1 Scope of Molecular Electronics

What's in a name?

1.1 INTRODUCTION

Molecular electronics is a relatively new and emerging technology, relating to the exploitation of organic and biological materials in electronic and opto-electronic devices. The subject has taken on a variety of definitions in different parts of the world, and at different times, but as it has matured over the last 30 years, molecular electronics can be divided broadly into two themes. The first, *molecular materials for electronics*, has its origins in materials science and concerns the development of electronic and opto-electronic devices that utilize the unique macroscopic properties of organic compounds. The most successful commercial product to date is the liquid crystal display, LCD. However, following many years of research, organic light-emitting devices based on dyes and polymers, plastic electronics circuitry and chemical and biochemical sensors are beginning to make their technological marks. The Nobel Prize in Chemistry for 2000 was awarded to three scientists working in this area: Alan Heeger, Alan MacDiarmid and Hideki Shirakawa, who have made significant contributions to the development of electrically conductive polymers.

More challenging is *molecular-scale electronics*. Here, the focus is on the behaviour of individual organic molecules or groups of molecules and the precise three-dimensional positional control of individual atoms and molecules. Topics as diverse as molecular switching, DNA electronics and molecular manufacturing have all been described in the literature. Much of the research activity is directed towards computational architectures that may, one day, rival silicon microelectronics. However, even the most optimistic researchers recognize that this is going to be some time away!

The two approaches to molecular electronics outlined above, to some extent, exemplify the 'top-down' and 'bottom-up' themes of nanotechnology. The former refers to making nanoscale structures, for example by machining, whereas bottom-up, or molecular, nanotechnology applies to building organic and inorganic architectures atom-by-atom, or molecule-by-molecule. Top-down methods for manufacturing involve the construction of parts through methods such as cutting, milling and moulding, or etching methods linked to photolithographic pattering. The progress of the microelectronics industry is an excellent example of the top-down approach. On the other hand, bottom-up manufacturing would provide components made of single molecules, held together by covalent forces that are far stronger than the forces that hold together macro-scale components.

The physicist Richard Feynman was one of the first to predict a future for molecular-scale electronics. In a lecture in December 1959, at the annual meeting of the American Physical Society, entitled 'There's Plenty of Room at the Bottom', he described how the laws of physics do not limit our ability to manipulate single atoms and molecules. Instead, it was our

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lack of the appropriate methods for doing so. Feynman correctly predicted that the time would come in which atomically precise manipulation of matter would be possible. Several advances have been made over the last 20 years to suggest that the prophesy was correct. The most notable of these has been the introduction of scanning probe microscopy.

1.2 MOLECULAR MATERIALS FOR ELECTRONICS

Liquid crystals represent a remarkable molecular electronics success story. However, the transformation of these organic compounds into the established display technology of today took many decades. In the latter half of the 19th nineteenth century, researchers discovered several materials whose optical properties behaved in a strange way near their melting points. In 1922, a liquid crystal classification scheme was presented by George Friedel, but it took until the 1960s for the potential of liquid crystals in display devices to be recognized. From this point, research into liquid crystals and their applications burgeoned. It is encouraging for workers in molecular electronics that the relatively unstable (thermally and chemically) liquid crystal compounds came to form the foundation of such a substantial worldwide industry.

Much of the 'molecular materials' theme to molecular electronics derives from the intriguing electrical and opto-electrical behaviour of organic materials. Two distinct groups of organic compounds have been studied – low molecular weight crystalline compounds (molecular crystals) and polymers. In the former category, the photoconductivity of anthracene was discovered in 1906 [1]. However, systematic study of the electrical behaviour of organic molecular solids did not begin until the 1950s [2–4]. The phthalocyanine compounds were one of the first classes of organic molecular crystals to be investigated [2, 3]. These large, flat, ring-shaped structures are relatively stable organic materials and demonstrate that the words 'organic' and 'thermally unstable' need not always go hand-inhand.

The first synthetic polymers were produced in the late 19th century. These were eventually developed into useful products in the 1940s and 1950s (exploiting their toughness, strength to weight ratio, low cost and ease of fabrication). At this time, polymeric materials were all good insulators, and the idea that a plastic material might conduct electricity was not generally considered. Polyacetylene is the simplest conductive polymer. Its chemical structure (Figure 1.1), consists of a hydrocarbon chain with the carbon atoms connected together by a system of alternating single and double bonds. This particular chemical bonding arrangement confers polyacetylene with its conductive properties.

Reports on acetylene polymers date back to the 19th century. However, the polymer was first prepared as a linear, high molecular weight polymer of high crystallinity and regular structure in 1958, by Giulio Natta (Nobel Prize for Chemistry in 1963) and co-workers [5].



Figure 1.1 Chemical structure of polyacetylene.

The material was discovered to be a semiconductor, with an electrical conductivity between 7×10^{-11} and 7×10^{-3} S m⁻¹, depending on how the polymer was produced. Some years layer, in 1967, a student of Hideki Shirakawa, working at the Tokyo Institute of Technology, produced, by accident, a polyacetylene film with a conductivity value similar to that of the best Natta material. Furthermore, the conductivity could be increased by a factor of about 10^9 by exposure to halogens. However, in the form in which the polymer was discovered, the material was practically useless; it was insoluble in any solvent and so could not be processed into any kind of useable structure, such as a thin film or a wire. This problem was solved by Jim Feast, a chemist at Durham University. This involved making a soluble groups attached to the side is first synthesized. These groups have the effect of making the polymer soluble, so the material can be formed into a film, a fibre or a wire. Only then, after processing, are the groups removed to leave the conductive polymer in the desired form.

In the 1980s, conductive polymers based on polyheterocyclic compounds (e.g. polyaniline, polypyrrole, polythiophene) were produced that were soluble in organic solvents and, consequently, could be processed into the form needed for many applications. Figure 1.2 depicts the very wide range of conductivity values that can now be found in conductive polymers.

Polymeric semiconductors can have significant advantages over their inorganic counterparts. For example, thin layers of polymers can easily be made by low-cost methods such as



Figure 1.2 Range of conductivities for conductive polymers compared with various inorganic materials.

spin-coating. High-temperature deposition from vapour reactants is generally needed for inorganic semiconductors. Since polymers are lightweight and can be manufactured into many different shapes, obvious uses are as components in portable batteries or as electrostatic or electromagnetic shielding, conducting adhesives, printed circuit boards and replacements for conventional electrolytes in electrolytic capacitors. Other electroactive properties of these organic compounds can also be exploited in electronic devices. Examples include components in photocopying machines, organic light-emitting displays, gas, vapour and biosensors and plastic transistors. The electrical properties of the last devices cannot be directly compared with those based on single crystal silicon and gallium arsenide. The mobilities (carrier velocity per unit electric field) of the charge carriers in organic field effect transistors are low and similar to those found in amorphous silicon. Nevertheless, the simple fabrication techniques for polymers have attracted several companies to work on polymer transistor applications, such as data storage and thin film device arrays to address liquid crystal displays. The long-term stability of organic materials has often been considered as a limitation to their exploitation in electronic devices. To some extent, this difficulty has now been resolved and some conductive polymers are now displaying adequate storage and operating lifetimes, e.g. estimated operating lifetimes of over 10⁶ hours for some organic light-emitting devices.

Certain organic compounds are superconducting, but usually at very low temperatures. A challenge has been to try to increase the transition temperature. Although there have been some theoretical predictions on the type of organic molecules that would be superconductive at room temperature, this 'Holy Grail' remains elusive. At the opposite extreme of the conductivity scale, nonconductive polymers can also play an important role in molecular materials for electronics. Pyroelectric, piezoelectric and ferromagnetic materials may find use in infrared detection, intruder alarms and nonlinear optics (e.g. second-harmonic generation). Similarly, some effort is being focused on organic magnetic materials. Due to the high density of iron, such molecular devices are generally inferior to conventional magnets on a 'magnet per unit weight or unit volume' basis. However, for more specialist applications, such as data storage, molecular systems may become important.

The development of effective devices for the identification and quantification of chemical and biochemical substances for process control and environmental monitoring is a growing need. Many sensors do not possess the specifications to conform to existing or forthcoming legislation; some systems are too bulky and/or expensive for use in the field. Inorganic materials such as the oxides of tin and zinc have traditionally been favoured as sensing elements. However, one disadvantage of sensors based on metallic oxides is that they usually have to be operated at elevated temperatures, limiting some applications. As an alternative, there has been considerable interest in trying to exploit the properties of organic materials. Many such substances, in particular phthalocyanine derivatives, are known to exhibit high sensitivity to gases. A significant advantage of organic compounds is that their sensitivity and selectivity can be tailored to a particular application by modifications to their chemical structure. Moreover, thin film technologies, such as self-assembly or layer-by-layer electrostatic deposition, enable ultra-thin layers of organic materials to be engineered at the molecular level.

This transition of materials from the micro-scale to the nano-scale offers several advantages. First, an enormous increase in surface area may be achieved; bulk properties become governed by surface properties. A material can be made light absorbing by coating its constituent particles with a dye. The particle size reduction also induces both mechanical

advantages and quantum effects. For instance, the hindered propagation of lattice defects leads to strong and hard metals, and enhanced diffusional creep leads to 'super-plastic' ceramics during processing at elevated temperatures. Quantum confinement allows for control over material 'constants', as demonstrated by the blue shift of the optical spectrum of nanoparticles. Colours can be controlled and manipulated. For example, titanium dioxide in nano-material form absorbs much more UV light than its bulk counterpart.

1.3 MOLECULAR-SCALE ELECTRONICS

The name 'molecular electronics' dates back to the 1950s in the USA, although its meaning was somewhat different to that accepted today. Although all branches of the US Military were interested in miniaturization, the form that interest took varied among the Services. The Air Force supported an idea known as 'molecular electronics'. The concept was radically different to any other attempt at miniaturization – to build a circuit in the solid without reproducing individual component function. The whole was to do more than the sum of the parts. Molecular electronics demanded a technological leap beyond even integrated circuits, which were really just discrete components formed in the same piece of silicon (with the two important problems of isolation and interconnection overcome). The idea was ahead of its time and certainly in advance of the technology available, and no significant progress was made.

Serious research on molecular electronics started in the USA in the 1970s with pioneering work by Ari Aviram at IBM, who proposed a structure for a molecular rectifier [6]. Impetus was provided by the enthusiasm of Forrest Carter working in the US Naval Research Laboratory [7] and the field was epitomized by the elegant experiments on monolayer films undertaken by Hans Kuhn in Göttingen [8].

However, emerging technologies must compete with existing ways to doing things. The microelectronics industry, based largely on the inorganic semiconductor silicon, has been developing since the 1950s and is continuing to make dramatic progress. To put molecular-scale electronics into context, a review of these developments is provided in the next section.

1.3.1 Evolution of Microelectronics

The workhorse of today's electronic computer is the metal–oxide–semiconductor transistor, or MOSFET; the basic structure of a silicon MOSFET is shown in Figure 1.3. This is a three-terminal device, comprising the source, drain and gate. A conductive channel in the silicon semiconductor is formed beneath the insulating gate oxide and between the source and drain contacts. Application of an electric field to the gate influences the conductivity of the channel; this is called the field effect. Because there are charge carriers with both positive and negative charges, there are two kinds of MOS transistor – n-channel and p-channel. The technology is therefore referred to as complementary MOS, or CMOS. Table 1.1 shows some of the significant dates in the evolution of electronics during the 20th century [9, 10]. Although a patent for a MOSFET was filed in 1930, most of the developments in electronics around this time exploited the valve (or vacuum tube) as a signal processing device. By the late 1940s, after 40 years of development, valve technology was mature.



Figure 1.3 Schematic diagram of a metal–oxide–semiconductor transistor or MOSFET. The length of the conductive channel is L and the thickness of the insulating gate oxide is given by d.

The first large-scale digital electronic computer that could be reprogrammed, ENIAC (Electronic Numerical Integrator And Computer), was built in 1946, in the Moore School of Electronic Engineering, University of Pennsylvania (although earlier computers had been built with some of these properties). ENIAC could add 5000 numbers per second. It could calculate the trajectory of an artillery shell in only 30 s (in contrast, a human would need about 40 h). ENIAC contained about 17 000 valves, weighed 27 000 kg, occupied about 500 m³ and consumed 174 kW. Its programme was wired into the processor and had to be mechanically altered.

The junction transistor was invented at Bell Laboratories, USA, in 1947 by John Bardeen, Walter Brattain and William Shockley. The three inventors shared the 1956 Nobel Prize for Physics. Even though transistors as discrete devices had significant advantages over vacuum tubes, and progress on transistors was steady during the 1950s, the directors of many large electronics companies believed that vacuum tubes held an unassailable competitive position. Arguably, the most significant breakthrough for technology came late in the 1960s, when the integrated circuit, IC, was introduced. The patent for the first IC was filed in February 1959 by Jack Kilby of Texas Instruments. His IC was two circuits constructed in a piece of germanium. Kilby, the acknowledged inventor of the microchip, died in 2005, during the

Date	Milestone
1930	MOSFET concept patent (Lilienfield, University of Liepzig, Germany)
1946	Stored-program computer (ENIAC, University of Pennsylvania)
1947	Bipolar transistor (Bardeen, Brattain, Shockley, Ball Laboratories, USA)
1952	IC concept (Dummer, Royal Radar Establishment, UK)
1959	Planar process (Hoerni, Fairchild, USA)
1959	IC patent (Kilby, Texas Instruments, USA)
1960	MOSFET (Kahng and Atalla, Bell, USA)
1962	MOS IC (Hofstein and Heiman, RCA, USA)
1968	CMOS (Westinghouse, GT&E, RCA, Sylvania, USA)
1969	Internet (ARPAnet, USA)
1971	Microprocessor (Hoff, Intel, USA)
1972	1024 bit DRAM (Intel, USA)
1980	256 k DRAM (NEC-Toshiba, NTT-Musashino, Japan)
1981	MS-DOS (Gates, Microsoft, USA)

Table 1.1Dates of key inventions in microelectronics [9, 10].

writing of this book. He was awarded the Nobel Prize for Physics in 2000. The microprocessor became a reality in the mid-1970s with the introduction of the large-scale integrated circuit (LSI) and later the very large-scale integrated circuit (VLSI), with many thousands of interconnected transistors etched into a single silicon substrate.

1.3.2 Moore's Laws

A common barrier to sustaining a high rate of growth in any industry is the existence of a fundamental limitation to the basic technologies on which the industry depends. A good example of this is the commercial aerospace industry, where fundamental limitations in the strength of materials and the cost of energy have resulted in a current generation of aircraft no faster or more comfortable than those of 40 years ago. Improvements have instead been evolutionary in nature and focused largely around operating cost reduction. By contrast, no fundamental limitation in the technologies enabling the electronics industry has yet arisen as a significant barrier to its continued growth.

The first microprocessor chip (the 4004), manufactured in 1971 by Intel using 10 μ m process technology, had a clock speed of 108 kHz and contained 2300 transistors. There are 169 × 10⁶ transistors on the Pentium[®] 4 chip (February 2005), fabricated using 90 nm technology, and operating at a clock speed of 3.73 GHz. The 2006 version of the Titanium[®] 2 Processor contains over 10⁹ transistors [11]. Furthermore, Intel is on track to manufacture chips on 300 mm Si wafers using 45 nm process technology by 2007.

Gordon Moore of Intel was the first to quantify the steady improvement in gate density when he noticed that the number of transistors that could be built on a chip increased exponentially with time. His observation, made in 1965, was that the number of transistors per unit area on integrated circuits, or functionality per chip, had doubled every year since the integrated circuit was invented. Moore predicted that this trend would continue for the foreseeable future. This is Moore's Law, or Moore's First Law. Although not strictly a 'law', this rule has been a consistent trend and key indication of successful leading-edge semiconductor products. In recent years, the pace slowed a little: the scaling of the microprocessor unit, MPU, is based more on a 2.5 year cycle (i.e. the functionality per chip doubles every 2.5 years) while the scaling of a dynamic random access memory, DRAM, is a 3 year cycle. Most experts expect Moore's Law to hold for at least until 2020.

The semiconductor industries have produced an *International Technology Roadmap for Semiconductors* on the future of CMOS technology [12]. Figure 1.4 shows the anticipated growth in the density of the transistors in both the MPU and the DRAM of a CMOS chip. The prediction is for a 13 nm minimum feature size (gate length, *L* in Figure 1.3) for the MPU and 4×10^{10} transistors per cm² for the DRAM (multi-level cell) by 2013. Longer term predictions give these values as 6 nm and 2×10^{11} cm⁻², respectively. All these figures are regularly updated. The transistors in Intel's new 65 nm process technology have gates measuring 35 nm. About 100 of these gates could fit inside the diameter of a human red blood cell.

Intel has already published experimental results on a transistor with 10 nm gate length [11]. Researchers from Intel and QinetiQ have also jointly developed prototype transistors with indium antimonide (InSb is compound semiconductor from based on elements from Groups 3 and 5 of the periodic table – a so-called III–V compound) which show promise for future high-speed and very low-power logic applications. These transistors could be used in



Figure 1.4 Predicted scaling for transistors in a dynamic random access memory (DRAM) and microprocessor unit (MPU). Taken from the *International Technology Roadmap for Semiconductors* [12].

Intel's logic products in the second half of the next decade and could be a factor in the continuation of Moore's Law well beyond 2015.

There are many recognized factors that could bring the Moore's Law scaling to an end. Some of the technical issues are explored in the next section. However, one significant factor is the economics of chip production. The cost of building fabrication facilities to manufacture chips has been increasing exponentially, by a factor of two for every chip generation. This is sometimes known as Moore's Second Law. The cost of manufacturing chips is increasing significantly faster than the market is expanding. Intel's Fab 22, a chip-fabrication facility which opened in Chandler, AZ, in October 2001, cost \$2 billion to construct and equip. The cost of building a Fab is projected to rise to \$15–30 billion by 2010 and could be as much as \$200 billion by 2015 [13]. This significant increase in cost is due to the extremely sophisticated tools that will be needed to form the increasingly small features of the devices.

1.3.3 Beyond Moore

As the dimensions of MOSFET devices decrease, the effect of the operating characteristics can be calculated [14]. The scaling can be done either to keep the electric field constant or to maintain the same operating voltage. For a scaling factor K(K > 1), Table 1.2 shows the effect on the operating parameters of the MOSFET for a constant field. The benefits of shrinking the device in terms of packing density, speed and power dissipation are evident. The scaling of depletion widths is achieved indirectly by scaling up the doping concentrations (which keeps the resistance unchanged). For ideal scaling, power supply voltages should also be reduced to keep the internal electric fields reasonably constant from one device generation to the next. In practice, however, power supply voltages are not scaled with the device dimensions, partly because of other system-related constraints.

One parameter that does not move in a favourable direction as the device dimensions are reduced is the current density, which is increased with the scale factor. Metal conductors

Parameter	Scaling factor
Device dimensions (channel length, gate width, oxide thickness)	1/K
Current, voltage	1/K
Current density	K
Impurity concentration	Κ
Gate capacitance	1/K
Time constant	1/K
Switching energy	$1/K^{3}$
Power per device	$1/K^{2}$

Table 1.2 Scaling rules for MOSFETs according to a scale factor *K*. The voltages are scaled to keep the electric fields constant [14].

have an upper current density limit imposed by the process of electromigration. This is a diffusive process in which the atoms of a solid move under the influence of electrical forces. This effect limits the maximum current that can be carried by a conductor without its rapid destruction. For example, the current density for aluminium conductors in integrated circuits must be kept below 10^{10} A m⁻².

Limits that are closely related to the basic physical laws are called fundamental limits. A basic concept of quantum mechanics is that a physical measurement performed in a time Δt (and computing may be considered as a 'measurement') must involve an energy ΔE :

$$\Delta E \ge \frac{h}{\Delta t} \tag{1.1}$$

where h is Planck's constant (= $6.63 \times 10^{-34} \text{ Js}$). The energy is dissipated as heat. The power P(= energy per unit time) dissipated during the measurement, or switching, process is

$$P = \frac{\Delta E}{\Delta t} \ge \frac{h}{\left(\Delta t\right)^2} \tag{1.2}$$

This can be considered as the lower band of power dissipation per unit operation. Equation (1.1) predicts a minimum energy dissipated in a nanosecond switching device (i.e. operating at 1 GHz) is about 10^{-25} J, which is currently orders of magnitude below the actual switching energy in an MOS device (the switching energy of silicon MOSFET devices that will be produced in 2016 is estimated as 4×10^{-18} J [12]).

The switching energy must generally be greater than the thermal energy, otherwise the device will switch on and off randomly. This requires

$$\Delta E > k_{\rm B}T \tag{1.3}$$

where $k_{\rm B}$ is Boltzmann's constant $(1.38 \times 10^{-23} \,\text{J K}^{-1})$ and *T* is the absolute temperature. At room temperature, $k_{\rm B}T = 4 \times 10^{-21} \,\text{J}$, once again many orders of magnitude below the actual switching energy in MOSFETs.

10 MOLECULAR ELECTRONICS

Equation (1.3) is not regarded as a fundamental limit to computing operations, as many methods are available to reduce noise in electronic systems [15]. An assertion, put forward by John von Neumann, in a 1949 lecture, was that a computer must dissipate an energy per reversible operation (or per bit in a binary computer) given by

$$\Delta E = k_{\rm B} T \log_{\rm e} 2 \tag{1.4}$$

which is about 3×10^{-21} J at room temperature. This can be considered as a fundamental limit.

A further issue is the time taken for a charge carrier to acquire energy from the applied electric field. The maximum rate of energy transfer (power) to an electron with an electrical charge $e(=1.6 \times 10^{-19} \text{ C})$ moving at a speed v in an electric field E is evE [i.e. = (force \times distance)/time]. The electron energy must be greater than the thermal energy $k_{\rm B}T$. The time to achieve this is therefore given by

time =
$$\frac{\text{energy}}{\text{power}} = \frac{k_{\text{B}}T}{evE}$$
 (1.5)

The maximum electron velocity in silicon is about $10^5 \,\mathrm{m \, s^{-1}}$ for an applied field of 5×10^7 V m⁻¹. This gives a limiting response time of approximately 5×10^{-15} s (5 fs) at room temperature. Devices will not respond so quickly as this the electrons will need to acquire energies $\gg k_{\rm B}T$ (10 $k_{\rm B}T$ or 100 $k_{\rm B}T$). However, this principle imposes a restriction on the operating frequency of silicon MOSFETs.

There are also a number of technological problems issues that will need to be overcome for the predictions for the CMOS-based roadmap to be realized. Not least are the materials limitations of the silicon/silicon dioxide system. For example, charge leakage becomes a problem when the insulating silicon dioxide layers are thinned to a few nm. Intel's 65 nm transistors have a gate oxide thickness of 1.2 nm. Quantum mechanical tunnelling through the oxide can become a serious problem if the tunnel currents become comparable to the other circuit currents. Alternative insulating materials, such as hafnium oxide, are currently under investigation by the large electronics companies.

Heat dissipation is a further important factor. A Pentium[®] chip, with around 10^8 transistors operating at the nanosecond rate, can emit up to 100 W of heat. Although the simple scaling shown in Table 1.2 predicts that the power per device decreases with the square of the scaling factor, the power density (power per unit area) will remain constant. This power density p is given by

$$p = \Delta E \nu n X \tag{1.6}$$

where *n* is the device density, v is the frequency of operation and X is the probability that the device switches in a clock cycle, typically $X \sim 0.1$. The maximum tolerable power density is about 100 W cm^{-2} . This means that the switching energy, operating frequency and device density are limited by

$$\Delta E \nu n \approx 1000 \,\mathrm{W} \,\mathrm{cm}^{-2} \tag{1.7}$$

At high frequency, a high device density is desirable, and therefore a low energy per bit is desirable. These three limits are depicted in the switching energy-time diagram in Figure 1.5.



Figure 1.5 Switching time versus switching energy for MOSFETs based on (Equation (1.7)). The three different curves correspond to different device densities *n* (in units of cm⁻²). The vertical line corresponds to $100k_{\rm B}T(=4 \times 10^{-19} \text{ J})$, the optimum value for the energy to write a bit of information at room temperature.

Beyond 2016 and the demise of the top-down lithographic technologies which are currently employed, bottom-up nanomaterials fabrication for nanoelectronics has the potential to move electronic materials, computers and devices into a new era of sustainable growth.

The promise of molecular-scale electronics is compelling. The device density offered by silicon technology and outlined above is remarkable and offers the means to store significant amounts of data (Table 1.3) [16]. However, molecular-scale electronics has the potential for further increases in device density. For example, using 1-3 nm organic molecules as the processing elements, $10^{13}-10^{14}$ 'devices' could be fitted into 1 cm^2 . Discrete organic processing devices (diodes and transistors) and simple circuits based on these already exist. What is now needed is to make them work faster (the maximum operational speed of such plastic circuits is around a few MHz) and more reliably.

Molecular-scale technology will, of course, also need to address all the problems of the silicon microelectronics industry – plus many more! New approaches are needed. It will not be sufficient to reproduce the functionality of discrete silicon devices in molecules and then

Application	Typical information content (bytes)
Colour photograph	10 ⁵
Average book	10^{6}
Desktop computer	10^{8}
Genetic code	10^{10}
Human brain	10^{13}
Library of Congress	10 ¹⁵

 Table 1.3
 Information content of various sources [16]. (1 byte = 8 bits)

attempt to connect all the devices together in the same way that a silicon integrated circuit is built.

As computational devices shrink in size, the tolerance of their architectures to defects in the individual processing elements becomes more important. Even if the rate of defects in a chemically fabricated molecular circuit were only one per 10^9 components, which exceeds the best practices in chip fabs, it would still result in 10^6 defects in a system containing 10^{15} components. The largest defect-tolerant computer built so far is Hewlett Packard's experimental machine known as Teremac. Although Teremac was constructed by means of conventional technology, many of its problems resemble the challenges that face scientists who are exploring molecular electronics.

Teremac was built from a large number of components that had significant defect probabilities. To keep the construction costs reasonable, the machine was built using components that were defective and inexpensive. Furthermore, the techniques used to connect all the components together were error prone. Teremac is a reconfigurable multiarchitecture computer with 10^6 gates that operate at 1 MHz or a total of 10^{12} bit operations per second (hence 'tera'). It is based on field-programmable gate arrays (FPGAs). These are essentially lookup tables connected by a huge number of wires and switches that are arranged to form crossbars, which permit the connection of any input to any output. In principle, FPGAs substitute memory for logic whenever possible. Perhaps the most significant fact about Teremac is that it was comatose at birth. Three-quarters of the FPGAs contained defects that would be fatal to an isolated chip. Teremac contained 220 000 wiring and gate defects - a total of 3% of all its resources. For the first 24 h of its existence, Teremac was connected to a workstation to undergo a series of tests in order to find out where the defective resources were. These locations were then written to a configuration table as being 'in use' to ensure that the defective components would not be assessed by a running programme.

1.4 THE BIOLOGICAL WORLD

Scientists and technologists working in the field of molecular electronics frequently draw attention to the analogy between the devices they are working on and those found in Nature. There are very many examples. For instance, the brain is nature's computer. Although the brain works in a different way to silicon microprocessors (exploiting ions rather than electrons, and utilizing parallel processing, instead of the serial approach in silicon systems), it is nonetheless constructed from a large number of individual processing elements. Nature's 'gates' are the neurons. There are about 10^{11} neurons in the human brain, and each is connected to 10^3-10^4 others. This gives a crude 'bit count' of $10^{11}-10^{15}$. An equivalent artificial 'brain' might therefore be built from 10^5 8 Gbit chips.

Living systems are able to exist because of the vast amount of highly ordered molecular machinery from which they are built. The information required to build a living cell or organism is stored in the DNA and is then transferred the proteins by the processes called transcription and translation. These are all executed by various biomolecular components, mostly protein and nucleic acids. Such molecular-scale machinery is highly sophisticated and has evolved over millions of years. For example, bacteria may be considered as 'micro-robots,' moving throughout the human body and taking part in highly complex biochemical processes.

Electronics at the molecular scale is concerned with atomic precision and molecular manipulation and, in principle, has much to learn from Nature. This rapidly developing field is known as biomimetics. However, it might be argued that attempts to reproduce Nature's complex molecular architectures in the laboratory or factory using mechanical and chemical processes are too ambitious and doomed to failure (after all, humans' most successful flying machines are constructed from metal and not feathers!). A better approach for molecular-scale electronics is to learn from Nature rather than to copy it. For example, fundamental studies into the operation of Nature's molecular motors may, one day, lead to a new technology for energy production.

The other field in which molecular-scale manipulation of matter is receiving considerable attention is medicine. Since all living organisms are composed of molecules, molecular biology has become the primary focus of biotechnology. Countless diseases have been cured by our ability to synthesize small molecules – drugs – that interact with the protein molecules which make up the molecular machinery that keeps us alive. Our understanding of how proteins interact with DNA, phospholipids and other biological molecules is fundamental to progress.

1.5 FUTURE OPPORTUNITIES

The growth of the electronics industry has been driven by the development of disruptive technologies in parallel with evolutionary improvements in enabling device technologies. The development of personal computers, PCs, was a disruptive applications technology. Its progress, however, was greatly accelerated by rapid evolutionary improvements in technology for manufacturing semiconductor devices (increasing significantly the number of transistors on a chip). Other 'killer' applications have included cell phones, personal electronics (e.g. games), digital imaging and video, along with plasma and LCD flat panel displays. Digital video (or versatile) discs, DVDs, have enjoyed the most rapid and unexpected acceptance of any new home entertainment technology. The introduction of advanced optical discs with the required storage capacity, along with increasingly widespread adoption of high-definition television, HDTV, will help drive a high rate of growth in this sector of consumer electronics for the immediate future. Indeed, management of the current menagerie of discrete personal electronic devices may well be the most important driver for early implementation of some of the concepts embodied in 'ambient intelligence'.

The concept of ambient intelligence, AmI, was first outlined by Marc Weiser [17]. The idea was that small computer chips would be embedded in everyday objects all around us ('ubiquitous computing') and would respond to our presence, needs and wishes by way of wireless connectivity. It was imagined that these devices would undertake important tasks without active manipulation and so unobtrusively that we would notice only their effects. Weiser referred to this as 'calm technology', since it would allow us to focus on our work and on our social and recreational activities without requiring that we 'interact' directly with these devices as we currently do today with PCs, TVs, VCRs (video cassette recorders) and other home and workplace electronic items and appliances. Ambient intelligence has the potential to fulfil an important societal need – the requirement to simplify human interactions with the plethora of electronic devices that surround us today and to take advantage of the unfulfilled capabilities of electronic devices to make work and home life easier and more

productive. If this technology is widely accepted and adapted, it will certainly establish rapid and sustainable growth in the electronics industry.

Since the original concept paper by Weiser, the vision of calm technology has expanded to include context awareness (i.e. analysing context, adapting to people who live in it, learning from their behaviour and eventually recognizing and demonstrating emotion). Such AmI systems would be aware of your physical and emotional state and react accordingly; for example, suggesting the need for, or requesting, medical attention, or simply adjusting ambient light, sound and colour to suit your mood.

The *International Technology Roadmap for Semiconductors* offers a similar viewpoint on the way ahead [12]. Figure 1.6 shows how non-CMOS devices can be integrated with the Roadmap. The essential functions of a silicon integrated circuit – or system-on-chip (SoC) – are those of data storage and digital signal processing. However, many functional requirements, such as wireless communication, sensing and actuating and biological functions do not scale with Moore's Law. In these cases, non-CMOS solutions can be used. In the future, the integration of CMOS and non-CMOS technologies within a single package – or system-in-package (SiP) – will become increasingly important.

A good example of the diversity of electronic systems is the 'lab-on-a-chip' technology, under development by many commercial organisations [18]. There is considerable interest in reducing the size of sensing systems and integrating them with some functionality. This has



Figure 1.6 Moore's Law and diversification. Taken from the *International Technology Roadmap for Semiconductors* [12].

been made possible by the emergence of novel sensors. A completed system would, in essence, reduce the functionality of a complete chemistry laboratory to a single chip. For example, Sandia's handheld µChemlab system is about the size of a palmtop computer but is capable of using both gas and liquid chromatographic techniques to separate the various constituents of complex chemical mixtures [19]. Samples are drawn into the device by a micropump and then passed through a series of channels where the mixture is separated into its basic components. A microcomputer measures and identifies the components and displays results on the device screen. Advanced microsensor technology is used to perform chemical analysis after separation of the mixture. The system incorporates miniaturized surface acoustic wave detectors, laser-induced fluorescence analysis and electrochemical detection components. Future lab-on-a-chip technologies may allow the manipulation and measurement of individual molecules. This would provide many new opportunities for studying biochemical reactions and life processes [20].

1.6 CONCLUSIONS

Organic compounds possess a wide range of fascinating physical and chemical properties that make them attractive candidates for exploitation in electronic and opto-electronic devices. It is not anticipated, however, that these materials will displace silicon in the foreseeable future as the dominant material for fast signal processing. It is much more likely that organic materials will find use in other niche areas of electronics, where silicon and other inorganic semiconductors cannot compete. Examples already exist, such as liquid crystal displays and certain chemical sensors. Organic light-emitting structures and plastic circuitry for identification tags and smart cards are likely to make a major impact in the market place over the next 10 years.

Over the first decades of the 21st century, classical CMOS technology will come up against a number of technological barriers. The bottom-up approach to molecular electronics provides an alternative and attractive way forward and, as such, it is currently an area of exciting interdisciplinary activity. However, the challenges in fabricating molecular switches and connecting them together are formidable. Living systems use a different approach. These assemble themselves naturally from molecules and are extremely energetically efficient when compared with man-made computational devices. More radical approaches to materials fabrication and device design, exploiting self-organization, may be needed to realize fully the potential offered by molecular-scale electronics.

BIBLIOGRAPHY

Amos M. Genesis Machines. London: Altantic Books; 2006.

- Bar-Cohen Y (Editor). *Biomimetics: Biologically Inspired Technologies*. Boca Raton, FL: Taylor and Francis; 2006.
- Braun E, MacDonald S. Revolution in Miniature. Cambridge: Cambridge University Press; 1977.

Cuniberti G, Fagas G, Richer K (Editors). *Introducing Molecular Electronics*. Berlin: Springer; 2005. Drexler KE. *Engines of Creation*. London: Fourth Estate; 1990.

Feast WJ, Tsibouklis J, Pouwer KL, Groenendaal, Meijer EW. Synthesis, processing and material properties of conjugated polymers. *Polymer* 1996; **37**: 5017–5047.

- Ferraro JR, Williams JM. Introduction to Synthetic Electrical Conductors. Orlando, FL: Academic Press; 1987.
- Feynman RP. There's plenty of room at the bottom. Lecture of the American Physical Society at California Institute of Technology, December 1959. Available from URL http://www.zyvex.com/nanotech/feynman.html.
- Flood AH, Stoddart JF, Steuerman DW, Heath JR. Whence molecular electronics. Science 2004; 306: 2055–2056.
- Gardner JW. Microsensors Principles and Applications. Chichester: John Wiley & Sons, Ltd; 1994.
- Gardner JV, Varadan VK, Awadelkarim OO. *Microsensors, MEMS and Smart Devices*. Chichester: John Wiley & Sons, Ltd; 2001.
- Gershenfeld N. The Physics of Information Technology. Cambridge: Cambridge University Press; 2000.
- Greer J, Korkin A, Labanowski J (Editors). *Nano and Giga Challenges in Microelectronics*. Amsterdam: Elsevier; 2003.
- Jones RAL. Soft Machines. Oxford: Oxford University Press; 2004.
- Leff HS, Rex AF (Editors). *Maxwell's Demon: Entropy, Information, Computing.* Bristol: Adam Hilger; 1990.
- Mansoori GA. Principles of Nanotechnology. Singapore: World Scientific; 2005.
- Petty C, Bryce MR, Bloor D (Editors). An Introduction to Molecular Electronics. London: Edward Arnold; 1995.
- Reitman EA. Molecular Engineering of Nanosystems. New York: Springer; 2001.
- Wallace GG, Spinks GM, Kane-Maguire LAP, Teasdale PR. Conductive Electroactive Polymers: Intelligent Materials Systems. Boca Raton, FL: CRC Press; 2002.
- Whitesides GM. The once and future nanomachines. Sci. Am. 2001; 285: 78-83.
- Whitesides GM, Love JC. The art of building small. Sci. Am. 2001; 285: 38-47.
- Wright JD. Molecular Crystals. Cambridge: Cambridge University Press; 1995.

REFERENCES

- [1] Pocchetino A. Sul comportamento foto-elettrico dell'antracene. *Atti Acad. Naz. Lincei Rend.* 1906; 15: 355–368.
- [2] Eley DD. Phthalocyanines as semiconductors. Nature 1948; 162: 819.
- [3] Varanyan AT. Poluprovodnikovye svoistva organicheskikh krasitelei. 1. Ftalotsianiny. Zh. Fiz. Khim. 1948; 22: 769–789.
- [4] Akamatu H, Inokuchi H. On the electrical conductivity of violanthrone, isoviolanthrone, and pyranthrone. J. Chem. Phys. 1950; 18: 810–811.
- [5] Natta G, Mazzanti G, Corradini P. Polimerizzazione stereospecifica dell'acetilene. Atti Acad. Naz. Lincei, Cl. Sci. Fis. Mat. Tend. 1958; 25: 3–12.
- [6] Aviram A, Ratner MA. Molecular rectifiers. Chem. Phys. Lett. 1974; 29: 277–283.
- [7] Carter FL. Molecular-level fabrication techniques and molecular electronic devices. J. Vac. Sci. Technol. B 1983; 1: 959–968.
- [8] Kuhn H. Organized monolayers building blocks in constructing supramolecular devices. In FT Hong (editor). *Molecular Electronics: Biosensors and Computers Symposium*. New York: Plenum Press; 1989, pp. 3–24.
- [9] Dummer GWA. Electronic Inventions and Discoveries, 4th ed. Bristol: Institute of Physics; 1997.
- [10] Braun E, MacDonald S. *Revolution in Miniature*. Cambridge: Cambridge University Press; 1977.
- [11] Intel. Available from URL http://www.intel.com/.
- [12] International Technology Roadmap for Semiconductors. Semiconductor Industries Association. Available from URL http://public.itrs.net/.
- [13] Dettmer R. Grand designs. IEE Rev. 2003; 49: 30-33.

- [14] Kasap SO. Principles of Electrical Engineering Materials and Devices. Boston: McGraw-Hill; 1997.
- [15] Landauer R. Computation: a fundamental physical view. In HS Leff and AF Rex (Editors). Maxwell's Demon: Entropy, Information, Computing. Bristol: Adam Hilger; 1990, pp. 260–267.
- [16] Tour JM. Molecular Electronics. Singapore: World Scientific; 2003.
- [17] Weiser M. The computer for the 21st century. Sci. Am. 1991; 265: 66-75.
- [18] Janasek D, Franzke J, Manz A. Scaling and the design of miniaturized chemical-analysis systems. *Nature* 2006; 442: 374–380.
- [19] Research and technology development performed by Sandia's California laboratory for the Department of Energy. Available from URL http://www.ca.sandia.gov/casite/index.html.
- [20] Craighead C. Future lab-on-a-chip technologies for interrogating individual molecules. *Nature* 2006; **442**: 387–393.