



纳米科学与技术

纳米技术 光、电及可再生能源

Nanotechnology for
Electronics, Photonics, and Renewable Energy

Anatoli Korkin Predrag S. Krstić Jack C. Wells



科学出版社



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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

表面分子组装》，是对相关工作的归纳总结。

多年来，本人的研究组开展固体表面分子组装研究，不但发展表面组装方法，还一直试图找到分子结构-固体种类-组装结构间的关系，也不放过发现组装结构中重要现象的机会并阐明原因，意欲探索表面分子组装规律，利用分子组装实现表面功能化。书中在介绍固体表面的结构特点和 STM 技术等表面分子组装基础知识之后，顺序介绍了简单烷烃/烷烃衍生物分子的组装结构、复杂配合物分子的组装、主客体组装以及功能化组装等，随后介绍结构转化研究、手性结构研究、电化学环境下的组装和相变化，最后是可能的表面功能化，内容安排尽量承上启下、先易后难且逻辑相关。

借此机会，我要感谢我研究组的研究生们，他们倾心科学，随我多年耕耘于固体表面分子组装研究领域，努力工作，夜以继日，他们终学有所成，也留下了丰富的科研结果。陈婷、严会娟、殷雅侠、陈庆、张旭、崔博、管翠中、郑轻娜等还参与了书稿内容整理、文献核对等工作。感谢科学出版社杨震、张淑晓和刘冉诸位编辑的悉心指导，感谢国家出版基金对本书的出版资助。感谢国家自然科学基金委员会、科技部和中国科学院，多年来，我的研究工作一直得到他们的支持，本书中的研究内容大多是在他们的资助下获得的科研成果。

还要感谢我的妻子姜红，她不厌其烦地整理我写下的零散片段，帮助打字输入我的手写书稿，保存相关资料，愿本书的出版给她带去一份快乐！

分子组装研究历史已久，内容丰富，且时有挑战课题出现，也有轰动性和里程碑性成果问世。限于水平和时间，书中不妥之处在所难免，恳请各位前辈和同行不吝赐教。出版本书意在抛砖引玉，以诱导、鼓励更多的科技工作者，尤其是青年科技工作者加入该研究行列，发展新技术，探索规律，攻坚克难；同时，发现新问题和解决新问题，推动分子组装研究不断发展。

葛之骅

Preface

Tutorial lectures given by world-renowned researchers have become one of the important traditions of the *Nano and Giga Challenges* (NGC) conference series. Soon after preparations had begun for the first forum, NGC2002,¹ in Moscow, Russia, the organizers realized that publication of the lectures notes would be a valuable legacy of the meeting and a significant educational resource and knowledge base for students, young researchers, and senior experts. Our first book was published by *Elsevier* and received the same title as the meeting itself—*Nano and Giga Challenges in Microelectronics*.² Our second book, *Nanotechnology for Electronic Materials and Devices*,³ based on the tutorial lectures at NGC2004⁴ in Krakow, Poland, the third book from NGC2007⁵ in Phoenix, Arizona, and the current book from joint NGC2009 and CSTC2009⁶ meeting in Hamilton, Ontario, have been published in Springer's *Nanostructure Science and Technology* series. Hosted by McMaster University, the meeting NGC/CSTC 2009 was held as a joint event of two conference series, Nano and Giga Challenges (*Nano & Giga Forum*) and Canadian Semiconductor Technology Conferences (CSTC), bringing together the networks and expertise of both professional forums.

Informational (electronics and photonics), renewable energy (solar systems, fuel cells, and batteries), and sensor (nano and bio) technologies have reached a new stage in their development in terms of engineering limits to cost-effective improvement of current technological approaches. The latest miniaturization of electronic devices is approaching atomic dimensions. Interconnect bottlenecks are limiting circuit speeds, new materials are being introduced into microelectronics manufacture at an unprecedented rate, and alternative technologies to mainstream CMOS are being considered. The low cost of natural energy sources and ignorance of the limits and environmental impact from use of natural carbon-based fuels have been long-standing economic barriers to the development of alternative and more efficient solar systems, fuel cells, and batteries. Nanotechnology is widely accepted as a source of potential solutions in securing future progress in information and energy technologies.

Nanotechnology as the art (i.e., science and technique) of control, manipulation, and fabrication of devices with structural and functional attributes smaller than 100 nm is perfectly suited to advanced CMOS technology. This technology

holds the capacity for massive production of high-quality nanodevices with an enormous variety of applications from computers to biosensors, from cell phones to space shuttles, and from large display screens to small electronic toys. Driven by scaling electronic devices to smaller and smaller sizes, the electronic industry has developed a set of sophisticated methods for deposition of ultra-thin films with very precise composition and nanoscale lithographic patterning. Enormous investment in nanotechnology for electronics R&D from companies and governments of many developed countries now finds a “new source of revenue”—solar energy applications. Based on the same core materials—silicon and other semiconductors—photovoltaics has for a long time been a “poor relative” of micro- and optoelectronics. That is not the case any more. The need for clean and renewable energy is becoming evident for the global community from the limited resources of mineral fuel and from the growing environmental impact of our current highly wasteful use of natural resources. Moreover, the world-wide energy crisis may spark a global political crisis and threaten the existence of human civilization.

The success of the NGC/CSTC 2009 conference, which resulted in the publication of this book and in other contributions making up special issues of *Nanotechnology*⁷ and *Nanoscale Research Letters*,⁸ would not have been possible without generous support from many sponsors and research institutions. We gratefully acknowledge the contributions and support of McMaster University (conference host and co-organizer), Arizona State University, Springer, Canadian Ministry of Foreign Affairs and Trade, Russian Nanotechnologies Corporation, Nokia, Oak Ridge National Lab, Ontario Centres of Excellence, Sematech International, CMC Microsystems, and many other local, national, international, and individual supporters.

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Notes

¹<http://asdn.net/ngcm2002/>

²*Nano and Giga Challenges in Microelectronics*, eds. J. Greer, A. Korkin, J. Labanowski (Elsevier, Amsterdam, Netherlands, 2003)

³*Nanotechnology for Electronic Materials and Devices*, eds. A. Korkin, E. Gusev, J. Labanowski, S. Luryi (Springer, New York, USA, 2007)

⁴<http://asdn.net/ngcm2004/>

⁵<http://asdn.net/ngc2007/>

⁶<http://asdn.net/ngc2009/>

⁷Selected and invited papers from NGC/CSTC 2009 symposium on semiconductor technology (guest editors Stephen Goodnick, Anatoli Korkin, Predrag Krstic, Peter Mascher, John Preston, and Alexander Zaslavsky) published in *Nanotechnology* **21**(13) (2010)

⁸Nanoscale science and technology for electronics, photonics and renewable energy applications: Selected papers from NGC2009 & CSTC2009 conference. (guest editors Anatoli Korkin, Predrag Krstic, Zoran Miskovic, Hongbin Yu, and Igor Zhitomirsky) published in the open-access journal, *Nanoscale Research Letters* **5**(3) (2010).

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Chapter 1

Molecular Electronics: Challenges and Perspectives

Paolo Lugli, Simone Locci, Christoph Erlen, and Gyorgy Csaba

Abstract Molecular electronics has lately attracted increasing attention due to some appealing features such as possibly very higher integration capabilities, their low production cost, flexibility in the substrate choice, and possibility for large-area deployment. Two parallel approaches characterize this field: on one side molecules can be contacted and their transport characteristics exploited to achieve electronic functionalities; on the other side existing device structures, as well as novel ones, can be realized using organic layers instead of or together with inorganic materials. While in the latter case theoretical investigations on such devices can be carried out on adapting conventional simulators to the new materials and physics involved, completely new tools have to be developed in the former case. In this chapter, the operational principles of molecular systems will be presented based on a series of theoretical results obtained from our groups. Challenges and perspectives are also discussed.

Introduction

Molecular electronics has witnessed increased interest in recent years, triggered by the forecast that silicon technology might reach its scalability limits in a few years [1–4]. In order for molecular electronics to become a valuable alternative to silicon technology, it will not be sufficient to fabricate molecular electronic devices with outstanding characteristics, but appropriate circuit and architectural solutions will also be needed. While a lot of effort has been dedicated to the demonstration of electronic functionalities of single molecules and organic films, research at the circuit and system level is still in its infancy [5–9].

Investigation on single molecules or nanotube-based devices promises to keep Moore's law alive once miniaturization of silicon-based structures becomes

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impractical. As first proposed by Aviram and Ratner [10], one can imagine to squeeze entire nonlinear circuit elements (such as diodes or transistors) into single molecules. In principle, such devices could be significantly faster and smaller than end-of-the-roadmap solid-state electron devices. Despite an enormous progress on the experimental characterization of single-molecule conduction in the last years, only few device concepts have emerged and it is still unclear whether individual molecular devices could be integrated into a larger-scale computing circuit. In any case, we can be sure that molecular circuits and architectures will be very different from what we are used to in today's systems. Several architectures, which would be suitable for the realization of electronic logic circuits or memory cells based on molecular devices, have been proposed. One possibility is to synthesize complex molecules whose arms can be separately contacted to provide the same electrical input/output of conventional logic gates. Such fascinating idea, suggested by Ellenbogen and Love [11], is unfortunately extremely challenging from the chemical-synthesis point of view, and it has not been realized up to now. Another possibility is to create a programmable interconnected network of nanoparticles and molecular entities ("nanocells") [12]: conducting metallic nanoparticles are randomly deposited on a substrate (which can be a silicon one) and subsequently bridged via molecular connections, to create electrical pathways between previously patterned metallic leads. The molecular linkers should exhibit nonlinear IV characteristics, in the form of negative differential resistance or hysteretic behavior and the network is connected to a limited number of input/output pins at the edges of the nanocell, which could then be accessed, configured, and programmed from the edges. Simulations have demonstrated the capability of the nanocell to act as logic gate [12, 13].

Integration with CMOS technology will certainly be the first step for devices based on single molecules, with solutions that follow a road that has been called "More than Moore" [14], in an attempt to extend the standard chip functionalities already offered by silicon technology. Such hybrid systems would benefit from the speed and reliability of CMOS, while offering at the same time the versatility and intrinsically nanometer footprint of molecular devices. Two architectures which are in principle compatible with silicon technology are the "Quantum Cellular Automata" [15] and the "cross bar" [16, 17]. While the latter employs solutions based on standard interconnections, the former relies on a highly innovative approach. In fact, devices and their interconnections can no longer be separated in a straightforward way in single-molecule electronics and it is not clear if the paradigm of classical circuit theory for building a complex system can still be followed [18, 19]. It is very timely to explore alternative ideas to interconnect molecular building blocks inside the molecular circuit and the molecules to the outer world without metal wires [20], using electric or magnetic fields. One very interesting hybrid architecture is the semiconductor/nanowire/molecular one ("CMOL"), proposed by Likharev and coworkers [21, 22]. The basic difference with respect to crossbars is that in CMOL the interface between CMOS circuitry and nanowires is provided by pins distributed all over the circuit area. Thus, a much larger integration should be achieved, with relaxed requirement concerning alignment of the wire interconnects.

Besides single-molecule structures, molecular electronics refers also to the employment of organic materials as substitutes for the solid-state layers of traditional semiconductor devices. Since their carrier mobility is relatively low, organic devices cannot compete with silicon-based circuits in high-speed, high-performance computing applications, but can become competitive in the market of large-area devices, because their process technology is potentially inexpensive and circuits can be realized on virtually any substrate (e.g., on plastics, paper, or textiles) [23].

We will present our theoretical analysis on organic transistors, inverters, and ring oscillators, describing the simulation tools used and its applications to device and circuit modeling. In the areas of chemical sensing, light emission, and light sensing, organic materials could make far more versatile devices as their semiconductor counterparts, because of the wide selection of possible sensor and light-emitting materials [24]. The first products have already entered the marketplace (e.g., OLED-displays), whereas others will follow soon. Due to their versatility in terms of fabrication and performance, organic films could also be integrated with silicon circuitry, embracing again the “More than Moore” paradigm.

Modeling and simulation of these device classes, which imitate traditional solid-state devices with organic materials, seems quite straightforward, as the existing semiconductor simulation approaches, like the well-established drift-diffusion method [25], can be applied. In spite of many open issues, mainly related to the charge transport in organic semiconductors as well as to their morphology [26], simulating organic devices do not require the development of fundamentally new approaches. In parallel to numerical simulation, analytical approaches have also been developed, which can help in the analysis of transport phenomena (e.g., trapping) and device operation [27]. Circuits employing organic thin-film transistors (OTFTs) are based on the same building block of conventional electronics, namely the inverter, but, due to the difficulty of realizing n-type organic transistors, typical circuits rely only on p-type devices, without being of complementary types [28].

A quite different approach is required for single-molecule devices, where quantum mechanical tools are needed. Quantum chemistry methods have reached a high level of maturity and are credited with good predictive power for the determination of formation energies and molecular geometries. It seems natural to extend these methods beyond their original purpose to treat non-equilibrium transport processes through single (or few) molecules and to analyze their device performance. To such purpose, density functional theory (DFT) [29] usually provides the description of the electronic properties of the molecular system, while the non-equilibrium Green’s function (NEGF) [30] allows one to compute the transport characteristics. With such tools, it is possible to calculate the current–voltage characteristics of a molecule connected to two metallic electrodes [31, 32]. Due to the computational complexity of the DFT–NEGF algorithms, it is basically impossible to extend them to the design of even very elementary circuits and memory cells. It is therefore necessary to develop approaches which allow us to go from the atomistic description of the single molecular element to design tools capable of full circuit simulations. Construction of equivalent circuit models and circuit-level simulations serve this purpose [33], as will be discussed afterwards.

Single Molecules

Electronic conduction through a variety of different molecules has been studied experimentally by many research groups [31, 32, 34–36] and novel design architectures for memories and logic circuits have been explored. However, the exact nature of the transport mechanisms in many of such systems remains still open to scientific debate. To correctly treat these problems, complex *ab initio* computations are needed. First-principles computations [29, 37, 38] are normally based on density-functional methods, which are, however, limited to molecular systems made up of a small number of atoms. In addition, a precise estimation of energy band gaps requires sophisticated many-body corrections. Since we are interested in the transport properties of molecules, which are not isolated entities but rather connected to metallic electrodes, we need first to clarify how the interactions between molecule and contacts determine the energy levels of the complete system. We have used the density-functional tight-binding (DFTB) method [39, 40–45], which allows a first-principles treatment of systems comprising a large number of atoms. This method, implemented in the code gDFTB, has been extended to the non-equilibrium Green's function (NEGF) approach [30], by generalizing the calculation of the atomic charges using the non-equilibrium (DFT) density matrix and solving a three-dimensional Poisson solver [40]. The implementation of NEGF is similar to other codes based on first-principles approaches [46, 29]. Thus, the computation of the tunneling current between two contacts is possible in a manner consistent with the open boundaries and non-equilibrium conditions that naturally arise in coherent transport problems.

The main approximations of gDFTB are (i) the use of limited basis functions (mainly the minimal basis) and (ii) the use of two-center approximation in the calculation of the Hamiltonian matrix elements. The use of such approximations makes the scheme computationally extremely fast and makes the approach suitable to treat systems with several thousands of atoms, thus applicable to nanostructured devices. The gDFTB scheme can be considered as a highly efficient high-level computational tool which works surprisingly well despite the large number of simplifying assumptions. It enables, for instance, the computation of the tunneling current flowing between two or more contacts in a manner consistent with the open boundaries and non-equilibrium conditions that naturally arise in coherent transport problems. Molecular dynamics simulation can be performed within the present approach, and time-dependent currents can be calculated accounting for molecular vibration effects [40, 47]. Recently, the approach has also been extended to account for electron–phonon interactions [48].

The density-functional tight-binding (DFTB) formalism has been described in detail in many articles and reviews [49]. All matrix elements and orbital wavefunctions are derived from density-functional calculations. The advantage of the method relies on the use of a small basis set and the restriction to two center integrals, allowing extensive use of look-up tables. What distinguishes our approach from empirical methods is the explicit calculation of the basis wavefunctions, which allows deeper physical insights into and better control of the approximations used.

The method solves the Kohn–Sham equations self-consistently using a Mulliken charge projection [43]. In the traditional DFTB code a minimal basis set of atomic orbitals is used in order to reduce the matrix dimensions for diagonalization speed-up. This approach has proved to give transferable and accurate interaction potentials, and the numerical efficiency of the method allows molecular dynamic simulations of large super-cells, containing several hundreds of atoms, particularly suitable to study the electronic properties and dynamics of large mesoscopic systems and organic molecules such as CNTs, DNA strands or adsorbates on surfaces, and semiconducting heterostructure [50].

We briefly describe here the self-consistent DFTB method. The electronic density is expanded as a sum of a reference density $n^0(r)$ (that can be chosen as the superposition of neutral atomic densities) and a deviation, $\delta n(r)$, such that $n(r) = n^0(r) + \delta n(r)$. The total energy of the system can be described, up to second order in the local density fluctuations, as

$$E_{\text{tot}}[n] = \sum_k n_k \langle \psi_k | H^0 | \psi_k \rangle + E_{\text{rep}}[n^0] + E^{(2)}[\delta n]. \quad (1.1)$$

The first term in Eq. (1.1) can be written in terms of the TB Hamiltonian, which is given by

$$\begin{cases} H_{\mu\nu}^0 = \varepsilon_{\mu}^{\text{free-atom}}, & \mu = \nu \\ \langle \phi_{\mu} | T + v_{\text{eff}}[n_i^0 + n_j^0] | \phi_{\nu} \rangle, & \mu \in i, \nu \in j \end{cases}, \quad (1.2)$$

where ϕ_{μ} and ϕ_{ν} are the atomic orbitals localized around the atomic centers i and j ; T is the kinetic energy operator; and v_{eff} is the effective one-particle potential, which depends on the density of the two atomic centers i and j .

The term $E_{\text{rep}}[n^0]$ in Eq. (1.1) is the repulsive energy between the ions, screened by the electronic distribution and the exchange energy. The third term in Eq. (1.1) is the second-order correction that can be written as

$$E^2[\delta n] = \frac{1}{2} \iint \left[\frac{1}{|r - r'|} + \frac{\delta^2 E_{\text{xc}}}{\delta n(r) \delta n(r')} \right] \delta n(r) \delta n(r') dr dr', \quad (1.3)$$

where the Hartree and exchange–correlation potentials have been separated. This quantity is greatly simplified by retaining only the monopole term in the radial expansion of the atom-centered density fluctuations [51].

Within the LDA approximation the exchange contribution vanishes for large atomic distances. Hence in Eq. (1.3) the second-order correction to E_{xc} can be neglected with respect to the Coulomb interaction. For short ranges Coulomb and XC contributions are accounted with on-site Hubbard parameters, which are calculated for any atom type within LDA-DFT as the second derivative of the total energy of the atom with respect to the occupation number of the highest occupied atomic orbital. These values are therefore neither adjustable nor empirical parameter [43]. By applying the variational principle to the energy functional of Eq. (1.1),