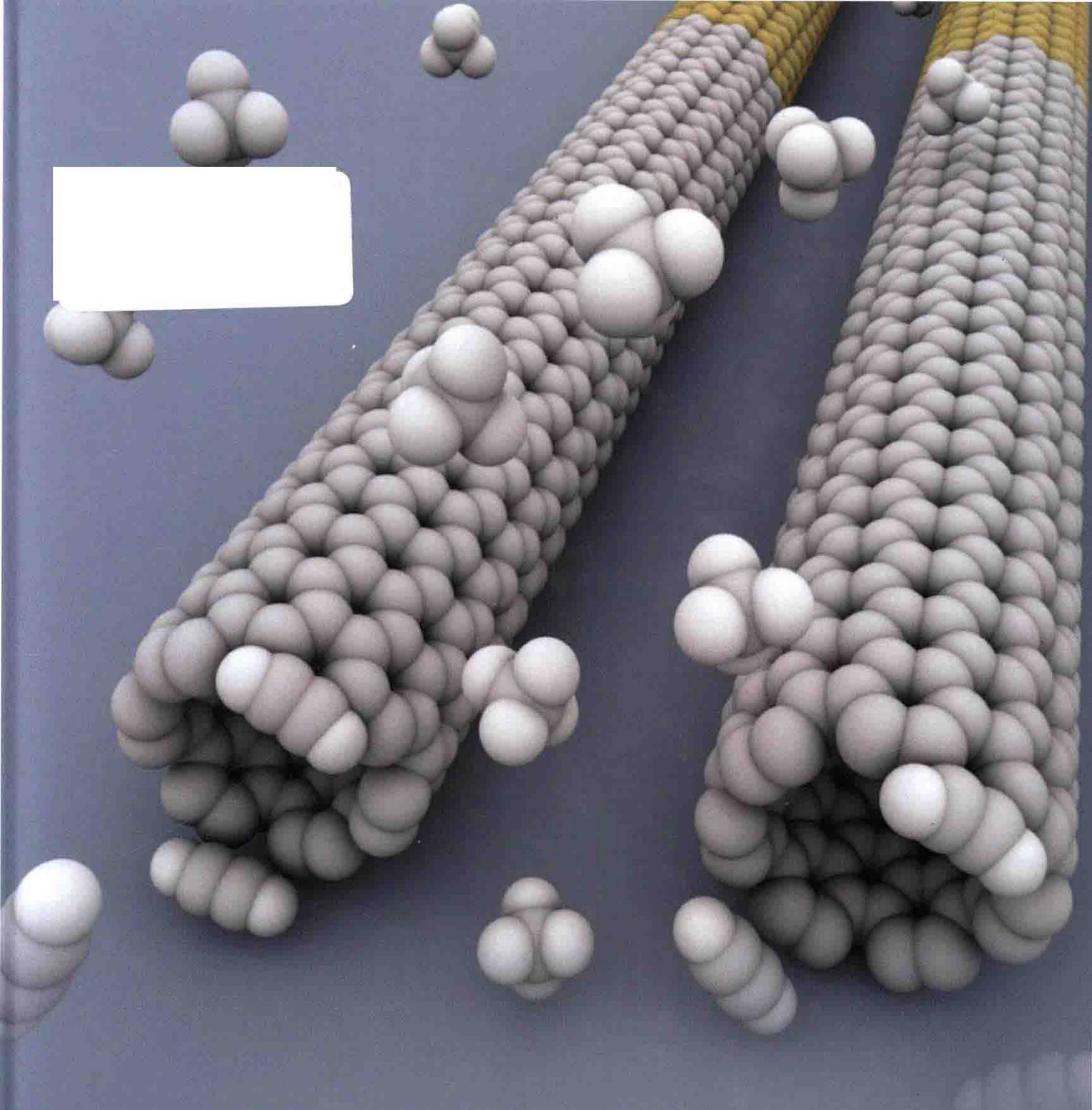

Handbook of

Applications of Carbon Nanotubes

Synthesis, Properties and Applications

Prancias Houterberg
Editor

Handbook of APPLICATIONS OF CARBON NANOTUBES

Synthesis, Properties and Applications

VOLUME 2

Editor

Dr Prancias Houterberg

University of Leoben

AURIS Reference

AURIS REFERENCE LTD.

London, UK

Handbook of Applications of Carbon Nanotubes: Synthesis, Properties and Applications

Revised Edition 2014

Published by

Auris Reference Ltd., UK
www.aurisreference.com

ISBN: 978-1-78154-301-6 (Set)

Editor: Dr Prancias Houterberg

Printed in UK

10 9 8 7 6 5 4 3 2 1

British Library Cataloguing in Publication Data
A CIP record for this book is available from the British Library

For information about Auris Reference Ltd and its publications, visit our website at www.aurisreference.com

Handbook of
APPLICATIONS OF CARBON NANOTUBES
Synthesis, Properties and Applications

Preface

A Carbon Nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale. A nanometer is one-billionth of a meter, or about one ten-thousandth of the thickness of a human hair. The graphite layer appears somewhat like a rolled-up chicken wire with a continuous unbroken hexagonal mesh and carbon molecules at the apexes of the hexagons. Carbon Nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. Although they are formed from essentially the same graphite sheet, their electrical characteristics differ depending on these variations, acting either as metals or as semiconductors. As a group, Carbon Nanotubes typically have diameters ranging from <1 nm up to 50 nm. Their lengths are typically several microns, but recent advancements have made the nanotubes much longer, and measured in centimetres. Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa). (For illustration, this translates into the ability to endure tension of a weight equivalent to 6422 kg (14,158 lbs) on a cable with cross-section of 1 mm^2.) Further studies, such as one conducted in 2008, revealed that individual CNT shells have strengths of up to ~100 GPa, which is in agreement with quantum/atomistic models. Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 g/cm^3, its specific strength of up to 48,000 $kN \cdot m \cdot kg^{-1}$ is the best of known materials, compared to high-carbon steel's 154 $kN \cdot m \cdot kg^{-1}$. Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% and can increase the maximum strain the tubes undergo before fracture by releasing strain energy.

Although the strength of individual CNT shells is extremely high, weak shear interactions between adjacent shells and tubes leads to significant reductions in the effective strength of multi-walled carbon nanotubes and carbon nanotube bundles down to only a few GPa's. This limitation has been recently addressed by applying high-energy electron irradiation, which crosslinks inner shells and tubes, and effectively increases the strength of these materials to ~60 GPa for multi-walled carbon nanotubes and ~17 GPa for double-walled carbon nanotube bundles. Multi-walled nanotubes are multiple concentric nanotubes precisely nested within one another. These exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell, thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already, this property has been utilized to create the world's smallest rotational motor. Future applications such as a gigahertz mechanical oscillator are also envisioned. Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high-pressure carbon monoxide disproportionation (HiPco), and chemical vapour deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

The present book has been designed to outline the basic and fundamental aspects of this subject to be understood in its right perspective. The book uses straight forward, less-technical jargon and manages to introduce each chapter with a basic concept, which ultimately evolves into a more specific detailed principle.

—Editor

Contents

VOLUME-2

They are inverse of the well-known resistance unit h/e^2, which is roughly equal to 25812.8 ohms, and referred to as the von Klitzing constant R_K (after Klaus von Klitzing, the discoverer of exact quantisation). Since 1990, a fixed conventional value R_{K-90} is accepted.

Examples of nanowires include inorganic molecular nanowires ($Mo_6S_{9-x}I_x$, $Li_2Mo_6Se_6$), which can have a diametre of 0.9 nm and be hundreds of micrometres long. Other important examples are based on semiconductors such as InP, Si, GaN, etc., dielectrics (e.g. SiO_2,TiO_2), or metals (e.g. Ni, Pt).

There are many applications where nanowires may become important in electronic, opto-electronic and nanoelectromechanical devices, as additives in advanced composites, for metallic interconnects in nanoscale quantum devices, as field-emitters and as leads for biomolecular nanosensors.

Synthesis of Nanowires

There are two basic approaches of synthesizing nanowires: top-down and bottom-up approach. In a top-down approach a large piece of material is cut down to small pieces through different means such as lithography and electrophoresis. Whereas in a bottom-up approach the nanowire is synthesized by the combination of constituent ad-atoms. Most of the synthesis techniques are based on bottom-up approach.

Nanowire structures are grown through several common laboratory techniques including suspension, deposition (electrochemical or otherwise), and VLS growth. Ion track technology enables growing homogeneous and segmented nanowires down to 8 nm diametre.

Suspension

- A suspended nanowire is a wire produced in a high-vacuum chamber held at the longitudinal extremities. Suspended nanowires can be produced by:
- The chemical etching, or bombardment (typically with highly energetic ions) of a larger wire
- Indenting the tip of a STM in the surface of a metal near its melting point, and then retracting it

VLS Growth

A common technique for creating a nanowire is the Vapour-Liquid-Solid (VLS) synthesis method. This technique uses as source material either laser ablated particles or a feed gas (such as silane). The source is then exposed to a catalyst. For nanowires, the best

Chapter 10

Nanowire

A nanowire is a nanostructure, with the diametre of the order of a nanometre (10^{-9} metres). Alternatively, nanowires can be defined as structures that have a thickness or diametre constrained to tens of nanometres or less and an unconstrained length. At these scales, quantum mechanical effects are important — which coined the term "quantum wires". Many different types of nanowires exist, including metallic (e.g., Ni, Pt, Au), semiconducting (e.g., Si, InP, GaN, etc.), and insulating (e.g., SiO_2, TiO_2). Molecular nanowires are composed of repeating molecular units either organic (e.g. DNA) or inorganic (e.g. $Mo_6S_{9-x}I_x$).

The nanowires could be used, in the near future, to link tiny components into extremely small circuits. Using nanotechnology, such components could be created out of chemical compounds.

Typical nanowires exhibit aspect ratios (length-to-width ratio) of 1000 or more. As such they are often referred to as one-dimensional (1-D) materials. Nanowires have many interesting properties that are not seen in bulk or 3-D materials. This is because electrons in nanowires are quantum confined laterally and thus occupy energy levels that are different from the traditional continuum of energy levels or bands found in bulk materials.

Peculiar features of this quantum confinement exhibited by certain nanowires manifest themselves in discrete values of the electrical conductance. Such discrete values arise from a quantum mechanical restraint on the number of electrons that can travel through the wire at the nanometre scale. These discrete values are often referred to as the quantum of conductance and are integer values of

$$\frac{2e^2}{h} \simeq 77.41 \mu S$$

the bulk material. As a nanowire shrinks in size, the surface atoms become more numerous compared to the atoms within the nanowire, and edge effects become more important.

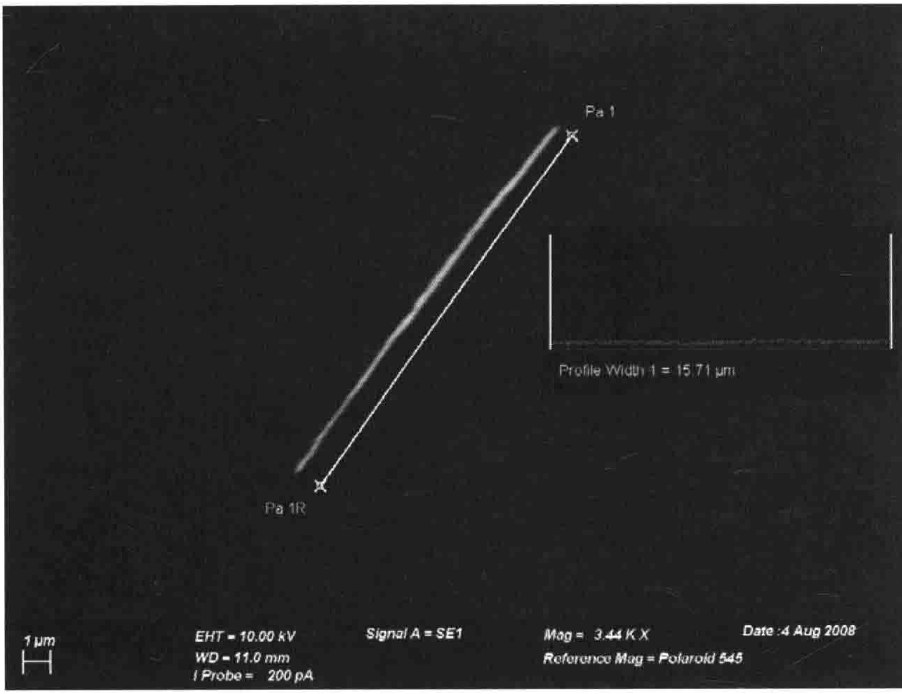

Figure: *An SEM image of a 15 micrometre nickel wire.*

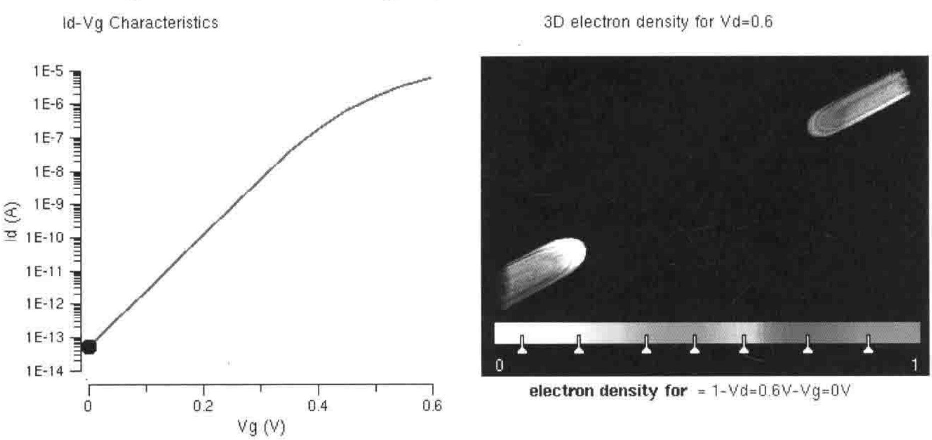

Figure: *Atomistic simulation result for formation of inversion channel (electron density) and attainment of threshold voltage (IV) in a nanowire MOSFET. Note that the threshold voltage for this device lies around 0.45V.*

Furthermore the conductivity can undergo a quantisation in energy: i.e. the energy of the electrons going through a nanowire can assume only discrete values, multiple of the Von Klitzing constant $G = 2e^2/h$ (where e is the charge of the electron and h is the Planck constant). The conductivity is hence described as the sum of the transport by separate *channels* of different quantised energy levels. The thinner the wire is, the smaller the number of channels available to the transport of electrons.

The conductivity of a nanowire can be studied suspending it between two electrodes. This has been proven by measuring the conductivity of a nanowire while pulling it: as its diametre is reduced, its conductivity decreases in a stepwise fashion and the plateaus correspond to multiples of G. The quantised conductivity is more pronounced in semiconductors like Si or GaAs than in metals, due to lower electron density and lower effective mass. Quantised conductance can be observed in 25 nm wide silicon fins, resulting in increased threshold voltage.

Welding Nanowires

To incorporate nanowire technology into industrial applications, researchers in 2008 developed a method of welding nanowires together: a sacrificial metal nanowire is placed adjacent to the ends of the pieces to be joined (using the manipulators of a scanning electron microscope); then an electric current is applied, which fuses the wire ends. The technique fuses wires as small as 10 nm.

For nanowires with diametres less than 10 nm, existing welding techniques, which requiring precise control of the heating mechanism and may introducing the possibility of damage, will be not practical. Recently scientists discovered that single-crystalline ultrathin gold nanowires with diametres ~3-10 nm can be "cold-welded" together within seconds by mechanical contact alone, and under remarkably low applied pressures (unlike macro- and micro-scale cold welding process). High-resolution transmission electron microscopy and in situ measurements reveal that the welds are nearly perfect, with the same crystal orientation, strength and electrical conductivity as the rest of the nanowire.

The high quality of the welds is attributed to the nanoscale sample dimensions, oriented-attachment mechanisms and mechanically assisted fast surface diffusion. Nanowire welds were also demonstrated between gold and silver, and silver and silver nanowires (with diametres ~5-15 nm) at near room temperature, indicating that this technique may be generally applicable for ultrathin metallic nanowires. Combined with other nano- and microfabrication technologies, cold welding is anticipated to have potential applications in the future bottom-up assembly of metallic one-dimensional nanostructures.