The **building blocks**
of tomorrow's materials

One approach to constructing nanocomponents consists in assembling matter atom by atom or molecule by molecule to build nano-objects that are then integrated into more complex systems. Among these elementary building blocks, carbon nanotubes possess exceptional structures and properties that make them choice nano-objects for many applications. Fluorescent semiconductor nanocrystals, a valuable feature of which is the possibility of varying emission wavelengths by setting particle size, should find broad-ranging applications in biology and optoelectronics. Nanowires are also attracting interest because of their unusual physical properties and their potential applications in opto- and microelectronics.

Artechnique/CEA

Carbon nanotubes deposited on a silicon substrate.

Carbon nanotubes, top research performers

The unexpected discovery of nano-objects (molecules of fullerene in 1985 and carbon nanotubes in 1991) caused much excitement in the scientific community, further fuelled by the awareness of the huge industrial potential offered by nanotechnology. Carbon nanotubes are robust, light and flexible, possess remarkable mechanical and electrical properties that promise many useful applications, and are expected to enter industrial production in the near future. Intense scientific research is also in progress on these entities.

Graphite and **diamond** were the only known **crystalline** forms of pure carbon until 1985, when Harold W. Kroto (University of Sussex, Great Britain), and Richard E. Smalley and Robert F. Curl jr. (Rice University, USA) discovered a new organized form of carbon, the C_{60} **molecule**, made up of 60 carbon atoms positioned at the apices of a regular polyhedron with hexagonal and pentagonal faces. In 1996 they obtained the Nobel Prize in chemistry for their work. This molecule was named *buckminsterfullerene* in honour of the architect Buckminster Fuller who designed the geodesic dome for the 1967

Universal Exhibition in Montreal, which had the same polyhedral shape. Somewhat later, in 1991, Sumio Iijima (NEC, Tsukuba, Japan), examining a by-product of the synthesis of C_{60} under an electron microscope, discovered carbon nanotubes. He described nanotubes for the first time as hollow tube-shaped objects of **nanometric** diametre and **micrometric** length.

Nanotubes can be made by the evaporation of carbon, usually graphite, using an electric arc or a laser in an atmosphere of helium or argon. However, the high temperature that was necessary for the process initially limited the amounts of material that could be obtained. Different specific methods of synthesis were subsequently developed that made it possible to conduct laboratory studies of the structure and physical and chemical properties of these objects. Research in this field has developed dramatically owing to the spectacular nature of the structure of nanotubes and their interesting properties in varied domains ranging from mechanics to nanoelectronics to nanochemistry.

Here we review the basic characteristics of these nano-objects, outline their structural diversity, and describe some of their exceptional electronic properties. We also give a few illustrations of their potential uses in nanoelectronics.

The importance of geometry

Carbon nanotubes are made of graphite sheets rolled into cylinders and closed at each end by a semi-**fullerene** unit. There are two types, according to the number of rolled sheets: single-walled nanotubes (SWNTs), which are made of a single sheet and can be used as building blocks in nanotube-based electronics, and multi-walled nanotubes (MWNTs), which are more complex systems that can contain several tens of concentric sheets. These nanotubes have diametres in the 2 - 30 nm range and lengths of up to several micrometres.
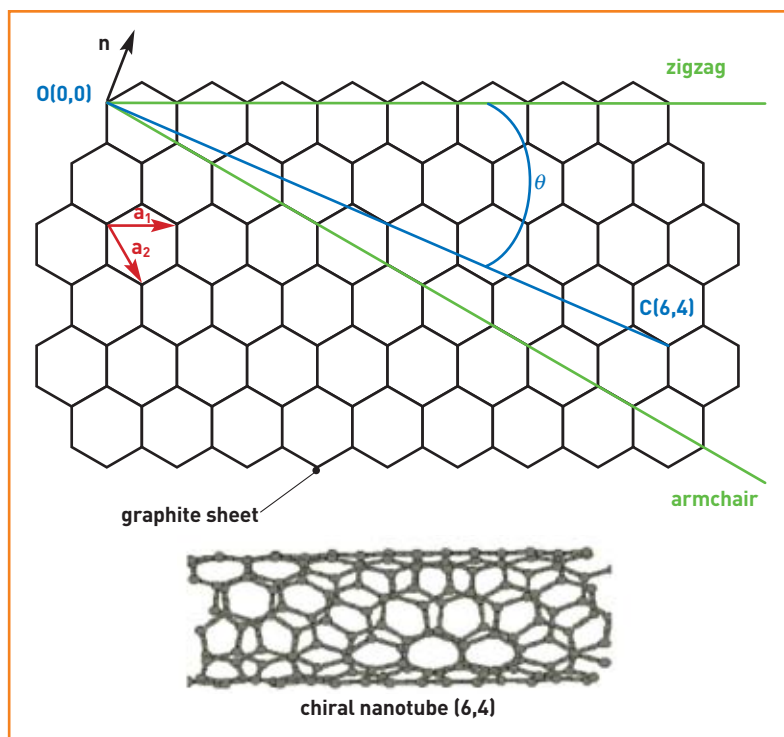
The geometry of nanotubes is of fundamental importance because it determines most of their physical properties. The reasons for this become clear if we consider how they are formed. If we take a sheet of graphite (Figure 1), we can designate two equivalent points O and C on the hexagonal lattice. If we cut a strip bounded by the straight lines passing through these two points and perpendicular to OC, and then bring points O and C together, we obtain a nanotube. Characterized by the coordinates (n,m) of point C in the base ($\mathbf{a}_1$,$\mathbf{a}_2$) of the hexagonal lattice, this nanotube will have as its axis the vector $\mathbf{n}$ orthogonal to **OC**. n and m, called the *chiral indices* of the nanotube, define its helicity. Scientists sometimes prefer to give values of diametre d and chiral angle θ, which are linked to n and m. The SWNTs are classified into three families according to their symmetry properties: "zigzag" nanotubes for $m = 0$, "armchair" for $n = m$, and "chiral" in all other cases.

Exceptional mechanical properties

For the SWNTs, the material obtained displays very interesting mechanical properties. Compared to steel, it is about 100 times stronger, 6 to 7 times stif-

Centura reactor, installed at CEA Grenoble, dedicated to the large-scale growth of carbon nanotubes by the chemical vapour deposition (CVD) process.


chiral nanotube (6,4)

Figure 1.
Geometric construction of a carbon nanotube from a single plane sheet of graphite (graphene): example of a nanotube (6,4). The chiral indices (6,4) are the coordinates of the vector **OC** in the base (**a**$_1$,**a**$_2$) of the graphene lattice. When the strip of graphene of width **OC** is rolled edge to edge perpendicular to **OC** to form a cylinder, a chiral nanotube (6,4) is obtained (bottom). The directions of the vector **OC** for "zigzag" and "armchair" tubes, which are non-chiral, are also represented.

fer and 6 times lighter. Let us imagine a cylinder of outside diametre 10 cm and wall thickness 4 cm, connecting two walls 2 m apart. If this cylinder was as stiff as a nanotube 10 million times smaller, then even under a load of 1,000 tons it would bend by only 1 cm at its midpoint! Carbon nanotubes are also highly resistant to breakage. They do not break even when bent at an angle of 70°, and because of their exceptional elasticity they will spring back to their original shape.

Remarkable electronic properties

The electrical properties of nanotubes depend closely on their geometry, defined by the chiral indices n and m. Depending on how the atoms are arranged around the circumference, it is possible to obtain a fully conducting or a **semiconductor** material. Carbon nanotubes are to this day the only known materials that display this behaviour. The theoretical study of the electronic properties of SWNTs predicts that they will be metallic when ($n - m$) is a multiple of 3. If not then the electronic structure of the nanotubes will present an energy **gap** and the sys-

300 nm

200 nm

Scanning electron microscope images of carbon nanotubes on a silicon substrate grown in the Centura reactor (left 100,000x, right 150,000x).
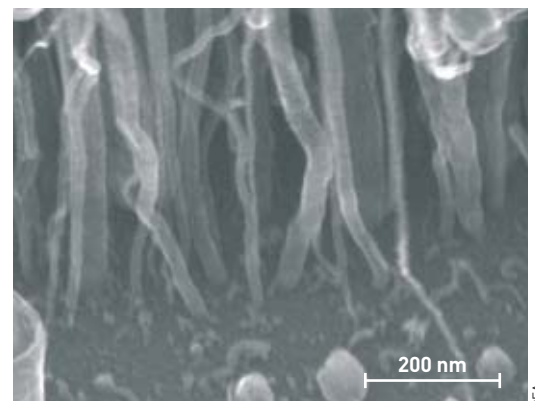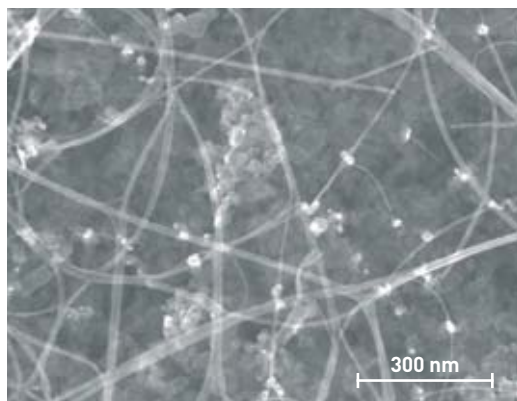
tem will behave like a semiconductor (Box). The gap of a semiconductor nanotube is inversely proportional to its diametre, which makes it fairly easy to control. Typically, a semiconductor nanotube of diametre about 1.4 nm has a gap of about 0.6 **eV**.

For the experimental study of the electronic properties of this type of molecular system, the scanning tunnelling microscope (STM) has been found to be an especially powerful tool (see *Local probe microscopy: contact and manipulation*). The theoretical predictions of the electronic properties of carbon nanotubes have been confirmed by near-field scanning tunnelling spectroscopy (STS). In this experimental technique, the **tunnel current** I is measured as a function of the polarization voltage V_{bias} applied between the tip and the substrate (Box G, ***The tunnel effect, a quantum phenomenon***). If a molecular system is located between the tip and the substrate the differential **conductance** dI/dV is proportional to the local electronic state density of the system. In the case of nanotubes, the presence or absence of an energy gap, and the peaks in the state density (Van Hove singularities due to the **quantum** confinement along the circumference) have been clearly observed experimentally. Figure 2 shows the STM image of the junction of two nanotubes with different helicities obtained by the group of Charles M. Lieber (Harvard, USA). The very high

resolution of these images allowed the helicity of the two segments (22,-5) and (21,2) to be determined, and predicted that the first one would be metallic and the second semiconducting. These predictions were confirmed by the STS spectra (local electronic state densities) measured on each segment (Figure 2b): a **bandgap** of 0.45 eV was observed for the nanotube (21,2).

Intramolecular junctions ideal as transistors

As we have just seen, the helicity of a nanotube determines whether it is metallic or semiconducting. Figure 2 shows that there is experimental evidence for the existence of junctions between nanotubes with different helicities, although the operator is not yet able to control their formation during synthesis. Theoretically, it is possible to predict which nanotube pairs are likely to form a chemically stable junction. For example, introducing a pentagon-heptagon pair into the hexagonal lattice can turn a (n,m) nanotube into a $(n\pm1,m\pm1)$ nanotube. Semiconductor(1)/semiconductor(2) intramolecular junctions, *e.g.*, (10,0)/(11,0), or metal/semiconductor junctions such as (8,0)/(7,1), can thus be created. The junction depicted in Figure 2 theoretically requires three pentagon-heptagon pairs arranged along the circumference, but the STM image
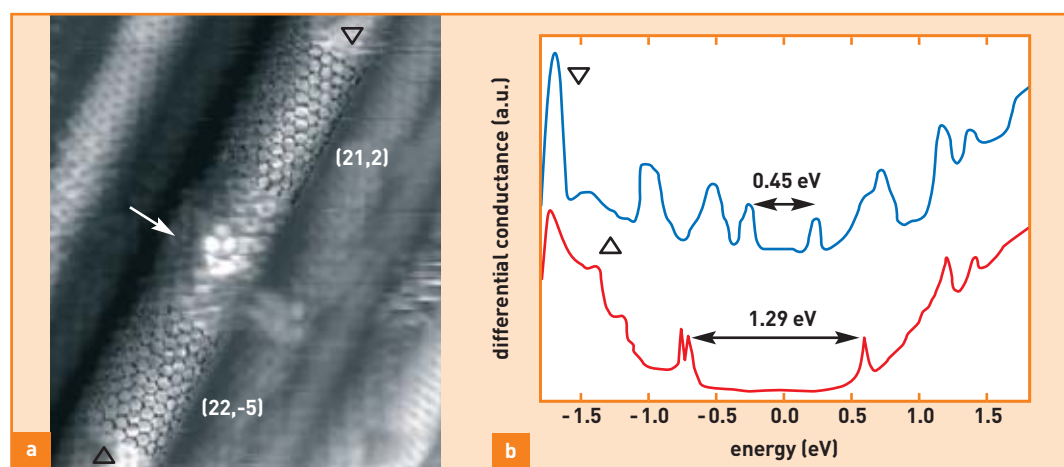

Figure 2.
a, tunnelling microscope image of an intramolecular junction between a metallic nanotube (22,-5) and a semiconductor nanotube (21,2). The arrow points to the junction between the two nanotubes, which has poor resolution at the atomic scale. Black hexagonal networks are superimposed on the image in order to determine helicities. b, local tunnelling spectroscopy measurements giving electronic state density over the metallic segment (bottom curve) and semiconductor segment (top curve) (from T. Odom, J. Huang and C. Lieber, "STM studies of single-walled carbon nanotubes", *J. Phys.: Condens. Matter*, 14, R145-R167, 2002).
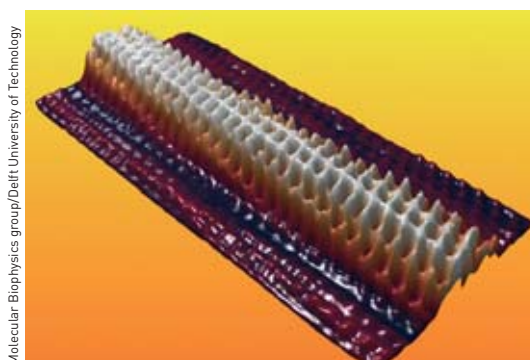
does not have a high enough resolution in this region for any of these structural defects to be observed. These theoretical constructs can be generalized to include metal/semiconductor/metal dual junctions, which form heterojunctions that are ideal for making **field-effect transistors** (Figure 3). Such heterojunctions may provide us with ultimately small intra-molecular transistors with exciting properties. Figure 4 shows the conductance of the particular hetero-junction represented in Figure 3 according to the charge injection energy. For too-short semiconductor **channel** lengths ($L < 3$ nm), the system is unable to work as a transistor because of a non-negligible tunnelling current at all energies. For $L > 5$ nm, the charge injection is correctly blocked in the band-gap energy zone, and so the heterojunction can operate like a transistor.

Potential applications in nanoelectronics

Another important characteristic of charge transport in nanotubes is low sensitivity to disorder, which results in mean free paths greater than a **micron**. This makes it possible to obtain very good **ballistic** charge conductors and field-effect transistors based on semiconductor nanotubes operating in the ballistic regime.

Also, because of their small diametre and their electrical properties, carbon nanotubes are an ideal material to replace the conductors and semiconductors contained in today's **integrated circuits**. With nanotubes, it will, for example, be possible to place more transistors in an integrated circuit and so greatly increase the power of the microprocessors used in computers and cellphones. This has propelled research laboratories and industry in a frantic race to build a new generation of electronic components based on carbon nanotubes. Now that the miniaturization of **silicon**-based integrated circuits is approaching its technological limits, the era of high-density molecular nanocircuits is ready to begin.

In 1998, the first molecular transistor made of a semiconducting single-walled carbon nanotube was constructed by the group of Cees Dekker at the University of Delft (Netherlands). The nanotube is connected to two metal **electrodes** and subjected to the influence of an **electrostatic gate**. This gate makes it possible to shift the **energy bands** of a nanotube to line up the **valence band** or the **conduction band** with the **Fermi level** defined by the electrodes, thereby allowing the current to pass. Other experimental groups such as that of Phaedon Avouris (IBM T.J. Watson Center, USA) or that of Hongjie Dai (Stanford University, USA) soon built transistors based on the same principle. According to the nature of the contact electrodes and the characteristics of the semicon-

ductor nanotubes, their diametre in particular, nanotube-based field-effect transistors can behave either like classical **MOSFET transistors** with "ohmic" contacts, or like **Schottky-type transistors**, in which charge injection mechanisms at the metal-nanotube interface dominate the current-voltage characteristics of the device. The term "ohmic contact" is used when the **tunnel barrier** at the interfaces is sufficiently small and narrow for the **tunnel effect** to outweigh the thermo-ionic effect. The contact resistance is then only weakly temperature-dependent, and the current-voltage characteristic is linear even at low voltages (no **diode** effect).

This type of study interests both public research

3D structure of a carbon nanotube, obtained by tunnelling microscope images. The tunnelling microscope is a very powerful tool for the study of the electronic properties of these nano-objects.
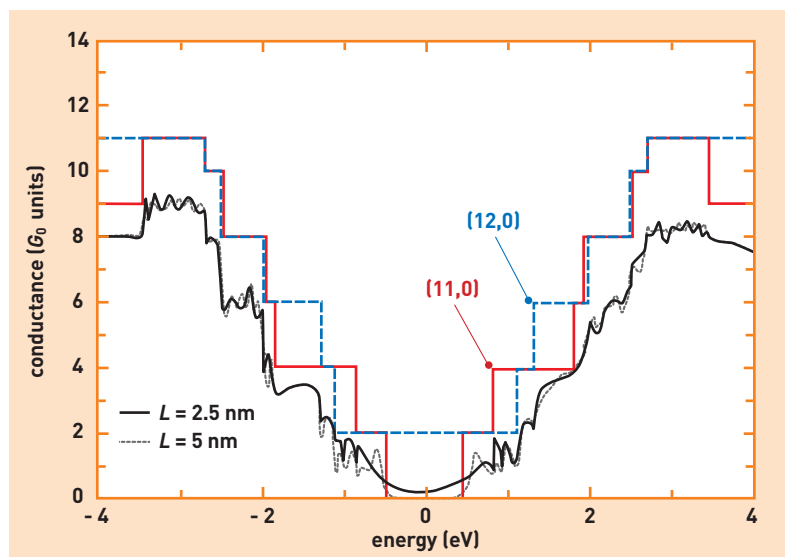

Figure 4.
Conductance as a function of energy of the metal (12,0)/semiconductor (11,0)/metal (12,0) intramolecular heterojunction for a semiconductor channel length L of 2.5 nm (solid line) and 5 nm (dotted line). If the system is electrically neutral (no **gate**), the **Fermi level** is at $E = 0$ and the conductance is nil for L greater than about 5 nm, because the **tunnel barrier** formed by the semiconductor tube is too high. The conductance of the metallic segment (blue dotted line) and semiconductor segment (red line) is also represented. The unit on the y-axis is the **quantum** conductance: $G_0 = 2e^2/h = (12.9$ k$\Omega)^{-1}$.
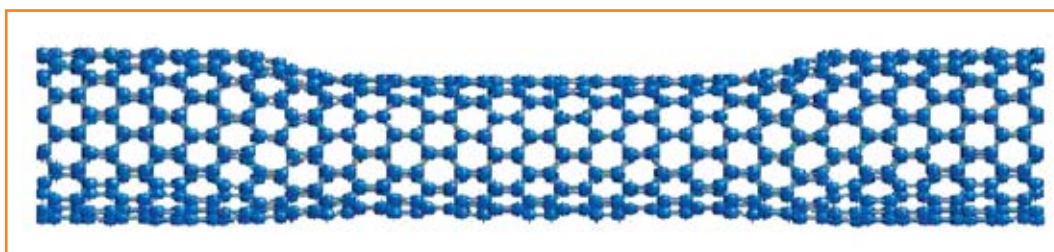

Figure 3.
Diagram of a metal/semiconductor/metal intramolecular junction with theoretically predicted stability. The helicities of the segments are respectively (12,0), (11,0) and (12,0).

Theoretical modelling and numerical simulation of nano-objects

Nanotechnology, which operates at a scale where it is difficult to measure everything, can greatly benefit from the use of numerical simulation. In the early 80s the American physicist Richard P. Feynman was critical of the ability of numerical simulation of quantum physics equations to help gain greater knowledge and control of nanometric processes. The so-called "first principles" methods, or *ab initio* model, are based on solving fundamental equations of quantum mechanics solely from knowledge of approximate atomic positions. These approaches, based in particular on density functional theory, provide a good description of the structural and electronic properties of metallic or semiconductor nanostructures, in close agreement with the experimental characterization of these objects. However, the study of charge transfer or electron transport within these systems is still a real challenge, given the great complexity of these processes. The cost of computation rises dramatically as the number of atoms increases. Despite the increased power of data processors and the use of parallel computation, the development of *multiscale* approaches will be the only way to solve such complex problems. Thus, by combining *ab initio* approaches and so-called *semi-empirical* approaches based on a simplified description of a system parameterized on the basis of *ab initio* calculations, researchers at the Department of Fundamental Research on Condensed Matter (CEA/DRFMC: Département de recherche fondamentale sur la matière condensée) have developed methods for calculating the electronic structure of nano-objects and quantum transport through chemically doped carbon nanotubes, at scales of the order of a micron. These methods are applicable to semiconductor nanowires, and even make it possible to envisage the simulation of new types of components such as ultrasensitive (bio)chemical sensors, floating gate molecular memories (see *Giving nano-objects new properties by molecular grafting*, Figure 4) or photosensitive transistors.

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bodies and R&D departments in the integrated circuits industry (IBM, Infineon, etc.). Each group is developing original and varied solutions for the synthesis of nanotubes, connection to metal electrodes or the integration of transistors. Overall, interest for carbon nanotubes is still fast-growing, both for their potential applications in nanoelectronics and for pure research in materials science.

Today the CEA is strongly involved in the field of nanotubes. At Saclay, the group of Jean-Philippe Bourgoin at the Solid State, Atoms and Molecules Research Department (Drecam: Département de recherche sur l'état condensé, les atomes et les molécules) is working, among other topics, on the optimization of transistors and on their interaction with the environment (chemical or optical sensors), see *Molecular electronics, a domain at the crossroads of chemistry, physics and engineering.* At CEA Grenoble, the team of Jean Dijon at the Electronics and Information Technology Laboratory (Leti: Laboratoire d'électronique et de technologie de l'information) is

developing flat panel displays based on field emission from a dense "carpet" of nanotubes (see *Nanotubes, multipurpose electron guns*). "Atomistic simulation" (Box) is being developed jointly by the Department of Fundamental Research on Condensed Matter (DRFMC: Département de recherche fondamentale sur la matière condensée) and the Leti, with valuable input from the Molecular Electronics Laboratory at CEA Saclay. Finally, research teams at the DRFMC and the Department of Energy and Nanomaterials Technology (DTEN: Département des technologies pour l'énergie et les nanomatériaux) are working on the growth of single-walled nanotubes using the CVD process for their large-scale integration in silicon-based electronics.

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Molecular Biophysics Group/Delft University of Technology
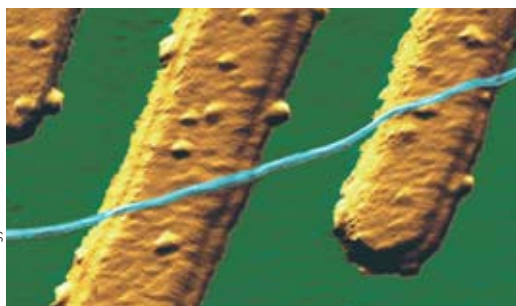
Atomic force microscopy image of a single-walled carbon nanotube between electrodes.

FOR FURTHER INFORMATION

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A From the macroscopic to the nanoworld, and vice versa...

In order to gain a better idea of the size of microscopic and nanoscopic* objects, it is useful to make comparisons, usually by aligning different scales, *i.e.* matching the natural world, from molecules to man, to engineered or fabricated objects (Figure). Hence, comparing the "artificial" with the "natural" shows that artificially-produced nanoparticles are in fact smaller than red blood cells.

Another advantage of juxtaposing the two is that it provides a good illustration of the two main ways of developing nanoscale systems or objects: *top-down* and *bottom-up*. In fact, there are two ways

* From the Greek *nano meaning* "very small", which is also used as a prefix meaning a billionth (10^{-9}) of a unit. In fact, the **nanometre** (1 nm = 10^{-9} metres , or a billionth of a metre), is the master unit for nanosciences and nanotechnologies.

Artechnique

300-mm silicon wafer produced by the Crolles2 Alliance, an illustration of current capabilities using top-down microelectronics.

into the nanoworld: molecular manufacturing, involving the control of single atoms and the building from the ground up, and extreme miniaturization, generating progressively smaller systems.

Top-down technology is based on the artificial, using macroscopic materials that we chip away using our hands and our tools: for decades now, electronics has been applied using silicon as a substrate and what are called "wafers" as workpieces. In fact, microelectronics is also where the "top-down" synthesis approach gets its name from. However, we have reached a stage where, over and above simply adapting the miniaturization of silicon, we also
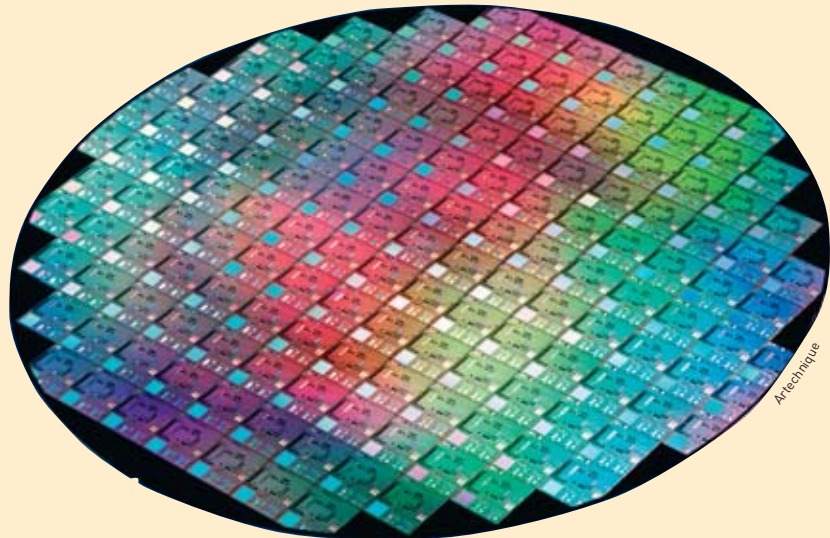
have to take on or use certain physical phenomena, particularly from quantum physics, that operate when working at the nanoscale.

The bottom-up approach can get around these physical limits and also cut manufacturing costs, which it does by using component self-assembly. This is the approach that follows nature by assembling molecules to create proteins, which are a series of amino acids that the super-molecules, *i.e.* nucleic acids (DNA, RNA), are able to produce within cells to form functional structures that can reproduce in more complex patterns. Bottom-up synthesis aims at structuring the material using

"building blocks", including atoms themselves, as is the case with living objects in nature. Nanoelectronics seeks to follow this assembly approach to make functional structures at lower manufacturing cost.

The nanosciences can be defined as the body of research into the physical, chemical or biological properties of nano-objects, how to manufacture them, and how they self-assemble by auto-organisazation.

Nanotechnologies cover all the methods that can be used to work at molecular scale to reorganize matter into objects and materials, even progressing to the macroscopic scale.

natural world

bottom-up

molecule
a few Å

DNA ,
3.4 nm

virus,
0.1 μm

red blood cell,
5 μm

a hair, 50 μm
(diameter)

pollen grain,
10 μm to 20 μm

flea,
1 mm

ant,
1 cm

butterfly,
5 cm

man,
2 m

0.1 nm	1 nm	10 nm	100 nm	1 μm	10 μm	100 μm	1 mm	1 cm	10 cm	1 m

nanoworld

10^{-10} m	10^{-9} m	10^{-8} m	10^{-7} m	10^{-6} m	10^{-5} m	10^{-4} m	10^{-3} m	10^{-2} m	10^{-1} m

atome,
0.1-1 nm

quantum dot,
5 nm

nanoparticle,
10 nm

nanotransistor,
20 nm

"Cooper"
transistor,
1 μm

integrated circuit
interconnects,
1 to 10 μm

microsystem,
10 to 100 μm

card chip,
1 cm

mobile phone,
10 cm

private vehicle,
2 m

artificial world

top-down

B A guide to quantum physics

Quantum physics (historically known as quantum mechanics) covers a set of physical laws that apply at microscopic scale. While fundamentally different from the majority of laws that appear to apply at our own scale, the laws of quantum physics nevertheless underpin the general basis of physics at all scales. That said, on the macroscopic scale, quantum physics in action appears to behave particularly strangely, except for a certain number of phenomena that were already curious, such as superconductivity or superfluidity, which in fact can only explained by the laws of quantum physics. Furthermore, the transition from the validating the paradoxes of quantum physics to the laws of classical physics, which we find easier to comprehend, can be explained in a very general way, as will be mentioned later.

Quantum physics gets its name from the fundamental characteristics of quantum objects: characteristics such as the angular momentum (spin) of discrete or discontinuous particles called quanta, which can only take values multiplied by an elementary quantum. There is also a quantum of action (product of a unit of energy multiplied by time) called Planck's cons-
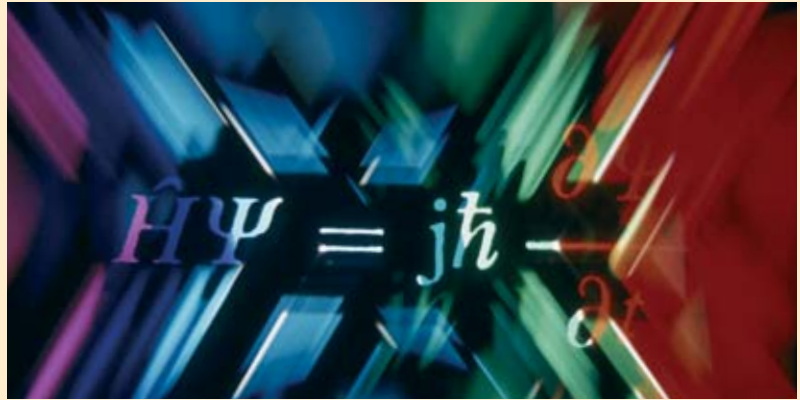
An "artist's impression" of the Schrödinger equation.

tant (symbolized as h) which has a value of 6.626×10^{-34} joule·second.

While classical physics separates *waves* from *particles*, quantum physics somehow covers both these concepts in a third group, which goes beyond the simple wave-particle duality that Louis de Broglie imagined. When we attempt to comprehend it, it sometimes seems closer to waves, and sometimes to particles. A quantum object cannot be separated from how it is observed, and has no fixed attributes. This applies equally to a particle - which in no way can be likened to a tiny little bead following some kind of trajectory - of light (photon) or matter (electron, proton, neutron, atom, etc.).

This is the underlying feature behind the Heisenberg uncertainty principle, which is another cornerstone of quantum physics. According to this principle (which is more *indeterminacy* than *uncertainty*), the position and the velocity of a particle cannot be measured *simultaneously* at a given point in time. Measurement remains possible, but can never be more accurate than *h*, Planck's constant. Given that these approximations have no intrinsically real value outside the observation process, this simultaneous determination of both position and velocity becomes simply impossible.

At any moment in time, the quantum object presents the characteristic of *superposing* several states, in the same way that one wave can be the *sum* of several others. In quantum theory, the amplitude of a wave (like the peak, for example) is equal to a **probability amplitude** (or probability wave), a complex number-valued function associated with each of the possible sates of a system thus described as quantum. Mathematically speaking, a physical state in this kind of system is represented by a **state vector**, a function that can be added to others *via* superposition. In other words, the sum of two possible state vectors of a system is *also* a possible state vector of that system. Also, the product of two vector spaces is also the sum of the vector products, which indicates **entanglement**: as a state vector is generally spread through space, the notion of local objects no longer holds true. For a pair of entangled particles, *i.e.* particles created together or having already interacted, that is, described by the *product* and not the *sum* of the two individual state vectors, the fate of each particle is linked - entangled - with the other, regardless of the distance between the two. This characteristic, also called *quantum state entan-glement*, has staggering consequences, even before considering the potential applications, such as quantum cryptography or - why not? - teleportation. From this point on, the ability to predict the behaviour of a quantum system is reduced to probabilistic or statistical predictability. It is as if the quantum object is some kind of "juxtaposition of possibilities". Until it has been measured, the measurable size that supposedly quantifies the physical property under study is not strictly defined. Yet as soon as this measurement process is launched, it destroys the **quantum superposition** through the "collapse of the wave-packet" described by Werner Heisenberg in 1927. All the properties of a quantum system can be deduced from the equation that Erwin Schrödinger put forward the previous year. Solving the **Schrödinger equation** made it possible to determine the energy of a system as well as the **wave function**, a notion that tends to be replaced by the probability amplitude.

According to another cornerstone principle of quantum physics, the **Pauli exclusion principle**, two identical half-spin ions (**fermions**, particularly electrons) cannot simultaneously share the same position, spin and velocity (within the limits imposed by the uncertainty principle), *i.e.* share the same *quantum state*. **Bosons** (especially photons) do not follow this principle, and can exist in the same quantum state.

The coexistence of **superposition states** is what lends **coherence** to a quantum system. This means that the theory of **quantum decoherence** is able to explain why macroscopic objects, atoms and other particles, present "classical" behaviour whereas microscopic objects show quantum behaviour. Far more influence is exerted by the "environment" (air, background radiation, etc.) than an advanced measurement device, as the environment radically removes all *superposition of states* at this scale. The larger the system considered, the more it is coupled to a large number of degrees of freedom in the environment, which means the less "chance" (to stick with a probabilistic logic) it has of maintaining any degree of quantum coherence.

TO FIND OUT MORE:

Étienne Klein, *Petit voyage dans le monde des quanta*, Champs, Flammarion, 2004.

C Molecular beam epitaxy

Quantum wells are grown using Molecular Beam Epitaxy (from the Greek *taxi*, meaning order, and *epi*, meaning over), or MBE. The principle of this physical deposition technique, which was first developed for growing III-V semiconductor crystals, is based on the evaporation of ultra-pure elements of the component to be grown, in a furnace under ultra-high vacuum (where the pressure can be as low as $5·10^{-11}$ mbar) in order to create a pure, pollution-free surface. One or more thermal beams of atoms or molecules react on the surface of a single-crystal wafer placed on a substrate kept at high temperature (several hundred °C), which serves as a lattice for the formation of a film called epitaxial film. It thus becomes possible to stack ultra-thin layers that measure a millionth of a millimetre each, *i.e.* composed of only a few atom planes.

The elements are evaporated or sublimated from an ultra-pure source placed in an **effusion cell** (or Knudsen cell; an enclosure where a molecular flux moves from a region with a given pressure to another region of lower pressure) heated by the Joule effect. A range of structural and analytical probes can monitor film growth *in situ* in real time, particularly using surface quality analysis and grazing angle phase transitions by LEED (*Low energy electron diffraction*) or RHEED (*Reflection high-energy electron diffraction*). Various **spectroscopic** methods are also used, including Auger **electron** spectroscopy, secondary **ion** mass spectrometry (SIMS), **X-ray** photoelectron spectrometry (XPS) or **ultraviolet** photoelectron spectrometry (UPS).

As *ultra-high-vacuum* technology has progressed, molecular beam epitaxy has branched out to be applied beyond III-V semiconductors to embrace metals and insulators. In fact, the vacuum in the growth chamber, whose design changes depending on the properties of the matter intended to be deposited, has to be better than 10^{-11} mbar in order to grow an ultra-pure film of exceptional crystal quality at relatively low substrate temperatures. This value corresponds to the vacuum quality when the growth chamber is at rest. Arsenides, for example, grow at a residual vacuum of around 10^{-8} mbar as soon as the arsenic cell has reached its set growth temperature.

The pumping necessary to achieve these performance levels draws on several techniques using ion pumps, cryopumping, titanium sublimation pumping, diffusion pumps or turbomolecular pumps. The main impurities (H_2, H_2O, CO and CO_2) can present partial pressures of lower than 10^{-13} mbar.

D The transistor, fundamental component of integrated circuits

The first transistor was made in germanium by John Bardeen and Walter H. Brattain, in December 1947. The year after, along with William B. Shockley at Bell Laboratories, they developed the bipolar transistor and the associated theory. During the 1950s, transistors were made with silicon (Si), which to this day remains the most widely-used semiconductor due to the exceptional quality of the interface created by silicon and silicon oxide

(SiO_2), which serves as an insulator. In 1958, Jack Kilby invented the integrated circuit by manufacturing 5 components on the same substrate. The 1970s saw the advent of the first microprocessor, produced by Intel and incorporating 2,250 transistors, and the first memory. The complexity of integrated circuits has grown exponentially (doubling every 2 to 3 years according to "Moore's law") as transistors continue to become increasingly miniaturized.

The transistor, a name derived from transfer and resistor, is a fundamental component of microelectronic integrated circuits, and is set to remain so with the necessary changes at the nanoelectronics scale: also well-suited to amplification, among other functions, it performs one essential basic function which is to open or close a current as required, like a switching device (Figure). Its basic working principle therefore applies directly to processing binary code (0, the current is blocked, 1 it goes through) in logic circuits (inverters, gates, adders, and memory cells).

The transistor, which is based on the transport of electrons in a solid and not in a vacuum, as in the electron tubes of the old triodes, comprises three electrodes (anode, cathode and gate), two of which serve as an electron reservoir: the source, which acts as the emitter filament of an electron tube, the drain, which acts as the collector plate, with the gate as "controller". These elements work differently in the two main types of transistor used today: bipolar junction transistors, which came first, and field effect transistors (FET).

Bipolar transistors use two types of charge carriers, electrons (negative charge) and holes (positive charge), and are comprised of identically doped (p or n) semiconductor substrate parts
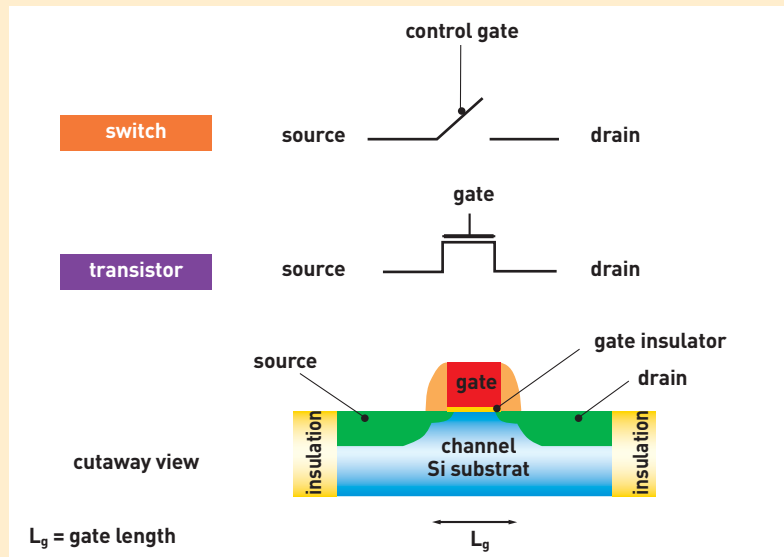

Figure.
A MOS transistor is a switching device for controlling the passage of an electric current from the source (S) to the drain (D) via a gate (G) that is electrically insulated from the conducting channel. The silicon substrate is marked B for Bulk.

separated by a thin layer of inversely-doped semiconductor. By assembling two semiconductors of opposite types (a p-n junction), the current can be made to pass through in only one direction. Bipolar transistors, whether n-p-n type or p-n-p type, are all basically current amplifier controlled by a gate current[1]: thus, in an n-p-n transistor, the voltage applied to the p part controls the flow of current between the two n regions. Logic circuits that use bipolar transistors, which are called TTL (for transistor-transistor logic), consume more energy than field effect transistors which present a zero gate current in off-state and are voltage-controlled.

Field effect transistors, most commonly of **MOS** (metal oxide semiconductor) type, are used in the majority of today's **CMOS** (C for complementary) logic circuits[2]. Two n-type regions are created on a p-type silicon crystal by doping the surface. These two regions, also called drain and source, are thus separated by a very narrow p-type space called the **channel**. The effect of a positive current on the control electrode, naturally called the **gate**, positioned over the semiconductor forces the holes to the surface, where they attract the few mobile electrons of the semiconductor. This forms a conducting channel between source and drain (Figure). When a negative voltage is applied to the gate, which is electrically insulated by an oxide layer, the electrons are forced out of the channel. As the positive voltage increases, the channel resistance decreases, letting progressively more current through.

In an integrated circuit, transistors together with the other components (**diodes**, condensers, resistances) are initially incorporated into a "chip" with more or less complex functions. The circuit is built by "sandwiching" layer upon layer of conducting materials and insulators formed by **lithography** (Box E, *Lithography, the key to miniaturization*). By far the most classic application of this is the microprocessor at the heart of our computers, which contains several hundred million transistors (whose size has been reduced 10,000-fold since the 1960s), soon a billion. This has led to industrial manufacturers splitting the core of the processors into several subunits working in parallel!

The very first transistor.
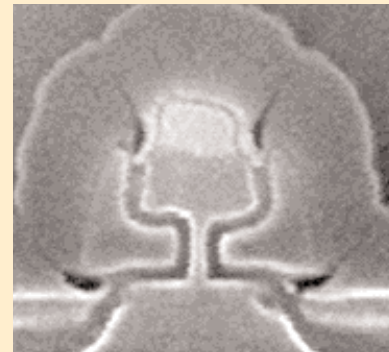
8 nanometre transistor developed by the Crolles2 Alliance bringing together STMicroelectronics, Philips and Freescale Semiconductor.

Lucent Technologies Inc./Bell Labs

STMicroelectronics

(1) This category includes **Schottky transistors** or **Schottky barrier transistors** which are field effect transistors with a metal/semiconductor control gate that, while more complex, gives improved charge-carrier mobility and response times.
(2) Giving **MOSFET** transistor (for Metal Oxide Semiconductor Field Effect Transistor).

E Lithography, the key to miniaturization

Optical lithography (photolithography) is a major application in the particle-matter interaction, and constitutes the classical process for fabricating integrated circuits. It is a key step in defining circuit patterns, and remains a barrier to any future development. Since resolution, at the outset, appears to be directly proportional to wavelength, feature-size first progressed by a step-wise shortening of the wavelength λ of the radiation used.

The operation works via a reduction lens system, by the *exposure* of a photoresist film to energy particles, from the ultraviolet (UV) photons currently used through to X photons, ions, and finally electrons, all through a mask template carrying a pattern of the desired circuit. The aim of all this is to transfer this pattern onto a stack of insulating or conducting layers that make up the mask. These layers will have been deposited previously (the *layering* stage) on a wafer of semiconductor material, generally silicon. After this process, the resin dissolves under exposure to the air (*development*). The exposed parts of the initial layer can then be etched selectively, then the resin is lifted away chemically before deposition of the following layer. This lithography step can take place over twenty times during the fabrication of an integrated circuit (Figure).

In the 1980s, the microelectronics industry used mercury lamps delivering near-UV (g, h and i lines) through quartz optics, with an emission line of 436 nanometres (nm). This system was able to etch structures to a feature-size of 3 microns (μm). This system was used through to the mid-90s, when it was replaced by excimer lasers emitting far-UV light (KrF, krypton fluoride at 248 nm, then ArF, argon fluoride at 193 nm, with the photons thus created generating several electronvolts) that were able to reach a resolution of 110 nm, pushed to under 90 nm with new processes. In the 1980s, the CEA's Electronics and Information Technology Laboratory (Leti) pioneered the application of lasers in lithography and the fabrication of integrated circuits using excimer lasers, and even the most advanced integrated circuit production still uses these sources.

Photolithography section in ultra-clean facilities at the STMicroelectronics unit in Crolles (Isère).

Artechnique

The next step for high-volume production was expected to be the F_2 laser (λ = 157 nm), but this lithography technology has to all intents and purposes been abandoned due to complications involved in producing optics in CaF_2, which is transparent at this wavelength. While the shortening of wavelengths in exposure tools has been the driving factor behind the strong resolution gain already achieved, two other factors have nevertheless played key roles. The first was the development of polymer-lattice photoresists with low absorbance at the wavelengths used, implementing progressively more innovative input energy reflection/emission systems. The second was enhanced optics reducing diffraction interference (better surface quality, increase in numerical aperture).

Over the years, the increasing complexity of the optical systems has led to resolutions actually *below* the source wavelength. This development could not continue without a major technological breakthrough, a huge step forward in wavelength. For generations of integrated circuits with a lowest resolution of between 80 and 50 nm (the next "node" being at 65 nm), various different approaches are competing to offer particle projection at ever-shorter wavelengths. They use either "soft" X-rays at extreme ultraviolet wavelength (around 10 nm), "hard" X-rays at wavelengths below 1 nm, ions or electrons.

The step crossing below the 50 nm barrier will lead towards low-electron-energy (10 eV)-enabled nanolithography with technology solutions such as the scanning tunnelling microscope and molecular beam epitaxy (Box C) for producing "superlattices".

source

spin-coating of the resin

centrifuging, curing, baking

mask

deposition of the next layer

projection optics

resin lift-off

etching
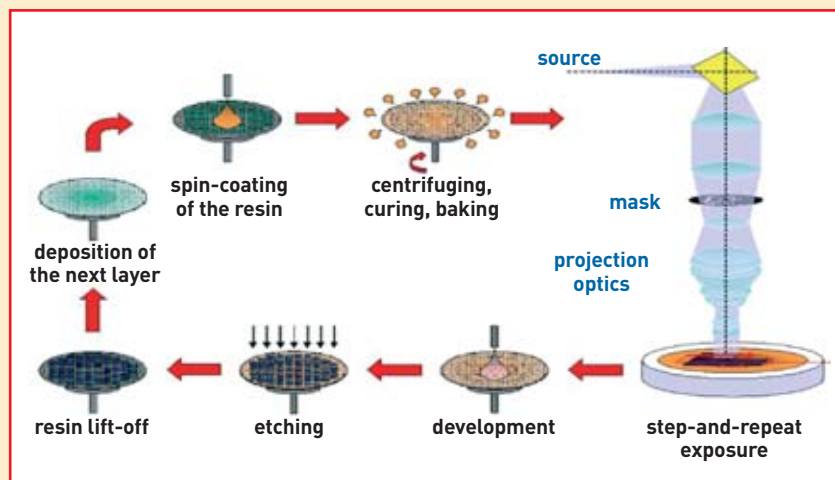
development

step-and-repeat exposure

Figure. The various phases in the lithography process are designed to carve features out of the layers of conducting or insulating materials making up an integrated circuit. The sequences of the operation are laying of a photoresist, then projecting the pattern on a mask using a reduction optics system, which is followed by dissolution of the resin that is exposed to the light beam (development). The exposed parts of the initial layer can then be etched selectively, then the resin is lifted away before deposition of the following layer.

G The tunnel effect, a quantum phenomenon

Quantum physics predicts unexpected behaviour that defies ordinary intuition. The tunnel effect is an example. Take the case of a marble that rolls over a bump. Classical physics predicts that unless the marble has enough kinetic energy it will not reach the top of the bump, and will roll back towards its starting point. In quantum physics, a particle (proton, electron) can get past the bump even if its initial energy is insufficient, by "tunnelling" through. The tunnel effect makes it possible for two protons to overcome their mutual electrical repulsion at lower relative velocities than those predicted by classical calculations.

Tunnel effect microscopy is based on the fact that there is a finite probability that a particle with energy lower than the height of a potential barrier (the bump) can still jump over it. The particles are electrons travelling through the space between two electrodes. These electrodes are a fine metal tip terminating in a single atom, and the metal or semiconductor surface of the sample. In classical physics a solid surface is considered as a well-defined boundary with electrons confined inside the solid. By contrast, in quantum physics each electron has wave properties that make its location uncertain. It can be visualized as an electron cloud located close to the surface. The density of this cloud falls off exponentially with increasing distance from the solid surface. There is thus a certain probability that an electron will be located "outside" the solid at a given time. When the fine metal tip is brought near the surface at a distance of less than a nanometre, the wave function associated with the electron is non-null on the other side of the potential barrier and so electrons can travel from the surface to the tip, and *vice versa*, by the tunnel effect. The potential barrier crossed by the electron is called the tunnel barrier. When a low potential is applied between the tip and the surface, a tunnel current can be detected. The tip and the surface being studied together form a local tunnel junction. The tunnel effect is also at work in Josephson junctions where a direct current can flow through a narrow discontinuity between two superconductors.

In a transistor, an unwanted tunnel effect can appear when the insulator or grid is very thin (nanometre scale). Conversely, the effect is put to use in novel devices such as Schottky barrier tunnel transistors and carbon nanotube assemblies.