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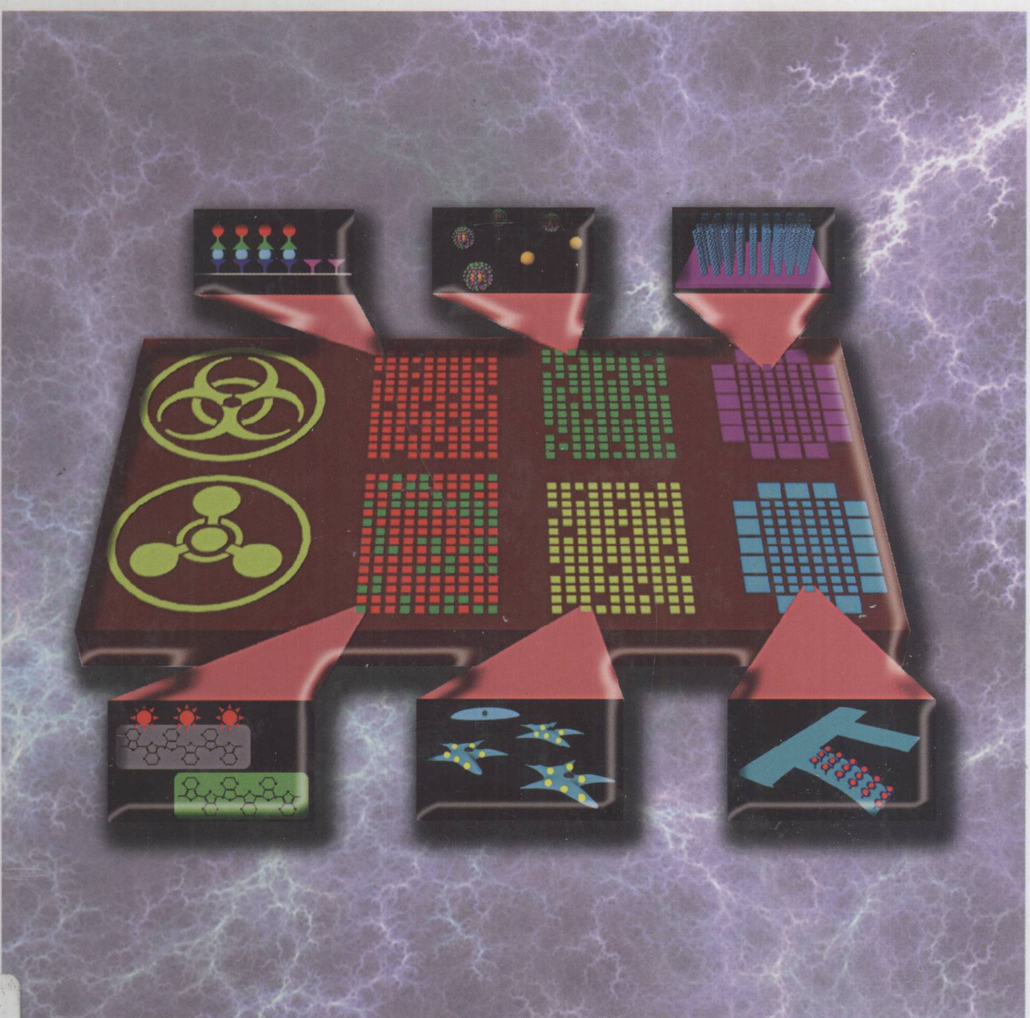
Nano and Microsensors for Chemical and Biological Terrorism Surveillance



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Nano and Microsensors for Chemical and Biological Terrorism Surveillance

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Jeffrey B.-H. Tok

Lawrence Livermore National Laboratory, Livermore, CA, USA and Micropoint Biosciences Inc., Sunnyvale, CA, USA

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Preface

The 9/11 attack on US soil has inadvertently heightened the need for our preparedness in other potential means of terrorist attack. In particular, both biological and chemical warfare have been at the top of the priority list of most governmental agencies as reagents can be covertly prepared and disseminated to result in both widespread fear and casualties. Among many others, one primary preventive step in preparing for the above attacks is to establish a network for efficient surveillance and rapid detection such that appropriate response to such attacks can be timely and effective.

Over the years, primarily due to technological advances, both chemical and biological agents that are able to inflict mass destructions have become more diverse and complex. Subsequently, improvement of sensing devices for rapid and sensitive detection should also be made to keep pace with these engineered or emerging threat agents. Advances in micro- and nanofabrication techniques to enable sensing devices are especially of interest as they have been shown to offer desired advantages such as improved and enhanced functionality, increased efficiency and speed in their readout, reduction in their fabrication cost, and also reduced reagent consumption. Indeed, numerous innovative and exciting reports which took advantage of the above-mentioned techniques for both chemical and biological sensing have appeared over the last decade. While it is not the intention of this book to detail each reported approach, the aim is to compile in depth several detection schematics such that the reader can be provided with a general sense of these micro- and nanoscale sensing systems and platforms.

In this book, I have assembled a series of chapters detailing both well-established and "next-generation" micro- and nanoscale sensors and/or sensing platforms. Briefly, these sensors or sensing platforms range from the novel utilization of nanotubes, cantilevers, nano- and/or microsized pores and engineered whole cells to polymeric transistors *etc.* for sensing purposes. It is truly gratifying to see a synergistic marriage of myriad techniques, ranging from

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chemical, engineering and biological, for the development of sensors, which was once traditionally thought to be reserved for immunologists. The enabling of the above technologies should soon result in a much improved sensing network for the detection and surveillance of both chemical and biological warfare agents.

Lastly, I thank the various members in my research group, namely Hansang Cho, Nick Fischer, Eric Schopf and Aaron Rowe, for their help in the completion of this book project.

Jeffrey B.-H. Tok
Livermore, California

Contributors

Matthew J. Aernecke, *Tufts University, Department of Chemistry, 62 Talbot Ave, Medford, MA 02155, USA*

Sarit S. Agasti, *Department of Chemistry, University of Massachusetts, 710 North Pleasant Street, Amherst, MA 01003, USA*

Daniel A. Bernards, *Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca 14850, USA*

Sibani Lisa Biswal, *Department of Chemical and Biomolecular Engineering, Rice University, MS 362, 6100 Main Street, Houston, TX 77005, USA*

Luca Cevenini, *Department of Pharmaceutical Sciences, University of Bologna, Via Belmeloro 6, 40126 Bologna, Italy*

Fabio Cicoira, *Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca 14850, USA and IFN-CNR, via alla Cascata 56/c, 38050 Povo (Trento), Italy*

Keith E. Herold, *Department of Bioengineering, University of Maryland, College Park, MD 20742, USA*

George G. Malliaras, *Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca 14850, USA*

Laura Mezzanotte, *Department of Pharmaceutical Sciences, University of Bologna, Via Belmeloro 6, 40126 Bologna, Italy*

Elisa Michelini, *Department of Pharmaceutical Sciences, University of Bologna, Via Belmeloro 6, 40126 Bologna, Italy*

Avraham Rasooly, *FDA Center for Devices and Radiological Health and NIH-National Cancer Institute, 6130 Executive Blvd. EPN, Rockville, MD 20852, USA*

Aldo Roda, *Department of Pharmaceutical Sciences, University of Bologna, Via Belmeloro 6, 40126 Bologna, Italy*

Vincent M. Rotello, *Department of Chemistry, University of Massachusetts, 710 North Pleasant Street, Amherst, MA 01003, USA*

Omar A. Saleh, *Materials Department and Biomolecular Science and Engineering Program, University of California, Santa Barbara, Santa Barbara, CA 93106-5050, USA*

Eric S. Snow, *Institute for Nanoscience, Naval Research Laboratory, Washington, DC 20375, USA*

Lydia L. Sohn, *Department of Mechanical Engineering, University of California, Berkeley, Berkeley, CA 94720-1740, USA*

David R. Walt, *Tufts University, Department of Chemistry, 62 Talbot Ave, Medford, MA 02155, USA*

Chang-Cheng You, *Department of Chemistry, University of Massachusetts, 710 North Pleasant Street, Amherst, MA 01003, USA*

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CHAPTER 1

Carbon-Nanotube-Network Sensors

ERIC S. SNOW

Institute for Nanoscience, Naval Research Laboratory, Washington, DC 20375, USA

1.1 Introduction

The growing threat of chemical, biological and radiological attack has created a demand for sensors that are capable of monitoring a large number of facilities for the preemptive detection or potential release of toxic agents. Such applications are highly demanding, requiring inexpensive sensors that are extremely sensitive while producing a low incidence of false alarms. Many such applications are beyond the capability of current technology, which has motivated the development of improved chemical and biological sensors.

Nanomaterials, because of their intrinsically high surface-to-volume ratio, offer the potential to advance the state of the art by serving as the active material for chemical, biological, radiological and explosive sensors. Among such nanomaterials single-walled carbon nanotubes (SWNTs) possess a number of intrinsic properties that make them particularly well suited for a wide range of sensor applications. SWNTs are single-atomic sheets of graphite rolled into a cylinder ~1 nm in diameter that can range in length from 10s of nanometers to 100s of microns depending on the method of growth and preparation.[1–3] Because SWNTs are composed entirely of surface atoms, molecular adsorbates can significantly perturb their electronic properties.[4,5] SWNTs also exhibit near-ballistic electron transport along the tube axis,[6] which provides a highquality electrical conduit for the transmission of such electrical perturbations to external contacts. Finally, the graphitic surface of SWNTs is chemically robust, enabling long-term stable operation.

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Initial laboratory results demonstrated the capability for SWNTs to electronically detect the adsorption of chemical and biological analytes.[4,7,8] However, a number of significant scientific and technological challenges inhibited the transition of these demonstrations to commercial sensor technology. These challenges include the development of an inexpensive, high-yield nanotube device fabrication process, addressing the high level of low-frequency noise, and achieving analyte specificity. Researchers have made significant strides at addressing each of these problems enabling the commercialization of SWNT sensor technology.

In this chapter we examine the current state of development of carbon nanotube chemical and biological sensors. Such sensors can take several forms, which include electrochemical sensors,[9–12] ionization sensors[13] and field-effect transistors (FETs)[14,15] with the SWNT FET platform perhaps the most developed of these. Each of these sensor platforms has its particular set of device physics, design issues and application areas, and it would be difficult to thoroughly discuss each of these in a limited space. Consequently, this chapter will focus on the SWNT FET used for the direct electronic detection of gases, chemical vapors and biological analytes. This chapter is divided into four sections, which include sensor design and fabrication, electronic transduction and noise, chemical vapor and gas detection, and biological detection. These topics cover the main areas of SWNT-FET-sensor research and development. For the interested reader, excellent reviews exist in the literature of other nanotube-based sensor platforms.[10–12]

1.2 Sensor Design and Fabrication

Initial demonstrations of the sensor properties of SWNTs were performed on FETs that contained a single SWNT as the conducting channel (see Figure 1.1).[4,5] In such devices the SWNT was grown or deposited on the surface of a thermal oxide on a conducting Si substrate. Metal source/drain electrodes formed the electrical contacts, and the Si substrate served as a back gate. Such devices were instrumental in investigating the charge-transfer properties of molecular adsorbates and in demonstrating the potential of SWNTs for sensor applications. However, such single-nanotube devices are not easily manufactured, because it is difficult to precisely position individual SWNTs, since the variation in SWNT electronic type (due to diameter and chirality variations[3]) produces large device-to-device non-uniformity, and because individual SWNTs produce a high level of low-frequency noise.[16–19] Consequently, factors such as these have impeded the commercialization of single-SWNT FET sensors.

1.2.1 SWNT Networks

A practical solution to the fabrication problem consists of fabricating field-effect transistors in which the conducting channel is composed of a SWNT random network.[20] SWNT networks are two-dimensional arrays of randomly

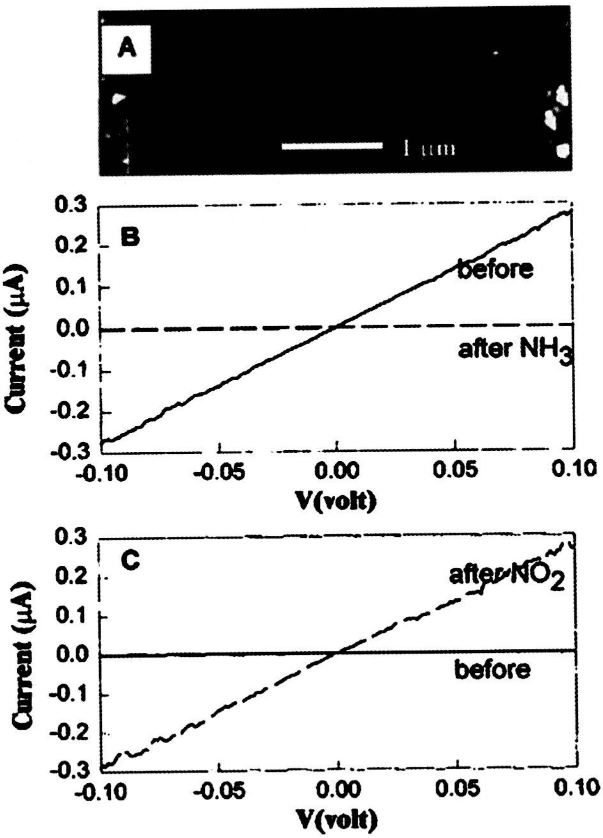

Figure 1.1 (A) Atomic-force-microscope image of a SWNT FET. Current-voltage characteristics recorded before and after exposure to NH_3 (B) and NO_2 (C). For (C) the current *versus* voltage curves were recorded under a gate bias of +4 V. Reproduced with permission from [4]. Copyright 2000 American Association for the Advancement of Science.

positioned SWNTs (Figure 1.2A). If the density of SWNTs in the channel is sufficient that they highly intersect then the SWNTs form an electrically continuous film over arbitrarily large dimensions. Sensors formed from such networks are inexpensive to manufacture using conventional microfabrication techniques and exhibit uniform properties that reflect the aggregate properties of many random, individual SWNTs.[21] The networks are typically grown directly on the thermal oxide of a Si substrate or deposited onto a substrate from solution. Under the appropriate conditions SWNT networks with sheet resistances typically between 10 and 1000 kΩ/square can be grown or deposited uniformly across the surface of large-area substrates.[22]

A key to the electronic properties of SWNT networks is the electrical contact that is formed between intersecting nanotubes lying on a surface. SWNTs adhere to surfaces *via* van der Waals forces.[23] Because SWNTs are extremely

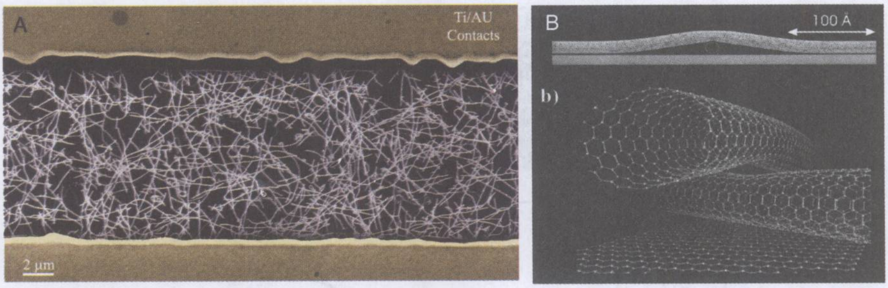

Figure 1.2 (A) Atomic-force-microscope image of a SWNT network FET. (B) Simulation of two intersecting SWNTs lying on a surface. The van der Waals forces acting on the top SWNT are sufficient to deform the SWNTs at the point of intersection. (B) reproduced with permission from [23]. Copyright 1998 the American Physical Society.

stiff (Young's modulus $\sim 10^{12}$ Pa),[24] when two SWNTs cross the van der Waals force pulling down on the top SWNT is transferred to the point of intersection. This force is sufficient to deform the two SWNTs forcing them closer together than the interplane spacing in graphite (see Figure 1.2B).[23] This close contact increases the inter-nanotube tunneling probability, which in the case of two metallic SWNTs can be as high as $0.1\,e^2/h$[25] (where $4\,e^2/h$ is the ideal ballistic conductance of a SWNT). Metal-semiconductor inter-SWNT contacts result in a higher resistance caused by the Schottky barrier formed between the two SWNTs.[25] Such electrical point contacts between intersecting SWNTs create an electrically continuous network over arbitrarily large dimensions, provided that the level of interconnectivity exceeds the percolation threshold for conductivity. Such films can range from semiconducting to metallic behavior depending on the density of SWNTs and the device geometry.[20,26]

It should be noted that recently the Rogers group at the University of Illinois has demonstrated that highly ordered arrays of SWNTs can be grown on certain substrates (see Figure 1.3).[27,28] If the cost of such ordered arrays can be kept sufficiently low it may be possible to manufacture sensors with precisely aligned SWNTs that avoid any deleterious effects of the inter-nanotube contacts present in a network. This approach offers promise for significant improvement in SWNT-sensor performance.

1.2.2 Sensor Fabrication

Sensors consist of microfabricated metal electrodes deposited on a patterned SWNT network that is typically formed on the thermal oxide of a conducting Si substrate.[29] The device structure is that of a thin-film transistor with a back gate that is formed by the Si substrate. A schematic of a sensor is shown in Figure 1.4. For biosensing the sensor is sometimes submerged in a saline solution that contains a Pt electrode used as an electrochemical gate.[30] SWNT

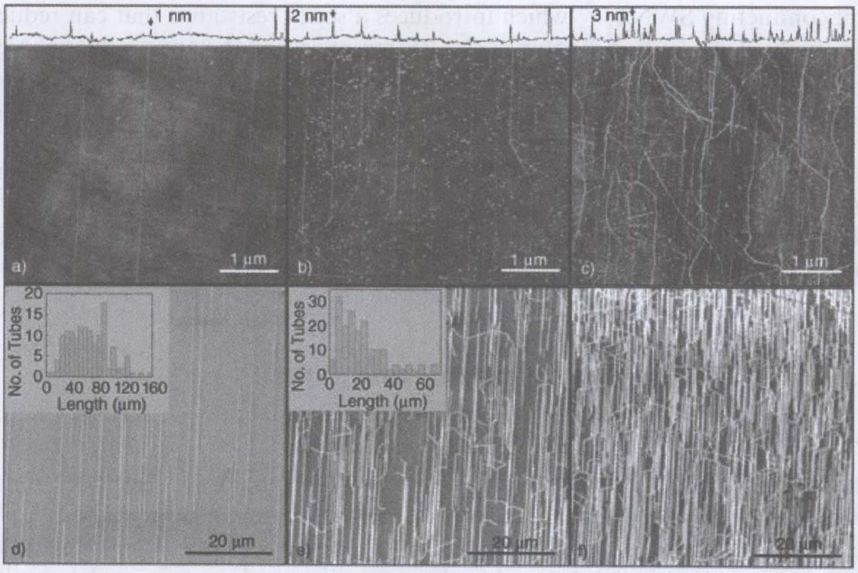

Figure 1.3 (a)–(c) AFM images of aligned SWNTs grown on single-crystal quartz substrate using different densities of catalyst particles. (d)–(f) Large-area SEM images of tubes grown in this fashion. These results indicate a decreasing degree of alignment with increasing tube density. Reprinted with permission from [28]. Copyright 2005 John Wiley and Sons, Inc.

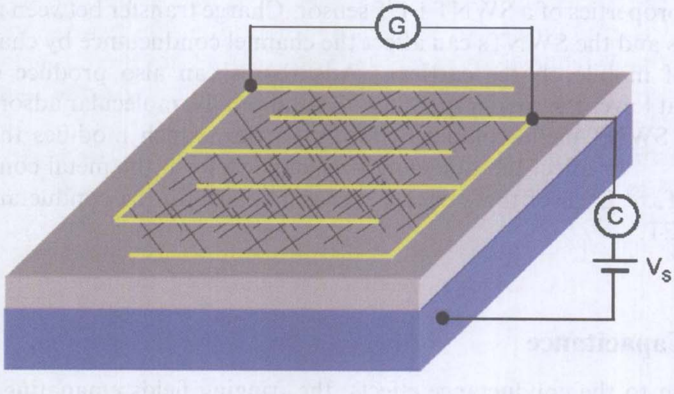

Figure 1.4 Schematic of a SWNT network FET sensor. A conducting Si substrate, separated from the network by a layer of SiO_2, serves as a back gate. Molecular adsorption on the SWNTs is detected as a change in the network conductance and/or the network capacitance. Reprinted with permission from [29]. Copyright 2005 American Chemical Society.

network sensors are simple to fabricate, and the design exposes the surface of the SWNTs to the environment for efficient molecular detection.

For both electronic and sensor applications, an important issue is the role of nanotube/metal contacts. Metal electrodes form a Schottky barrier to