spectroscopies, scanning probe microscopies, unusual methods for device fabrication, chemical techniques for tube functionalization, and computational tools to simulate device response. The team includes DuPont as a research collaborator, and as a potential path to commercialization. The interdisciplinary science and technology provide excellent educational, human resource and outreach opportunities.

The program consists of four thrusts: (1) producing macroscopic quantities of electronically homogenous, semiconducting SWNTs, (2) achieving high mobilities in semiconducting SWNT on plastic, (3) forming dense, aligned arrays of SWNTs on plastic and fabricating transistors using them, and (4) establishing a fundamental understanding of the operation of these devices

Research Results:
(1): Macroscopic Quantities of Electronically Homogeneous, Semiconducting SWNTs – Implementing SWNT into electronic systems requires means to separate the metallic from the semiconducting tubes in the mixtures of tubes that are generated using known synthetic procedures. Chemical functionalization of SWNTs with dichlorocarbene, octadecylamine, nitronium ions, and phenyl diazonium compounds may provide scalable routes to achieving electronic homogeneity. For direct application in SWNT based thin film transistors, covalent

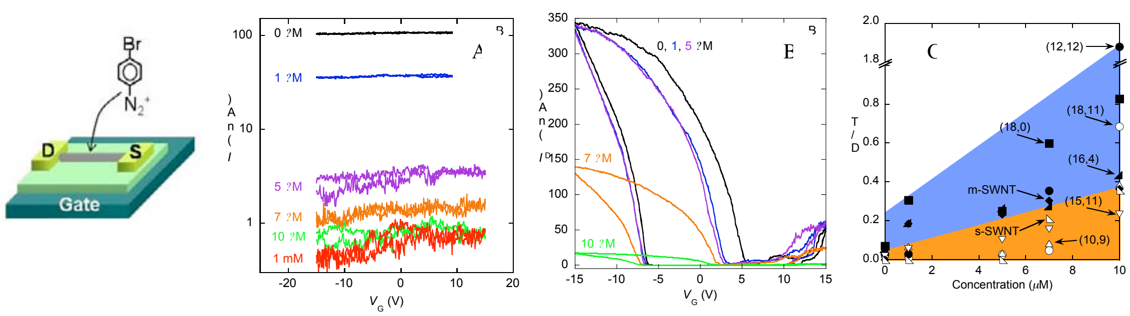

Figure 1. Schematic of electronically selective covalent chemistry on SWNT transistors. Electrical response of metallic (A) and semiconducting (B) SWNT. Raman spectroscopic measurement of reactivity of different chirality SWNTs (C) as represented by the changes in the ratio of intensities of disorder and tangential modes.

functionalization with preferential reactivity towards metallic tubes may be the most desirable approach. Such a selective reactivity would allow post-fabrication removal of metallic contributions to the conductivity that would otherwise cause electrical shorting and performance degradation of network or array TFTs. In this regard, the reaction with diazonium compounds provides one of the most convenient methods along with mild reaction conditions and readily available reagents. Our work over the last year demonstrated, for the first time, the application of this approach to high performance SWNT TFTs [2]. It also elucidated the basic mechanisms of the chemistry. which involves two step kinetics with an initial adsorption event that provides the selectivity, and the effects of bonding on the electronic properties of the tubes [3]. Figure 1 shows the response of single tube SWNT devices to various degrees of chemical functionalization with the diazonium chemistry. Increased on/off ratios in TFT devices, with negligible change in device mobility, indicate selective degradation of the conductance associated with transport through the metallic tubes [2].

(2) and (3): High mobilities in semiconducting SWNT on plastic and transistors that use them

We developed printing techniques to transfer high quality SWNT networks or arrays from high temperature growth substrates to low temperature plastic sheets [4]. Our findings show consistently that the pristine SWNTs grown using chemical vapor deposition techniques have superior electronic properties and reproducibity compared to solution suspensions of SWNTs generated by high pressure carbon monoxide or laser ablation techniques [5,6]. Figure 2 shows some 'all tube' TFTs on a plastic sheet of polyethyleneterephlatate [7]. In these devices, SWNT films (in the form of random networks) provide not only the semiconductor layers but also, at high coverages, films for the source, drain and gate electrodes. The resulting devices show good mobilities, and also optical transparency and extreme levels of bendability [4,7]. These characteristics make these devices potentially useful for a range of applications. Organized, densely packed arrays of SWNT represent the most desirable geometry for charge transport. As described in our HIGHLIGHT piece, this year we developed techniques for guided growth of such ordered arrays; we have also incorporated them into high performance TFTs [8].

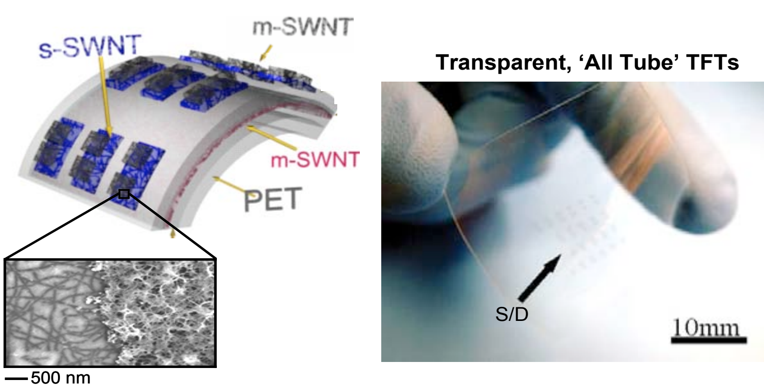

Figure 2. Transparent, bendable 'all tube' TFTs on a plastic substrate. These devices use thin film SWNT networks for all of the semiconducting and conducting layers.

(4): Fundamental understanding of the operation of these devices

The considerable work by other groups on fundamental properties of single tube transistor devices yields some information that is important to understanding the behavior of the TFTs. Many issues, however, remain unresolved. For example, both single tube devices and TFTs show large hysteresis in their operation. This hysteresis appears as a threshold voltage that depends on the history of the operation of the device. Our experimental work shows that

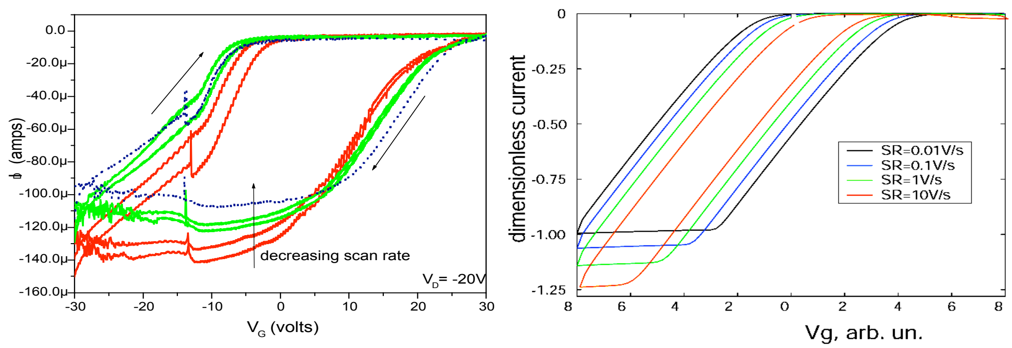

Figure 3. Experimental measurements (left) and theoretical calculations (right) of the hysteresis in the operation of SWNT TFTs. The modeling, which assumes that injection of electrons into the dielectric creates a field that is additive with the externally applied field, captures the magnitude and the sweep rate dependence of the measurements.

ultrahigh capacitance dielectrics, in the form of polymer electrolytes[9] or nanoscale organic layers[10], can eliminate this hysteresis. Our theoretical modeling shows that simple pictures that involve injection of electrons into the dielectric at high voltages can lead to hysteresis with properties (i.e. magnitudes, sweep rate dependences, etc) that reproduce the experimental observations. Figure 3 presents some data and calculations[11].

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