

纳米科学与技术



国家出版基金项目
NATIONAL PUBLICATION FOUNDATION

定向碳纳米管

物理、理念、制作与器件

Aligned Carbon Nanotubes
Physics, Concepts, Fabrication and Devices

Zhifeng Ren Yucheng Lan Yang Wang

 科学出版社



纳米科学与技术

定向碳纳米管：物理、理念、
制作与器件

Aligned Carbon Nanotubes : Physics ,
Concepts , Fabrication and Devices

Zhifeng Ren Yucheng Lan Yang Wang



科学出版社

北京

图：01-2014-4079

Reprint from English language edition:

Aligned Carbon Nanotubes : Physics, Concepts, Fabrication and Devices

by Zhifeng Ren, Yucheng Lan and Yang Wang

Copyright © Springer-Verlag Berlin Heidelberg 2013

Springer Berlin Heidelberg is a part of Springer Science+Business Media

All Rights Reserved.

This reprint has been authorized by Springer Science & Business Media for distribution in China Mainland only and not for export therefrom.

本影印版由施普林格科学商业媒体授权仅在中国大陆境内发行，不得出口。

图书在版编目 (CIP) 数据

定向碳纳米管：物理、理念、制作与器件 = Aligned carbon nanotubes: physics, concepts, fabrication and devices : 英文/(美)任志峰主编. — 影印本. — 北京：科学出版社，2014.7

(纳米科学与技术)

ISBN 978-7-03-041428-1

I. ①定… II. ①任… III. ①碳-纳米材料-英文 IV. ①TB383

中国版本图书馆 CIP 数据核字 (2014) 第 165806 号

丛书策划：杨震 / 责任编辑：王化冰
责任印制：钱玉芬 / 封面设计：陈敬

科学出版社出版

北京东黄城根北街 16 号

邮政编码：100717

<http://www.sciencep.com>

中国科学院印刷厂印制

科学出版社发行 各地新华书店经销

*

2014 年 7 月第一版 开本：720×1000 1/16

2014 年 7 月第一次印刷 印张：19 3/4

字数：403 000

定价：128.00 元

(如有印装质量问题，我社负责调换)

《纳米科学与技术》丛书编委会

顾 问 韩启德 师昌绪 严东生 张存浩

主 编 白春礼

常务副主编 侯建国

副主编 朱道本 解思深 范守善 林 鹏

编 委 (按姓氏汉语拼音排序)

陈小明 封松林 傅小锋 顾 宁 汲培文 李述汤

李亚栋 梁 伟 梁文平 刘 明 卢秉恒 强伯勤

任咏华 万立骏 王 琛 王中林 薛其坤 薛增泉

姚建年 张先恩 张幼怡 赵宇亮 郑厚植 郑兰荪

周兆英 朱 星

《纳米科学与技术》丛书序

在新兴前沿领域的快速发展过程中,及时整理、归纳、出版前沿科学的系统性专著,一直是发达国家在国家层面上推动科学与技术发展的重要手段,是一个国家保持科学技术的领先权和引领作用的重要策略之一。

科学技术的发展和应用,离不开知识的传播:我们从事科学研究,得到了“数据”(论文),这只是“信息”。将相关的大量信息进行整理、分析,使之形成体系并付诸实践,才变成“知识”。信息和知识如果不能交流,就没有用处,所以需要“传播”(出版),这样才能被更多的人“应用”,被更有效地应用,被更准确地应用,知识才能产生更大的社会效益,国家才能在越来越高的水平上发展。所以,数据→信息→知识→传播→应用→效益→发展,这是科学技术推动社会发展的基本流程。其中,知识的传播,无疑具有桥梁的作用。

整个 20 世纪,我国在及时地编辑、归纳、出版各个领域的科学技术前沿的系列专著方面,已经大大地落后于科技发达国家,其中的原因有许多,我认为更主要的是缘于科学文化的习惯不同:中国科学家不习惯去花时间整理和梳理自己所从事的研究领域的知识,将其变成具有系统性的知识结构。所以,很多学科领域的第一本原创性“教科书”,大都来自欧美国家。当然,真正优秀的著作不仅需要花费时间和精力,更重要的是要有自己的学术思想以及对这个学科领域充分把握和高度概括的学术能力。

纳米科技已经成为 21 世纪前沿科学技术的代表领域之一,其对经济和社会发展所产生的潜在影响,已经成为全球关注的焦点。国际纯粹与应用化学联合会(IUPAC)会刊在 2006 年 12 月评论:“现在的发达国家如果不发展纳米科技,今后必将沦为第三世界发展中国家。”因此,世界各国,尤其是科技强国,都将发展纳米科技作为国家战略。

兴起于 20 世纪后期的纳米科技,给我国提供了与科技发达国家同步发展的良好机遇。目前,各国政府都在加大力度出版纳米科技领域的教材、专著以及科普读物。在我国,纳米科技领域尚没有一套能够系统、科学地展现纳米科学技术各个方面前沿进展的系统性专著。因此,国家纳米科学中心与科学出版社共同发起并组织出版《纳米科学与技术》,力求体现本领域出版读物的科学性、准确性和系统性,全面科学地阐述纳米科学技术前沿、基础和应用。本套丛书的出版以高质量、科学性、准确性、系统性、实用性为目标,将涵盖纳米科学技术的所有领域,全面介绍国内外纳米科学技术发展的前沿知识;并长期组织专家撰写、编辑出版下去,为我国

纳米科技各个相关基础学科和技术领域的科技工作者和研究生、本科生等,提供一套重要的参考资料。

这是我们努力实践“科学发展观”思想的一次创新,也是一件利国利民、对国家科学技术发展具有重要意义的大事。感谢科学出版社给我们提供的这个平台,这不仅有助于我国在科研一线工作的高水平科学家逐渐增强归纳、整理和传播知识的主动性(这也是科学研究回馈和服务社会的重要内涵之一),而且有助于培养我国各个领域的人士对前沿科学技术发展的敏感性和兴趣爱好,从而为提高全民科学素养作出贡献。

我谨代表《纳米科学与技术》编委会,感谢为此付出辛勤劳动的作者、编委会委员和出版社的同仁们。

同时希望您,尊贵的读者,如获此书,开卷有益!



中国科学院院长

国家纳米科技指导协调委员会首席科学家

2011年3月于北京

Preface

Ever since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, there have been extensive research efforts on their synthesis, physics, electronics, chemistry, and applications due to the fact that carbon nanotubes were predicted to have extraordinary physical, chemical, mechanical, optical, and electronic properties. Among the various forms of carbon nanotubes: single-walled and multi-walled, random and aligned, semiconducting and metallic, aligned carbon nanotubes are especially important since fundamental studies and many important applications will not be possible without the alignment. The CNTs have been aligned by various in situ and ex situ techniques. These aligned CNTs have been widely applied in various fields including high energy storage batteries, extremely strong composites, highly sensitive sensors and devices, etc., covering physics, chemistry, biology, engineering, and more. Up to now there have been thousands of scientific publications on fabrication, characterization, physical properties, and applications of aligned CNTs in various aspects. It is the right time now to review the accomplishments on aligned CNTs.

Although there have been significant endeavors on growing carbon nanotubes in an aligned configuration since their discovery in 1991, little success had been made before our first report on growing individually aligned carbon nanotubes on various substrates by plasma enhanced chemical vapor deposition (PECVD) [1]. Aligned CNT arrays have been extensively studied as field emission devices, optical devices, chemical sensors, and biosensors. Based on a recent review article [2], we further expanded to include more recent work on aligned CNTs to write this book. In the book, we introduce the main results of aligned CNTs including CNT growth mechanisms and techniques, CNT microstructures and physical properties, alignment techniques, applications of aligned CNTs, and related physical mechanisms.

In this book, we first review the fundamental structures of CNTs and their unique anisotropic properties in Chap. 2 (*Carbon Nanotubes*), general growth methods in Chap. 3 (*Growth Techniques of Carbon Nanotubes*) and in Chap. 4 (*Chemical Vapor Deposition of Carbon Nanotubes*). Because of the wide and important application of DC-PECVD method to align CNTs, Chap. 5 (*Physics of*

Direct Current Plasma-Enhanced Chemical Vapor Deposition) is specially dedicated to discuss the experimental setup, physical principle, and experimental parameters in more detail. Various in situ and ex situ alignment techniques are introduced in Chap. 6 (*Technologies to Achieve Carbon Nanotube Alignment*). Major fabrication methods are illustrated in detail, particularly the most widely used PECVD growth technique on which various device integration schemes are based. The orientation of aligned CNT systems is vertical, parallel, or at other angles to the substrate surface. The techniques to examine the alignment of CNTs are discussed in Chap. 7 (*Measurement Techniques of Aligned Carbon Nanotubes*). These chapters provide the necessary initial techniques for the following in-depth introduction of the state-of-the-art applications of aligned CNT arrays that we talk about in Chap. 8 (*Properties and Applications of Aligned Carbon Nanotube Arrays*) and in Chap. 9 (*Potential Applications of Carbon Nanotube Arrays*). In these two chapters, we introduce the applications of aligned CNTs in field emission, optical antennas, nanocoax solar cells, subwavelength light transmission, electrical interconnects, nanodiodes, and many others. At the end, the current limitations and challenges are discussed to lay down the foundation for future developments.

In the book, we list detailed experimental procedures and explain the physical mechanisms of sensors and devices to help the readers to understand the aligned CNTs for practical devices. At the same time, a lot of references including review papers and books are also listed. The book can be used as a textbook on aligned CNTs for beginners, and a reference book for advanced readers. In order to understand the aligned CNT well, we strongly encourage the readers, especially beginners on CNTs to first read other books on CNTs, such as *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications* (Edited by M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, Springer, 2000), *Carbon Nanotubes: Preparation and Properties* (Edited by T. W. Ebbesen, CRC Press, 1996), and *Physics of Carbon Nanotube Devices* (Authored by F. Léonard, William Andrew Inc., 2008).

The writing is partly supported by the US Department of Energy under Contract Number DOE DE-FG02-00ER45805 (Z.F.R.), partly by the Defense Threat Reduction Agency under grants HDTRA1-10-1-0001 and HDTRA122221 (YCL).

Chestnut Hill, MA

Zhifeng Ren
Yucheng Lan
Yang Wang

References

1. Z.F. Ren, et al., *Science* **282**, 1105–1108 (1998)
2. Y.C. Lan, et al., *Adv. Phys.* **60**, 553–678 (2011)

Acronyms

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AAO	Anodized aluminum oxide
AC	Alternating current
AFM	Atomic force microscopy
CMOS	Complementary metal–oxide semiconductor
CNF	Carbon nanofiber
CNT	Carbon nanotube
CRT	Cathode ray tube
CVD	Chemical vapor deposition
DC	Direct current
DNA	Deoxyribonucleic acid
DWCNT	Double-walled carbon nanotube
EDS	Energy X-ray dispersive spectrum
FED	Field emission display
FIB	Focused ion beam
HRTEM	High-resolution transmission electron microscopy
IC	Integrated circuit
ITO	Indium tin oxide
IR	Infrared
LCD	Liquid crystal display
MWCNT	Multi-walled carbon nanotube
PECVD	Plasma-enhanced chemical vapor deposition
ppm	Parts per million
PPn	Polyphenol
ppb	Parts per billion
PS	Polystyrene
PVA	Polyvinyl alcohol
RC delay	Resistive capacitive delay
RF	Radio frequency

RNA	Ribonucleic acid
SAED	Selected area electron diffraction
SEM	Electron scanning microscopy
S/N ratio	Signal-noise-ratio
STM	Scanning tunneling microscopy
STEM	Scanning transmission electron microscopy
SWCNT	Single-walled carbon nanotube
TCO	Transparent conductive oxide
TEM	Transmission electron microscopy
TIM	Thermal interface material
XRD	X-ray diffraction

Contents

1	Introduction to Carbon	1
	References	4
2	Carbon Nanotubes	7
2.1	History of Carbon Nanotubes	8
2.1.1	History Before 1991	8
2.1.2	History Since 1991	10
2.1.3	History of Aligned Carbon Nanotubes	11
2.2	Structures of Carbon Nanotubes	16
2.2.1	Graphite	16
2.2.2	Single-Walled Carbon Nanotubes	17
2.2.3	Double-Walled Carbon Nanotubes	18
2.2.4	Multi-Walled Carbon Nanotubes	19
2.2.5	Bamboo-Like Carbon Nanotubes	19
2.2.6	CNT Y-Junctions	20
2.2.7	Carbon Nanobuds	21
2.2.8	CNT Nanotorus and Micro-Rings	23
2.2.9	Carbon Microtubes	24
2.2.10	Amorphous Carbon Nanotubes	25
2.2.11	Coiled Carbon Nanotubes	26
2.2.12	Flattened Carbon Nanotubes	26
2.2.13	Other Carbon Nanomaterials	28
2.3	Physical Properties of Carbon Nanotubes	30
2.3.1	Anisotropic Mechanical Properties	30
2.3.2	Anisotropic Electrical Properties	30
2.3.3	Anisotropic Thermal Conductivity	31
2.3.4	Anisotropic Thermal Diffusivity	32
2.3.5	Anisotropic Seebeck Coefficient	34
2.3.6	Other Anisotropic Physical Properties	34
	References	35

3	Growth Techniques of Carbon Nanotubes	45
3.1	Arc Discharge	45
3.2	Laser Ablation	47
3.3	Chemical Vapor Deposition	48
3.4	Hydrothermal Methods	52
3.5	Flame Method	56
3.6	Disproportionation of Carbon Monoxide	57
3.7	Catalytic Pyrolysis of Hydrocarbons	59
3.8	Electrolysis	59
3.9	Solar Energy	60
	References	61
4	Chemical Vapor Deposition of Carbon Nanotubes	67
4.1	Thermal Chemical Vapor Deposition	67
4.1.1	Hot-Wall Chemical Vapor Deposition	68
4.1.2	Hot-Wire Chemical Vapor Deposition	70
4.1.3	Thermal Chemical Vapor Deposition Growth Mechanism of Carbon Nanotubes	71
4.1.4	Experimental Condition of Carbon Nanotube Array Growth	73
4.2	Plasma-Enhanced Chemical Vapor Deposition	75
4.2.1	Direct Current Plasma-Enhanced Chemical Vapor Deposition	76
4.2.2	Radio-Frequency Plasma-Enhanced Chemical Vapor Deposition	78
4.2.3	Microwave Plasma-Assisted Chemical Vapor Deposition	78
4.2.4	Plasma-Enhanced Chemical Vapor Deposition Growth Mechanism of Carbon Nanotube Alignment . . .	80
4.2.5	Experimental Conditions of Plasma-Enhanced Chemical Vapor Deposition Growth	83
	References	86
5	Physics of Direct Current Plasma-Enhanced Chemical Vapor Deposition	93
5.1	Equipment Setup and Growth Procedure	93
5.2	Substrate and Underlayer	95
5.3	Growth Temperature	96
5.4	Plasma Heating and Etching Effects	97
5.5	Plasma States	99
5.6	Catalyst Crystal Orientation	100
5.7	Electric Field Manipulation	101
5.8	DC-PECVD Growth Mechanism	102
5.8.1	First Stage: Randomly Entangled CNT Growth	102

5.8.2	Second Stage: Partially Aligned CNT Growth	104
5.8.3	Third Stage: Fully Aligned CNT Growth	105
5.8.4	DC-PECVD Growth Mechanism	106
	References	107
6	Technologies to Achieve Carbon Nanotube Alignment	111
6.1	In Situ Techniques for Carbon Nanotube Alignment	112
6.1.1	Thermal Chemical Vapor Deposition with Crowding Effect.	112
6.1.2	Thermal Chemical Vapor Deposition Growth with Imposed Electric Field	116
6.1.3	Thermal Chemical Vapor Deposition Growth Under Gas Flow Fields	119
6.1.4	Thermal Chemical Vapor Deposition Growth with Epitaxy	123
6.1.5	Thermal Chemical Vapor Deposition Under Magnetic Fields.	128
6.1.6	Vertically Aligned Carbon Nanotube Arrays Grown by Plasma-Enhanced Chemical Vapor Deposition	128
6.1.7	Other In Situ techniques.	140
6.2	Ex Situ Techniques for Carbon Nanotube Alignment.	140
6.2.1	Ex Situ Alignment Under Electric Fields	141
6.2.2	Ex Situ Alignment Under Magnetic Fields	141
6.2.3	Ex Situ Mechanical Methods	143
6.2.4	Other Ex Situ Methods.	147
	References	147
7	Measurement Techniques of Aligned Carbon Nanotubes	157
7.1	Scanning Electron Microscopy	157
7.2	Bragg Diffraction	160
7.2.1	X-Ray Diffraction	160
7.2.2	Neutron Diffraction	164
7.2.3	Electron Diffraction.	164
7.2.4	Light Diffraction	166
7.3	Small-Angle Scattering.	168
7.3.1	Small-Angle X-Ray Scattering	168
7.3.2	Small-Angle Neutron Scattering	172
7.4	Raman Spectroscopy	173
7.5	Transmission Electron Microscopy	176
7.6	Scanning Tunneling Microscopy	178
7.7	Atomic Force Microscopy	179
7.8	Other Techniques	179
	References	180

8	Properties and Applications of Aligned Carbon Nanotube Arrays	
	Nanotube Arrays	183
8.1	Field Emission Devices	183
8.1.1	Field Emission of Aligned Carbon Nanotube Arrays	184
8.1.2	Carbon Nanotube Array Emitters	187
8.1.3	High-Intensity Electron Sources	188
8.1.4	Lighting	189
8.1.5	Field Emission Flat Panel Displays	191
8.1.6	Incandescent Displays	193
8.1.7	X-Ray Generators	194
8.1.8	Microwave Devices	195
8.1.9	Other Field Emission Devices	197
8.2	Optical Devices	198
8.2.1	Photonic Crystals	198
8.2.2	Optical Antennae	199
8.2.3	Optical Waveguides	202
8.2.4	SWCNT Array Solar Cells	204
8.2.5	Solar Cells Based on MWCNT Nanocoaxes	204
8.3	Nanoelectrode-Based Sensors	208
8.3.1	Nanoelectrode Arrays	208
8.3.2	Ion Sensors	213
8.3.3	Gas Sensors	215
8.3.4	Biosensors	222
8.4	Thermal Devices: Thermal Interface Materials	228
8.5	Electrical Interconnects and Vias	231
8.6	Templates	235
8.7	Aligned-CNT Composites and Applications	236
	References	236
9	Potential Applications of Carbon Nanotube Arrays	255
9.1	Mechanical Devices	255
9.1.1	Carbon Nanotube Ropes	256
9.1.2	TEM Grids	259
9.1.3	Artificial Setae	260
9.1.4	Piezoresistive Effects: Pressure and Strain Sensors	260
9.2	Electrical Devices	263
9.2.1	Random Access Memory	263
9.2.2	Low κ Dielectrics	264
9.2.3	Transistors	265
9.3	Acoustic Sensors	265
9.3.1	Artificial Ears	265
9.3.2	Thermoacoustic Loudspeakers	265
9.4	Electrochemical and Chemical Storage Devices	269
9.4.1	Fuel Cells	270

Contents	xiii
9.4.2 Supercapacitors	274
9.4.3 Lithium Ion Batteries	279
9.4.4 Hydrogen Storage	280
9.5 Electromechanical Devices: Actuators	280
9.6 Terahertz Sources	281
9.7 Other Applications.	282
References	283
Epilogue	291
Index	293

