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Bionanoelectronics

Bioinquiring and Bioinspired Devices

Daniela Dragoman　Mircea Dragoman

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by Daniela Dragoman and Mircea Dragoman
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《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

This is the first book on bionanoelectronics which deals with the applications of nanoelectronics in biology and medicine. Nanoelectronics is the most advanced area of nanotechnologies having huge applications in daily life. The mobile phones at which we are communicating every day as well as the desktop and laptop computers and iPhones are all results of the development of nanoelectronics, which is now able to fabricate with high reproducibility trillions of very large scale integrated circuits, integrating a huge number of transistors in a single chip. The nanoelectronics technologies are so effective that even 10 years ago the number of transistors contained in DRAM memories was greater than the number of grains of rice produced in the same year, and the price of a transistor was significantly lower than that of a grain of rice. These nanoscaled chips contain one billion transistors, which act as Boolean switches, connected in complicated paths, with a total length of 20 km, but confined and packed in an area of few cm^2. The nanoelectronics technology has developed so significantly according to the Moore law, which states that the dimensions of transistors reduce with 30% every 3 years, such that today the software of any iPhone is more powerful than that of the Apollo 11 lunar module, which landed on the Moon 30 years ago.

After publishing the second edition of the book *Nanoelectronics. Principles and Devices*, at Artech House, in 2009, which followed the first edition after only 3 years, we started to think that the last chapter of this book, called "Molecular and biological nanodevices," must be extended into a separate book, taking into account the amazing applications of bionanoelectronics in rapid DNA sequencing, tissue engineering, controlled drug delivery, bioinspired devices, targeted cancer therapy, or even nanoelectronic artificial organs such as the nose, liver, or lung. More than 20 therapy products based on nanotechnologies are already in use, with very promising results, and other hundreds of nanomedicine-related devices are researched and are under clinical tests. However, we were a bit reluctant to start such an endeavor. We have known that nanoelectronic devices are governed by the rules of quantum mechanics, which prevail for any nanoscale device, and are accompanied by other fundamental laws of physics that cannot be easily adapted to the complex systems of biology. While physics uses a reductive approach to get relatively simple equations

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with a universal character, also applicable in nanodevices, biology, and medicine are mainly observational science, since life manifestations are extremely complex. For example, in a human body, there are 10^{14} cells and, due to cell divisions, 25 millions of new cells are generated every second; a cell has an average dimension of 10 μm and weighs 1 ng; each cell contains the human genome having 3×10^9 base pairs, which means 750 MB of information; the human genome is 1 m long but is folded and packed in few microns and weighs 3 pg. Indeed, our nanoelectronics chips are simple toys compared to what nature has created. We have to recognize that human body is in itself a universe having at least a similar complexity to the cosmological universe from which we originate.

So we have thought how to make accessible to the engineering and physical community the amazing accomplishments of nanoelectronic devices and nanotechnologies applied in various areas of biology and medicine. The reason of such important steps forward in bionanoelectronics are due to the fact that the size of nanodevices and nanomaterials are similar to that of cells, and even of the DNA. The result of our efforts is the present book. The book is not focused on complicated biological, medical, or chemical considerations, although we inevitably use terms from these sciences, briefly explained in the text.

The main idea of the book is to provide to the reader the basic knowledge of nanosciences, i.e., the theoretical concepts and the basic technologies, as well as their applications in biosensing, imaging, bioarchitectures, molecular devices, bioinspired devices, controlled drug delivery, implants, biochips, etc. Thus, the book has achieved an internal coherence reflecting the dual interaction between nanoelectronics on one side and biology and medicine on the other, manifested by bioinquiring devices, when nanotechnologies are used to sense, control, or heal biological systems, and by bioinspired devices, when innovative nanoelectronic devices mimic the function of biological systems.

The first chapter of the book contains the basic principles and theoretical concepts of nanosciences and nanotechnologies, which are further used in the entire book. The second chapter is dedicated to the sensing of biomolecules, including single biomolecules such as DNA, using various techniques, for example, nanoelectronic devices based on nanowires, carbon nanotubes, or graphene, nanocantilevers, or plamonic devices. An artificial nose, which is able to sense various gases in very small quantities, of even few molecules, and to detect the gases associated with diseases such as lung cancer ends this chapter. Chapter 3 is dealing with the imaging tools used in nanotechnologies, such as atomic force microscopy (AFM), which are applied to determine important parameters of various biological systems. The manipulation of biomolecules using optical tweezers and dielectrophoresis is also described in this chapter. These three chapters form the basis for understating the bioinquiring nanodevices. Chapter 4 is focused on the applications in medicine of nanoelectronic devices, which perform complex tasks such as controlled drug delivery monitored by external signals, targeted cancer cell therapy, and mimicking organs such as lung.

Chapters 5, 6, and 7 are dedicated, respectively, to biomolecular architectures, molecular devices, and biocomputing. These chapters present biological

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devices that perform mechanical, optical, or electrical actions usually associated to nonbiological devices. On the contrary, Chap. 8 gathers examples of bioinspired devices, which refer to mechanical, optical, or electrical devices designed based on nature's lessons. The book ends with Chap. 9, which deals with nano-bio integration, a subject that could prove invaluable in the future innovative nanodevices. The applications of nanotechnologies in biology and medicine will produce soon a revolution similar to that of communications and computers, which made possible the occurrence of the internet, mobile phones, and laptops. In the case of bionanoelectronics and nanomedicine, we hope that the final result will be a better and healthier life, in a cleaner environment, the nanotechnologies contributing to the diagnosis and therapy of serious diseases as well as to the development of environmental-friendly technological processes.

Many thanks are addressed to Dr. Claus Ascheron from Springer Verlag, who has encouraged us during the writing of this book.

Bucharest

Mircea Dragoman
Daniela Dragoman

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Chapter 1
Fundamentals on Bionanotechnologies

Abstract This is the introductory chapter of the book. The basic theoretical and experimental facts regarding the application of electronics at the nanoscale and for biological systems are developed here. Transport phenomena at the nanoscale, the principles of nanotechnologies, the physical properties of biological materials, and micro/nanofluidics are reviewed and explained in this chapter. The knowledge gained in this chapter will then be used in the entire book.

1.1 Transport Phenomena at the Nanoscale

When electronic devices are scaled down from few microns up to nanoscale, they become comparable with living organisms, such as bacteria, viruses, or the dimensions of DNA bases. The nanoscale is represented in Fig. 1.1. This fact is of paramount importance for sensing, detecting, or manipulating microorganisms or biomolecules.

The reduced nanometer dimensions of electronic devices changes completely the transport properties. A nanoscale device is an electron device where one, two, or even all three spatial dimensions have few nm. If at a scale of few microns any electronic device can be described by macroscopic physical equations such as Ohm's law, at the nanoscale, microscopic equations are replaced by equations based on quantum mechanics. Quantum mechanical effects manifest at the nanoscale even at room temperature.

A homogenous semiconductor has a conduction band (the first empty band), a valence band (the last occupied band), and a bandgap that separates them. The distribution function of charge carriers in these bands is described by the Fermi–Dirac function

$$f(E) = 1/\{1 + \exp[(E - E_{\mathrm{F}})/k_{\mathrm{B}}T]\}, \quad (1.1)$$

where E_{F} is the Fermi energy level. In semiconductors, the Fermi level is located inside the energy bandgap. In Fig. 1.2, we have displayed the Fermi function at two temperatures.

D. Dragoman and M. Dragoman, *Bionanoelectronics*, NanoScience and Technology, DOI 10.1007/978-3-642-25572-4_1, © Springer-Verlag Berlin Heidelberg 2012

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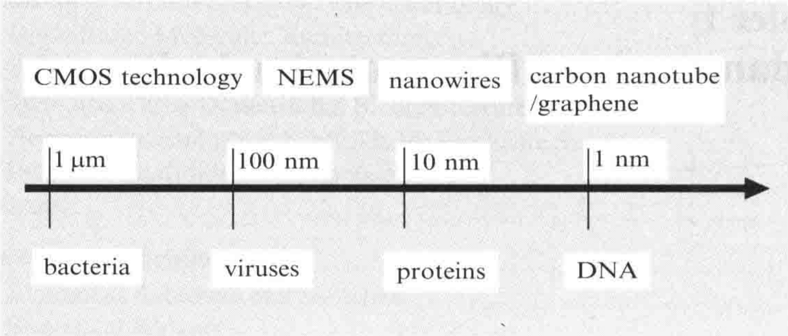
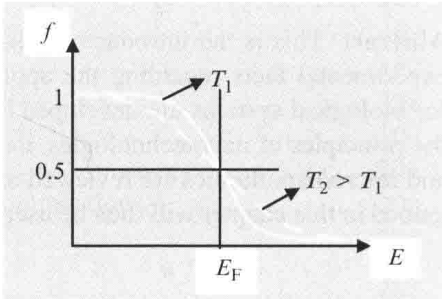


Fig. 1.1 Dimension scale of biological systems and electron devices, where NEMS stands for nanoelectromechanical systems

Fig. 1.2 The Fermi–Dirac distribution function



In the case of nanoscale devices, the confinement of carrier wavefunctions produces a discretization of the energy spectrum of charge carriers as well as discontinuities in the density of states. These effects cause further important changes in the transport properties of charge carriers depending on the number of dimensions along which the motion of carriers is restricted.

In bulk materials with dimensions of few millimeters, the transported carriers move randomly due to repeated scatterings with impurities and phonons. The carrier transport is thus of a diffusive type, which is modeled in general by a stochastic Boltzmann equation. The Boltzmann equation loses its validity as soon as the dimensions of the material shrink to nanoscale. The nanoscale is often termed as mesoscale since it is intermediate between the macroscopic scale and the atomic scale, where the atoms and molecules with sizes of the order of 1 Å $= 10^{-10}$ m are described by quantum mechanical laws.

At the nanoscale, the electron transport is dictated by the relation between the dimensions of the sample and three parameters (Datta 1997):

1. The mean-free path L_{fp}, which is the average distance between two electron collisions with phonons or impurities that cancel the initial momentum of a charge carrier.
2. The phase relaxation length L_{ph}, which represents the propagation distance after which the electron coherence, i.e., the phase memory of electrons, vanishes as a result of time-reversal breaking. Examples of such processes are

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electron–electron collisions, dynamic scatterings, or certain impurity scattering processes in which an internal degree of freedom changes; the phase relaxation length is often called the coherence length.

3. The electron Fermi wavelength, denoted as λ_F.

When one or more dimensions of a device are smaller than the mean-free path and the phase relaxation length, the number of scatterings reduces dramatically, and the transport in the device is termed ballistic. In this case, the electrons behave no longer as particles but as waves that follow all the reflection and refraction rules of common light or acoustic waves. As will be seen later, the ballistic transport manifests over distances of few hundreds of nanometers in carbon nanotubes (CNTs), graphene, or high-mobility transistors at room temperature.

In Fig. 1.3, we have schematically displayed a transistor with scaled down dimensions. The transport is diffusive when the transistor has gate lengths of 1 μm or greater and ballistic as soon as the gate channel shrinks to tens of nanometers. In the ballistic transport regime, the carriers traverse the gate channel in a much shorter time and with higher speeds.

The transport of ballistic charge carriers with electron effective mass m and constant energy E can be modeled by the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2}\{m^{\alpha}\nabla[m^{\beta}\nabla(m^{\alpha}\Psi)]\} + V\Psi = E\Psi, \tag{1.2}$$

when the coupling phenomena between different electron bands can be neglected (Dragoman and Dragoman 1999). In (1.2), Ψ denotes the envelope electron wavefunction, which has a slow variation over the unit cell of the crystalline lattice and V is the potential energy. The material-dependent parameters α and β are

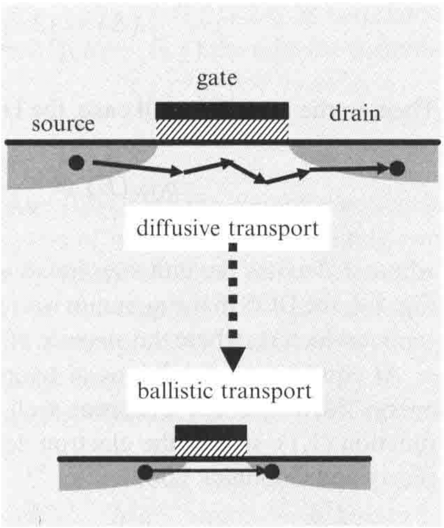

Fig. 1.3 The scaling down of a transistor

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related by $2\alpha + \beta = -1$ and are equal to $\alpha = 0$ and $\beta = -1$ in AlGaAs compounds, which were the first semiconductors that displayed ballistic transport.

The spatial restrictions on electron motion are expressed in the specific form of the boundary conditions imposed on the Schrödinger equation. A structure in which electrons are confined at the nanoscale by potential barriers along the, say, z direction but are free to travel along the transverse x and y directions is referred to as quantum well (QW). In a quantum well with infinite-height potential barriers, the Schrödinger equation is accompanied by the boundary conditions $\Psi(x, y, 0) = \Psi(x, y, L_z) = 0$, where L_z is the width of the quantum well.

If $V = 0$, the solution of the Schrödinger equation can be written as $\Psi(x, y, z) = (2/L_z L_x L_y)^{1/2} \sin(k_z z) \exp(i k_x x) \exp(i k_y y)$, where L_x and L_y are, respectively, the dimensions of the structure along x and y. In ballistic devices, L_z is comparable to the Fermi wavelength λ_F and $L_z < L_x, L_y \ll L_{fp}, L_{ph}$. Another effect of the boundary conditions is a discrete spectrum for the z component of the electron momentum $k_z = p\pi/L_z$, which induces a discretization of the energy levels along the direction of spatial restriction. The energy dispersion relation in the quantum well in which the bottom of the conduction band E_c is considered as reference is given by

$$E(k_x, k_y, k_z) = E_c + \frac{\hbar^2}{2m}\left(\frac{p\pi}{L_z}\right)^2 + \frac{\hbar^2}{2m}(k_x^2 + k_y^2) = E_{s,p} + \frac{\hbar^2}{2m}(k_x^2 + k_y^2), \quad (1.3)$$

where $E_{s,p}$ is the cutoff energy of the discrete subband labeled by the integer p; the subbands are also referred to as transverse modes. The difference in energy between adjacent subbands is greater for more confined electrons, i.e., for smaller L_z.

For an arbitrary energy distribution in the $\mathbf{k}$ space, which takes $E(\mathbf{k})$ constant values on a $\mathbf{k}$-space surface Σ, a spin-degenerate density of states (DOS) can be defined as

$$\rho(E) = (2\pi)^{-3} \int_{\Sigma} \frac{\mathrm{d}S}{|\nabla_{\mathbf{k}} E|_{E=\mathrm{const.}}}. \quad (1.4)$$

Then, in the quantum well case, the DOS particularizes to

$$\rho_{QW}(E) = \frac{m}{\pi \hbar^2 L_z} \sum_p \vartheta(E - E_{s,p}), \quad (1.5)$$

where ϑ denotes the unit step function. As follows from (1.5), and as illustrated in Fig. 1.4, the DOS in the quantum well is discontinuous, in contrast to the case of bulk semiconductors, where the absence of spatial constraints leads to a continuous DOS.

At equilibrium conditions at temperature T, the electrons occupy the discrete energy levels of the quantum well according to the Fermi–Dirac distribution function (1.1), so that the electron density per unit area at equilibrium is given by (Ferry and Goodnick 2009)

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