NanoScience and Technology

S.V. Rotkin
S. Subramoney (Eds.)

Applied Physics of Carbon Nanotubes

Fundamentals of Theory, Optics and Transport Devices

Springer

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With 200 Figures

Springer

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To my wife, Lolita, and my son, Lev, for their loving support
and patience, and for my mother and grandfather.

Slava V. Rotkin

Foreword

Back in 1991 Sumio Iijima first saw images of multi-walled carbon nanotubes in the TEM. Two years later, he and Donald Bethune synthesized the first single-walled nanotubes (SWNTs). Since then, we have seen tremendous advances in both the methods for nanotube synthesis and in the understanding of their properties. Currently, centimeter-long SWNTs can be readily grown at selected positions on a solid substrate, and large quantities of nanotubes can be produced for industrial applications. Significant progress has been made in producing nearly homogeneous samples of nanotubes of only a few diameters/chiralities. It is expected that the development of techniques for the synthesis of a single type of nanotube is not far away. At the same time, physical and chemical procedures for the separation of nanotube mixtures are being demonstrated. In addition to pure nanotubes, derivatized nanotubes with attached chemical or biochemical groups are being prepared. Nanotubes acting as containers for atoms, molecules (such as the "peapods") and chemical reactions are attracting significant attention.

In parallel with the synthetic effort there has been a race to decipher the properties of these materials. It is now clear that nanotubes possess unique mechanical, electrical, thermal and optical properties. Scientists and engineers around the world are exploring a wide range of technological applications that make use of these properties. For example, the outstanding mechanical properties of NTs are used in the fabrication of new, strong composites; their field-emission properties are employed to fabricate flat panel displays; the ballistic character of electronic transport in SWNT has been utilized to demonstrate SWNT transistors that outperform corresponding state-of-the-art silicon devices; while the sensitivity of their electrical characteristics on interactions with their environment is being used to produce chemical and biological sensors. Some of these technologies already have matured enough to enter the market place; others will require much more time. New uses of carbon nanotubes are continually being proposed, and it would not be an exaggeration to say that NTs are destined to become the key material of the 21st century.

This book, written by recognized experts in their areas, provides an up-to-date review of the science and technology of NTs. In the "theory and modeling" section, S. Rotkin discusses the classical and quantum mechanical behavior of different single-walled nanotube (SWNT) devices. He analyzes the current-voltage characteristics of long channel SWNT field-effect transistors operating in the quasi-diffusive regime, and he derives analytical expressions for both the geometrical and quantum capacitance of SWNTs. He investigates the changes in electronic structure resulting from the interaction (charge-transfer) between the SWNT with its substrate and the resulting breaking of the axial symmetry of the SWNT. He also discusses the possibility of "band-gap engineering" by external electric fields. He finds that an electric field can open a band-gap in a metallic nanotube, and conversely close the gap of a semiconducting tube. Ideas for new electronic devices are also presented. Damnjanovic et al. provide a detailed symmetry-based analysis of the electronic structure of both single-walled and double-walled nanotubes (DWNT). The results of simple tight-binding theory and density functional theory are compared. Using symmetry arguments again, they discuss the optical absorption spectra of nanotubes, SWNT phonons and their Raman and IR spectroscopies. Finally, the interactions between the walls of DWNTs are discussed. Analytical continuum models of the acoustic and optical phonon modes of finite length NTs are provided in the chapter by Stroscio et al., where both dispersion relations and mode amplitudes are given.

In the "synthesis and characterization" section of the book, Huang and Liu discuss the latest developments in the controlled synthesis of SWNTs. While the heterogeneous NT mixtures produced by various synthetic routes can be used in a number of applications, high technology applications, such as those in electronics, require control over the diameter, orientation and length of the SWNTs. The authors demonstrate the strong relation between catalyst particle size and the diameter of the resulting SWNTs in CVD growth. They go on to show that oriented growth of NTs can be induced simply by the laminar flow of the reaction gases. The CVD methods of Hunag and Liu are based on fast flow of the reaction gases coupled with a fast heating of the reacting mixture of gases and catalysts. This version of CVD leads not only to directional growth that allows SWNT structures such as crossbars to be generated, but also produces extraordinarily long nanotubes in the range of centimeters. Then, Okazi and Shinohara discuss the synthesis and properties of peapods, i.e. the compounds formed by the occlusion of fullerenes by SWNTs. Occlusion of both simple fullerenes and endohedral metallo-fullerenes is considered, and structural data and electrical properties of peapods provided by techniques such as STM, EELS and electron diffraction are presented. The use of SWNTs as containers for confined chemical reactions is also discussed. Strano et al. discuss how to use spectroscopic measurements, absorption, fluorescence and Raman, to study covalent and charge transfer interactions between small molecules and SWNTs. Examples discussed include the selective reaction of metallic SWNTs with diazonium molecules to form aryl C-C bonds and functionalize the side walls of SWNTs, and the selective protonation of NTs in the presence of oxygen.

In the section on "optical spectroscopy", Simon et al. focus on double-walled CNTs (DWNTs). They discuss the structure of these CNTs using Raman spectroscopy. They analyze the mechanism of the process by which SWCNTs incorporating C60, i.e. peapods, are converted into DWNTs through high energy electron beam irradiation. From Raman spectra they conclude that the walls of the inner tubes of DWNTs are structurally perfect and use the splitting of the radial breathing modes to decipher the interaction between the two carbon shells. A detailed account of the emission spectra of NTs is provided by B. Weisman. Fluorescence originating from the lowest excited state (E11) of SWNTs is readily observed upon resonant or higher state (e.g. E22) excitation. Weisman explains how, by combining, fluorescence, fluorescence excitation and resonant Raman spectra of SWNTs dispersed using surfactants, one can deduce the (n,m) indices that describe their structure. He points out that the energies of the individual transitions and the ratios between them show important deviations from expectations based on single electron tight-binding theory. The environment of SWNTs is found to affect both the widths and position of the excitation peaks. Such effects are predicted by theories that account for the many electron effects and exciton formation. (See also chapter by Avouris et al.)

In the section on "transport, electronic, electro-optical and electro-mechanical device applications", Avouris, Radosavljevic and Wind discuss the electronic structure, electrical properties and device applications of SWNTs. Special emphasis is placed on SWNT field-effect transistors (SWNT-FETs). The fabrication, switching mechanism, scaling properties and performance of p-, n- and ambipolar SWCNT-FETs are analyzed and compared with conventional silicon metal-oxide-semiconductor field-effect transistors (MOSFETs). The key role of Schottky barriers and the critical effects of the environment on the performance of SWNT-FETs are stressed. Then the nature of the excited states of nanotubes and their optoelectronic properties are discussed, and single SWNT light emitting and light detecting devices, both based on the SWNT-FET structure, are demonstrated. The authors suggest the possibility that a future integrated electronic and optoelectronic technology based on SWNTs may be possible. Jagota et al. discuss the interaction of SWNTs with biological systems. Such interactions are of interest because they (a) allow the manipulation and sorting of SWNTs, and (b) they can be used as the basis of sensors for biomolecules. The solubilization of SWNTs by complexing with DNA is discussed. This interaction is used in the separation of metallic from the semiconducting SWNTs. The authors also provide evidence that the separation of SWNTs according to their diameter may be possible by the same technique. A different separation method based on selective protonation of SWNTs is also discussed. The use of SWNTs as bio-sensors is demonstrated using the detection of cytochrome C as an example. Finally, Cumings and Zettl discuss a variety of mechanical and electrical experiments on multiwall NTs (MWNTs) and boron nitride nanotubes (BNNT). These include the peeling, sharpening and telescoping of MWNTs inside the TEM. They use MWNT telescoping as a means to study nanofrictional forces and determine the static and dynamic frictional components involved. They also use the same process to determine the length dependence of the conductance of an NT shell. Under their conditions, they find an exponential dependence of the resistance on length which they attribute to localization phenomena.

The mechanical properties of NTs are the subject of the chapter by Fisher et al. The authors discuss in some detail the construction of nanomanipulator systems which allow the manipulation of NTs and other nanostructures in 3D. They also describe measurements of mechanical properties, such as the tensile loading of single-wall and multi-wall NTs, the mechanics of carbon nanocoils, and the results of pull-out tests of single NTs from NT-polymer matrices.

Yorktown Hights, December 2004 *Phaedon Avouris*

Preface

Since the discovery of carbon nanotubes about a decade and a half ago by Sumio Iijima, the scientific community involved in various aspects of research related to carbon nanotubes and related technologies has observed a steady progress of the science, as is typical for any new and novel material. Right from day one, it was apparent to the scientists working on carbon nanotubes that the chirality of individual nanotubes would dictate their electronic properties, besides the well-established knowledge that individual sheets of sp2-bonded carbon had extremely attractive physical and mechanical properties. So, the field of carbon nanotubes took a giant leap in 1993 when research groups at NEC and IBM almost simultaneously discovered the single-walled variant of carbon nanotubes. Since then, we have observed the progress of science and technology as it relates to carbon nanotubes changing from the discovery of various methods to synthesize them to their structure-property relationships to how one might synthesize them in bulk quantities.

A number of edited books have been published in the last five to eight years outlining a variety of topics of current interest related to carbon nanotube research. The chapters in these books deal with topics ranging from synthesis methods to large-volume production concepts to the studies of the unique physical and mechanical properties of carbon nanotubes. Some of the chapters in these books deal with what might be unique about carbon nanotubes and where one might apply them to real-world commercial applications of the future. In fact, it is becoming very evident that carbon nanotubes (specifically single-walled nanotubes with unique electronic properties) will eventually replace silicon in electronic devices that dominate our present information/data driven world. Having stated that, the challenges to selectively obtain and manipulate carbon nanotubes into desired positions in these devices are enormous, and conventional silicon-based technologies will essentially be useless to achieve these goals. On a cumulative basis, the chapters in this book deal with a number of these very new challenges related to carbon nanotubes – how one might go about synthesizing nanotubes of specific chiralities and/or electronic properties and possible experimental routes to separate out the desirable nanotubes, and unique and novel measurement tools to characterize the chiralities of nanotubes. Other chapters deal with the measurement of the electronic properties of carbon nanotubes and how these may be used in real devices. Clearly, the authors who have contributed to this book have done an outstanding job in their respective arenas of interest. From a set-theory point of view, it is our sincerest hope that the reader will benefit immensely from the wealth of information from the individual sets (chapters) as well as from the intersection of the various sets.

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Contents

Part I Theory and Modelling