The background of the cover is a complex, colorful illustration. It features a large, detailed carbon nanotube structure in the upper right, rendered in shades of blue and yellow. Below and to the left, there are various molecular models, including a chain of blue spheres and a cluster of yellow and blue spheres. The overall color palette is dominated by blues, yellows, and greens, with a soft, ethereal lighting effect.

Physical Properties of Carbon Nanotubes

碳纳米管的物理特性

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Imperial College Press

世界图书出版公司

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Imperial College Press

ICP

Published by

Imperial College Press
57 Shelton Street
Covent Garden
London WC2H 9HE

Distributed by

World Scientific Publishing Co. Pte. Ltd.
5 Toh Tuck Link, Singapore 596224
USA office: Suite 202, 1060 Main Street, River Edge, NJ 07661
UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

First published 1998
Reprinted 1999, 2001, 2002, 2003

PHYSICAL PROPERTIES OF CARBON NANOTUBES

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ISBN 1-86094-093-5
ISBN 1-86094-223-7 (pbk)

This book is printed on acid-free paper.

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Physical Properties of Carbon Nanotubes

Preface

A carbon nanotube is a honeycomb lattice rolled into a cylinder. The diameter of a carbon nanotube is of nanometer size and the length of the nanotube can be more than $1\mu\text{m}$. The nanotube diameter is much smaller in size than the most advanced semiconductor devices obtained so far. Thus the availability of carbon nanotubes may have a large impact on semiconductor physics because of its very small size and the special electronic properties that are unique to carbon nanotubes. Because of the large variety of possible helical geometries known as chirality, carbon nanotubes provide a family of structures with different diameters and chiralities. One of the most significant physical properties of carbon nanotubes is their electronic structure which depends only on their geometry, and is unique to solid state physics. Specifically, the electronic structure of a single-wall carbon nanotube is either metallic or semiconducting, depending on its diameter and chirality, and does not require any doping. Thus we can imagine that the smallest possible semiconductor devices are likely to be based on carbon nanotubes. Further, the energy gap of semiconducting carbon nanotubes can be varied continuously from 1 eV to 0 eV, by varying the nanotube diameter. Thus, in principle, it may be possible to specify the desired semiconducting properties using only carbon atoms with a specified geometric structure.

The purpose of this book is to define the structure of carbon nanotubes as clearly as possible, starting from basic physics and chemistry. Since the uniqueness in the electronic structure comes directly from the uniqueness of the electronic structure of graphite, this volume provides background information about the structure and properties of graphite and related carbon materials. From our definition of the structure of carbon nanotubes, we can explain the electronic structure and phonon dispersion relations based on simple physical models, which the reader can follow with a pen and paper. Thus the contents of the book are rather theoretically oriented, and experimental results are used primarily to provide evidence for the validity of the theory. This is actually the

way that the field of carbon nanotubes developed. At an early stage, the theory stimulated experiments in carbon nanotube physics, since obtaining sufficient quantities of pure carbon nanotubes has been difficult in practice. The early experiments were made through electron microscope observation. The direct evidence provided by electron microscopy for the existence of carbon nanotubes was sensational to many physicists and chemists, and because of this fascination, the field of carbon nanotubes has grown explosively, with many active research groups worldwide working independently or in collaborative research projects.

In this book, using basic ideas of the lattice, electronic and phonon structures, the physical properties are discussed in the terminology of carbon nanotubes, which are characterized by the chiral index (n, m) . The chiral index (n, m) consists of a set of integers which specify each carbon nanotube uniquely. Since quantum effects are prominent in nanotube physics, the magnetic and transport quantum effects are very significant. Although progress in the field is still at an early stage, the book focuses on the basic principles behind the physical properties. Another unique property of a carbon nanotube is its stiffness, corresponding to the upper limit of the best carbon fibers, which are commonly used as a strong light-weight material. The special properties of carbon nanotubes are explained in the various chapters in this book.

Thus the physical properties of carbon nanotubes provide a new dimension for solid state physics, based on the great variety of possible geometries that are available for carbon nanotubes. In order to expand this field into the future, many researchers in different fields of science should contribute to this field. The authors hope that readers from any field of science can read this book without any special background requirements. This book is not intended to be a collection of all activities on carbon nanotubes worldwide because this field is already so extensive, and is moving forward so rapidly at the present time. When this book was started three years ago, the present status of the field could not have been anticipated. Thus future progress is beyond our imagination. We hope that through this book, we will find many new friends in this field. So please enjoy the book and please communicate to the authors any comments you might have about this book.

The authors would like to acknowledge many carbon nanotube researchers who have contributed to the contents of the book. The authors also thank the New Energy Development Organization (NEDO) of the Japanese Ministry for

International Trade and Industry (MITI), Japan Society for the Promotion of Science (JSPS), and their generous support for international collaboration which made the writing of this book possible. The authors especially thank Ms. Junko Yamamoto and Ms. Laura Doughty for their help in preparing the indexes and figures of the book.

Finally the authors wish to say to readers: "Welcome to Carbon Nanotube Physics."

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M.S. Dresselhaus, Cambridge, Massachusetts

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CHAPTER 1.

Carbon Materials

Carbon materials are found in variety forms such as graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes. The reason why carbon assumes many structural forms is that a carbon atom can form several distinct types of valence bonds, where the chemical bonds refer to the *hybridization* of orbitals by physicists. This chapter introduces the history of carbon materials and describes the atomic nature of carbon.

1.1 History

We provide here a brief review of the history of carbon fibers, which are the macroscopic analog of carbon nanotubes. The early history of carbon fibers was stimulated by needs for materials with special properties, both in the 19th century and more recently after World War II. The first carbon fiber was prepared by Thomas A. Edison to provide a filament for an early model of an electric light bulb. Specially selected Japanese Kyoto bamboo filaments were used to wind a spiral coil that was then pyrolyzed to produce a coiled carbon resistor, which could be heated ohmically to provide a satisfactory filament for use in an early model of an incandescent light bulb [1]. Following this initial pioneering work by Edison, further research on carbon filaments proceeded more slowly, since carbon filaments were soon replaced by a more sturdy tungsten filament in the electric light bulb. Nevertheless research on carbon fibers and filaments proceeded steadily over a long time frame, through the work of Schützenberger and Schützenberger (1890) [2], Pelabon [3], and others. Their efforts were mostly directed toward the study of vapor grown carbon filaments, showing filament growth from the thermal decomposition of hydrocarbons.

The second applications-driven stimulus to carbon fiber research came in

the 1950's from the needs of the space and aircraft industry for strong, stiff light-weight fibers that could be used for building lightweight composite materials with superior mechanical properties. This stimulation led to great advances in the preparation of continuous carbon fibers based on polymer precursors, including rayon, polyacrylonitrile (PAN) and later mesophase pitch. The late 1950's and 1960's was a period of intense activity at the Union Carbide Corporation, the Aerospace Corporation and many other laboratories worldwide. This stimulation also led to the growth of a carbon whisker [4], which has become a benchmark for the discussion of the mechanical and elastic properties of carbon fibers. The growth of carbon whiskers was also inspired by the successful growth of single crystal whisker filaments at that time for many metals such as iron, non-metals such as Si, and oxides such as Al_2O_3 , and by theoretical studies [5], showing superior mechanical properties for whisker structures [6]. Parallel efforts to develop new bulk synthetic carbon materials with properties approaching single crystal graphite led to the development of highly oriented pyrolytic graphite (HOPG) in 1962 by Ubbelohde and co-workers [7, 8], and HOPG has since been used as one of the benchmarks for the characterization of carbon fibers.

While intense effort continued toward perfecting synthetic filamentary carbon materials, and great progress was indeed made in the early 60's, it was soon realized that long term effort would be needed to reduce fiber defects and to enhance structures resistive to crack propagation. New research directions were introduced because of the difficulty in improving the structure and microstructure of polymer-based carbon fibers for high strength and high modulus applications, and in developing graphitizable carbons for ultra-high modulus fibers. Because of the desire to synthesize more crystalline filamentous carbons under more controlled conditions, synthesis of carbon fibers by a catalytic chemical vapor deposition (CVD) process proceeded, laying the scientific basis for the mechanism and thermodynamics for the vapor phase growth of carbon fibers in the 1960's and early 1970's.[9] In parallel to these scientific studies, other research studies focused on control of the process for the synthesis of vapor grown carbon fibers,[10]–[13] leading to current commercialization of vapor grown carbon fibers in the 1990's for various applications. Concurrently, polymer-based carbon fiber research has continued worldwide, mostly in industry, with emphasis on greater control of processing steps to achieve carbon fibers with ever-increasing modulus and strength, fibers with special characteristics, while decreasing costs

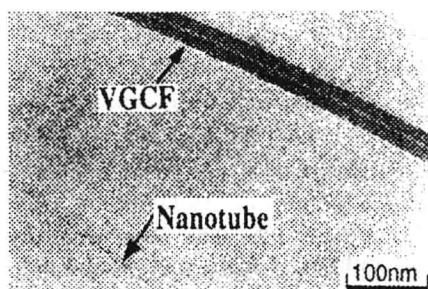


Fig. 1.1: High resolution TEM micrograph showing carbon nanotubes with diameters less than 10 nm [14–17].

of the commercial products.

As research on vapor grown carbon fibers on the micrometer scale proceeded, the growth of very small diameter filaments, such as shown in Fig. 1.1, was occasionally observed and reported [14, 15], but no detailed systematic studies of such thin filaments were carried out. In studies of filamentous carbon fibers, the growth of the initial hollow tube and the subsequent thickening process were reported. [16, 17] An example of a very thin vapor grown tubules ($< 100 \text{ \AA}$) is shown in the bright field TEM image of Fig. 1.1 [14–17].

Reports of such thin filaments inspired Kubo [18] to ask whether there was a minimum dimension for such filaments. Early work [14, 15] on vapor grown carbon fibers, obtained by thickening filaments such as the fiber denoted by VGCF (vapor grown carbon fiber) in Fig. 1.1, showed very sharp lattice fringe images for the inner-most cylinders corresponding to a vapor grown carbon fiber (diameter $< 100 \text{ \AA}$). Whereas the outermost layers of the fiber have properties associated with vapor grown carbon fibers, there may be a continuum of behavior of the tree rings as a function of diameter, with the innermost tree rings perhaps behaving like carbon nanotubes.

Direct stimulus to study carbon filaments of very small diameters more systematically [19] came from the discovery of fullerenes by Kroto and Smalley [20]. In December 1990 at a carbon-carbon composites workshop, papers were given on the status of fullerene research by Smalley [21], the discovery of a new synthesis method for the efficient production of fullerenes by Huffman [22], and a review of carbon fiber research by M.S. Dresselhaus [23]. Discussions at the workshop stimulated Smalley to speculate about the existence of carbon nanotubes of dimensions comparable to C_{60} . These conjectures were later followed

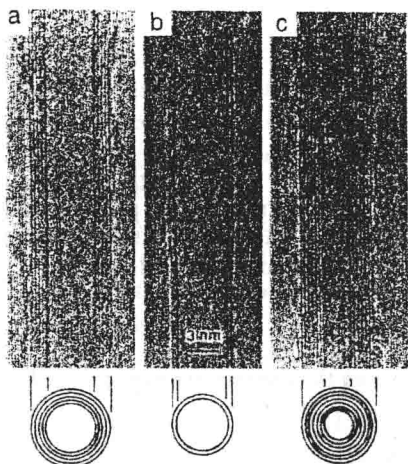


Fig. 1.2: The observation by TEM of multi-wall coaxial nanotubes with various inner and outer diameters, d_i and d_o , and numbers of cylindrical shells N : reported by Iijima using TEM: (a) $N = 5$, $d_o = 67 \text{ \AA}$, (b) $N = 2$, $d_o = 55 \text{ \AA}$, and (c) $N = 7$, $d_i = 23 \text{ \AA}$, $d_o = 65 \text{ \AA}$ [19].

up in August 1991 by an oral presentation at a fullerene workshop in Philadelphia by Dresselhaus [24] on the symmetry proposed for carbon nanotubes capped at either end by fullerene hemispheres, with suggestions on how zone folding could be used to examine the electron and phonon dispersion relations of such structures. However, the real breakthrough on carbon nanotube research came with Iijima's report of experimental observation of carbon nanotubes using transmission electron microscopy (see Fig. 1.2) [19]. It was this work which bridged the gap between experimental observation and the theoretical framework of carbon nanotubes in relation to fullerenes and as theoretical examples of 1D systems. Since the pioneering work of Iijima [19], the study of carbon nanotubes has progressed rapidly.

1.2 Hybridization in A Carbon Atom

Carbon-based materials, clusters, and molecules are unique in many ways. One distinction relates to the many possible configurations of the electronic states of a carbon atom, which is known as the hybridization of atomic orbitals. In this section we introduce the hybridization in a carbon atom and consider the family of carbon materials.

Carbon is the sixth element of the periodic table and is listed at the top

of column IV. Each carbon atom has six electrons which occupy $1s^2$, $2s^2$, and $2p^2$ atomic orbitals.* The $1s^2$ orbital contains two strongly bound electrons, and they are called core electrons. Four electrons occupy the $2s^2 2p^2$ orbitals, and these more weakly bound electrons are called valence electrons. In the crystalline phase the valence electrons give rise to $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals which are important in forming covalent bonds in carbon materials. Since the energy difference between the upper $2p$ energy levels and the lower $2s$ level in carbon is small compared with the binding energy of the chemical bonds,[†] the electronic wave functions for these four electrons can readily mix with each other, thereby changing the occupation of the $2s$ and three $2p$ atomic orbitals so as to enhance the binding energy of the C atom with its neighboring atoms. This mixing of $2s$ and $2p$ atomic orbitals is called hybridization, whereas the mixing of a single $2s$ electron with $n = 1, 2, 3$ [‡] $2p$ electrons is called sp^n hybridization [9].

In carbon, three possible hybridizations occur: sp , sp^2 and sp^3 ; other group IV elements such as Si, Ge exhibit primarily sp^3 hybridization. Carbon differs from Si and Ge insofar as carbon does not have inner atomic orbitals except for the spherical $1s$ orbitals, and the absence of nearby inner orbitals facilitates hybridizations involving only valence s and p orbitals for carbon. The lack of sp and sp^2 hybridization in Si and Ge might be related to the absence of "organic materials" made of Si[§] and Ge.

1.2.1 sp Hybridization: Acetylene, $HC\equiv CH$

In sp hybridization, a linear combination of the $2s$ orbital and one of the $2p$ orbitals of a carbon atom, for example $2p_x$, is formed. From the two-electron orbitals of a carbon atom, two hybridized sp orbitals, denoted by $|sp_a\rangle$ and $|sp_b\rangle$, are expressed by the linear combination of $|2s\rangle$ and $|2p_x\rangle$ wavefunctions of the carbon atom,

$$\begin{aligned} |sp_a\rangle &= C_1|2s\rangle + C_2|2p_x\rangle \\ |sp_b\rangle &= C_3|2s\rangle + C_4|2p_x\rangle \end{aligned} \quad (1.1)$$

*The ground state of a free carbon atom is 3P ($S = 1$, $L = 1$) using the general notation for a two-electron multiplet.

[†]In the free carbon atom, the excited state, $2s2p^3$ which is denoted by 5S is 4.18 eV above the ground state.

[‡]Because of the electron-hole duality, $n = 4$ and 5 are identical to $n = 2$ and 1 , respectively.

[§]It should be mentioned that the "organic chemistry" for Si is becoming an active field today.

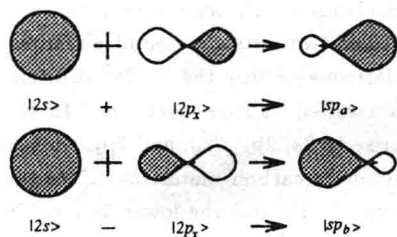


Fig. 1.3: sp hybridization. The shading denotes the positive amplitude of the wavefunction. $|2s\rangle + |2p_x\rangle$ is elongated in the positive direction of x (upper panel), while that of $|2s\rangle - |2p_x\rangle$ is elongated in the negative direction of x (lower panel).

where C_i are coefficients. Using the ortho-normality conditions $\langle sp_a | sp_b \rangle = 0$, $\langle sp_a | sp_a \rangle = 1$, and $\langle sp_b | sp_b \rangle = 1$, we obtain the relationship between the coefficients C_i :

$$\begin{aligned} C_1 C_3 + C_2 C_4 &= 0, & C_1^2 + C_2^2 &= 1, \\ C_3^2 + C_4^2 &= 1, & C_1^2 + C_3^2 &= 1. \end{aligned} \quad (1.2)$$

The last equation is given by the fact that the sum of $|2s\rangle$ components in $|sp_a\rangle$ and $|sp_b\rangle$, is unity. The solution of (1.2) is $C_1 = C_2 = C_3 = 1/\sqrt{2}$ and $C_4 = -1/\sqrt{2}$ so that

$$\begin{aligned} |sp_a\rangle &= \frac{1}{\sqrt{2}} (|2s\rangle + |2p_x\rangle) \\ |sp_b\rangle &= \frac{1}{\sqrt{2}} (|2s\rangle - |2p_x\rangle). \end{aligned} \quad (1.3)$$

In Fig. 1.3 we show a schematic view of the directed valence of the $|sp_a\rangle$ (upper panel) and $|sp_b\rangle$ (lower panel) orbitals. The shading denotes a positive amplitude of the wavefunction. The wavefunction of $|2s\rangle + |2p_x\rangle$ is elongated in the positive direction of x , while that of $|2s\rangle - |2p_x\rangle$ is elongated in the negative direction of x . Thus when nearest-neighbor atoms are in the direction of x axis, the overlap of $|sp_a\rangle$ with the wavefunction at $x > 0$ becomes large compared with the original $|2p_x\rangle$ function, which gives rise to a higher binding energy. If we select $|2p_y\rangle$ for $|2p_x\rangle$, the wavefunction shows a directed valence in the direction of y axis.

It is only when an asymmetric shape of the wavefunction (see Fig. 1.3) is desired for forming a chemical bond that a mixing of $2p$ orbitals with $2s$ orbitals occurs. The mixing of only $2p$ orbitals with each other gives rise to the rotation of $2p$ orbitals, since the $2p_x$, $2p_y$ and $2p_z$ orbitals behave like a vector, (x, y, z) . A wavefunction $C_x|2p_x\rangle + C_y|2p_y\rangle + C_z|2p_z\rangle$, where $C_x^2 + C_y^2 + C_z^2 = 1$, is the $2p$