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Nanoscale Devices

Fabrication, Functionalization, and Accessibility from the Macroscopic World

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Chapter 1
Matter on the Nanoscale

Nanotechnology may be defined as the set of techniques[1] and methods for the exploitation of the properties of matter on the nanoscale.

Nanotechnology may also be considered as the practical realization of the dreams of Feynman and Drexler:

- In a legendary talk titled *There's plenty of room at the bottom: An invitation to enter a new world of physics*, delivered on 29 December 1959 at the Winter Meeting in the West of the American Physical Society [1],[2] Feynman proposed the use of atoms as information storage elements, thus allowing a planar bit density on the scale of 10^{15} cm^{-2} – the petascale integration (PSI).
- Subsequently, in a series of publications started in 1982 and culminating in a book on *Nanosystems – Molecular Machines, Manufacturing and Computation* [3], Drexler suggested that the optimal scale for the exploitation of microscopic objects at the macroscopic scale is the molecular or supermolecular one.[3]

Drexler's conclusion, although reducing the maximum density of a surface arrangement from the petascale to the terascale, does, however, clarify that the exploitation of the potentials offered by molecular or supramolecular arrangements requires the development of a technology for assembling, addressing and probing objects on the nanometer length scale – just nanotechnology.

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[1] In this book the word "technique" is used with the meaning of "method of accomplishing a desired aim" (item 2b of Merriam–Webster Dictionary); "technology" will instead be used with the meaning of "combination of techniques aimed at a desired aim."

[2] A transcript of Feynman's talk is available online at http://www.zyvex.com/nanotech/feynman.html. In that site the talk is referred to as delivered to the "Annual Meeting," but Queisser informed the author that "it was the 'Winter Meeting in the West' of the American Physical Society in Pasadena. I was there, listened with enthusiasm to Feynman's physics and humor, even sat at the speaker's table; my boss Shockley arranged that for me. Shockley knew Feynman from his student days. The talk was very general, did not really address microelectronics as yet – but it provided a strong impetus for me" [2].

[3] The notion and even the name "nanotechnology" became, however, popular only after the appearance of *Engines of Creation. The Coming Era of Nanotechnology* [4], a visionary book listing the menu of what could reasonably be expected from a technology able to manipulate nanoscale objects.

1.1 Nanotechnology and the $(N+1)$ Problem

The collective properties of matter can be distinguished in the light of their scaling behavior: on the *macroscopic scale* (the one described by classical physics) they remain substantially unchanged when the size of the considered system is progressively reduced; replicas of the system have negligible statistical dispersion; on the *mesoscopic scale* they change substantially when the size of the system is progressively reduced so that replicas of the systems have usually large statistical dispersion; whereas on the *microscopic scale* (the one described by quantum physics) matter cannot be shrunk and all replicas of the system are rigorously identical.

The upper limit of the microscopic scale is the molecular one, whose length scale is centered on the nanometer, so that mesoscopic systems have sizes typically in the interval 3–30 nm – that allows them, in relation to their size, to be referred to as nanoscopic. Not only do nanoscopic objects display properties (often potentially useful properties) generally different from those observed on the macroscopic scale, but also *on the nanoscale the properties of a system with* $(N+1)$ *particles may be very different from those of a system with* N *particles*.[4]

The recognition that matter confined in geometries on a length scale of 3–30 nm manifests special behaviors has led to a systematic search for methods to permit their practical exploitation. The set of methods, processes, and materials allowing such exploitation forms the skeleton of nanotechnology.

Although eventually responsible for the birth of such a technology, the nanoscale property emphasized above, the so-called $(N+1)$ *problem* [6], is responsible for the difficulties in the development of nanotechnology.

In perturbative terms the $(N+1)$ problem may be restated saying that on the nanoscale the addition of another particle to a system of N particles cannot be considered as a small perturbation. Expressed in thermodynamic terms, it is equivalent to saying that the chemical potential of nanoscale systems is not a smooth function of N.

Clearly enough, the relevance of the $(N+1)$ problem increases with the strength of the interaction of the $(N+1)$th particle with the remaining N. The strength of this interaction is minimum when the particles are molecules interacting with each other by means of Van der Waals forces. Hence the *molecular road to nanotechnology*: exploiting the properties of packets of few molecules forming supramolecular complexes stabilized by Van der Waals interactions.

The molecular structure of matter was firmly established at the beginning of the twentieth century with the foundation of a theory of Brownian motion by Einstein and Smoluchowski and its experimental verification by Perrin. Molecules could however be individually sensed and manipulated only after Binnig and Rohrer's invention of the scanning tunnel microscope.

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[4] Interviewed by the Editor for the first issue of *ACS Nano*, Rohrer defined nanoscale as the "bifurcation point where ... materials have their properties and a cluster of 10 atoms does not yet have the same properties as 100 atoms" [5].

The availability of this tool has allowed the discovery that quantum properties of large potential interest (like interference or resonant tunnel) are typically manifested *inside* molecules, i.e., on the genuine nanometer length scale (0.3–3 nm).

Although one of the major aspects of current nanotechnology is just the functionalization of nanostructures with suitable molecules (e.g., for the lubrication of microelectromechanical systems, for drug delivery, for controlling hydrophobicity/ hydrophilicity, etc.), the properties imparted by the molecules are qualitatively similar, although quantitatively superior, to those manifested on a macroscopic length scale – but really few devices exploiting the genuine intramolecular quantum phenomena are known.

1.2 Microelectronics is a Nanotechnology

An integrated circuit (IC) is a collection of batch-processed single devices [usually complementary metal–oxide–semiconductor (CMOS) field-effect transistors (FETs)] interconnected in such a way as to perform sophisticated operations, like computation. At the forefront of the technology, ICs have complexity on the giga-scale integration; the gate length and width are of 45 nm, gate-insulator thickness is of 1–2 nm, and exploit, for some of their functions, genuine quantum phenomena (for instance, flash memories, with tunnel oxide thickness of 4–6 nm, are erased exploiting a typical quantum effect – Fowler–Nordheim emission). Thus, although usually referred to as *micro*electronics,[5] the IC technology is already a *nano*technology.[6]

Although quantum and ballistic phenomena certainly affect the behavior of metal–oxide–semiconductor (MOS) FETs on a size scale of 10 nm, the analysis of test vehicles with that size has however shown that they can to a large extent continue to be regarded simply as large devices scaled down to that gate length. Which technology, if any, will be developed for the exploitation of such devices is still obscure; rather, there is a general agreement in the field that some of the fundamental difficulties in developing devices scaled to the 10-nm length scale will result in a failure of the technology within one decade. This consideration suggests the idea of developing a radically new technology exploiting (rather than trying to cancel) the properties manifested on the nanometer length scale.

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[5] Actually, prefix "micro" in the present context may be deceptive: affixed to "meter," it denotes a *macro*scopic length scale; affixed to "electronics," it denotes a *nano*technology; while affixed to "scopic," it is almost synonymous with "quantum." To avoid the confusion deriving from its use, from now on the objects forming the ICs will be referred to mentioning the basic technology involved in their production – lithography.

[6] According to the United States Patent Office, for an invention to qualify as pertaining to nanotechnology, at least one of its dimensions should be between 1 and 100 nm in size, and the tiny size of the device must be essential to its function [7].

Macroscopic devices based on nanoscopic elements have already been developed (think, for instance, of quantum dots for single electron transistors). The $(N + 1)$ problem, however, makes their reproducibility extremely difficult. This fact makes difficult the preparation of dense arrays of such devices with uniform characteristics.

However, the size of the cluster, at which one property, say the energy gap, is half way between the bulk and individual atom, will differ from one material to the next, and depend strongly upon electronic bonding or coupling. Whereas strong coupling will result in nonsmooth dependence on N, weak coupling, like that occurring in noble gases and to a lesser extent in molecular solids, will result in smaller differences between the individual molecule and the cluster. A radically new approach to nanoelectronics is thus based on the exploitation of conduction or charge-storage properties of single molecules or of packets of few of them.

1.3 From Microlectronics to Molecular Electronics

The birth of molecular electronics can be dated with the appearance of Aviram and Ratner's seminal paper [8]; that work opened the road to the search for and determination of molecular properties (including strongly nonlinear conductance, bistability, etc.) that have analogues in electronic devices. Attention was correspondingly focused on the preparation of simple test vehicles for checking whether a molecule, or an assembly of a few molecules, manifests properties of interest for electronic applications. In turn, this focus has led to experiments (involving scanning tunneling microscopy, break junctions, etc.) for the determination of such properties. This state of affairs is well described by the following words by Reed [9]:

> We are still [2001] at the materials stage in this field [molecular electronics], working to understand fundamentally what is going on in the materials by measuring their transport characteristics. Electronics has to go one step further, to a point where we can actually interconnect all of the devices. How we are actually going to progress technologically to the point where we can connect molecules is still not clear... Learning how we can connect all of these structures at the molecular stage is the next stage.

Transforming discrete molecular *devices* into practically exploitable *circuits* (where billions of molecular devices work in concert and each of them is electrically accessible) indeed requires the development of a totally new technology. As emphasized by Tour [10, p. 251], a silicon–organic hybrid architecture seems an obvious solution:

> with the fundamental limits in solid-state structures being approached, molecules will become the devices of the future ultradense computational systems. Not only will they be smaller and less expensive than their solid-state counterparts, but in some instances they will show superior behavior which is hitherto unattainable from solid-state devices. The key, however, is that molecular systems will likely not supplant solid-state systems, but that they will be complements to traditional electronic devices.

The path to molecular electronics, however, is not expected to be so easy. In a critical analysis, Keyes [11, p. 20] objected that as molecular electronics requires the development of some novel architecture, “history does not encourage optimism.” Also, the technology requires the solution of a number of problems [11, p. 23]:

> Strains from attachment to a substrate will have an effect; inhomogeneities in a substrate surface may also modify properties. Gradients of temperature will create differences between different regions. Also, one must ask what is necessary to ensure that all of a large number of molecules actually do have the same chemical composition. Quantitative questions will arise. What standards of reagent purity will be required in order to obtain satisfactory yield in an assembly of 10^6, 10^8, or 10^{10} molecules? What sort of clean environment will be wanted to control the contamination that plagues electronic manufacturing?

None of the above questions has been answered yet.

Assuming optimistically that the concerted research effort in this area will succeed in giving positive answers, in this book the attention will be concentrated on (although not limited to) the molecular property which has attracted major interest for its possible implementation in hybrid circuits – the dramatic change of conductance resulting from the excitation of an ionized donor–acceptor pair [12] or from the ionization of a suitable molecular center [13]. If the excited states are metastable, the molecular bistability can be exploited for the preparation of memories.

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