From **assembly** to **functionalization**
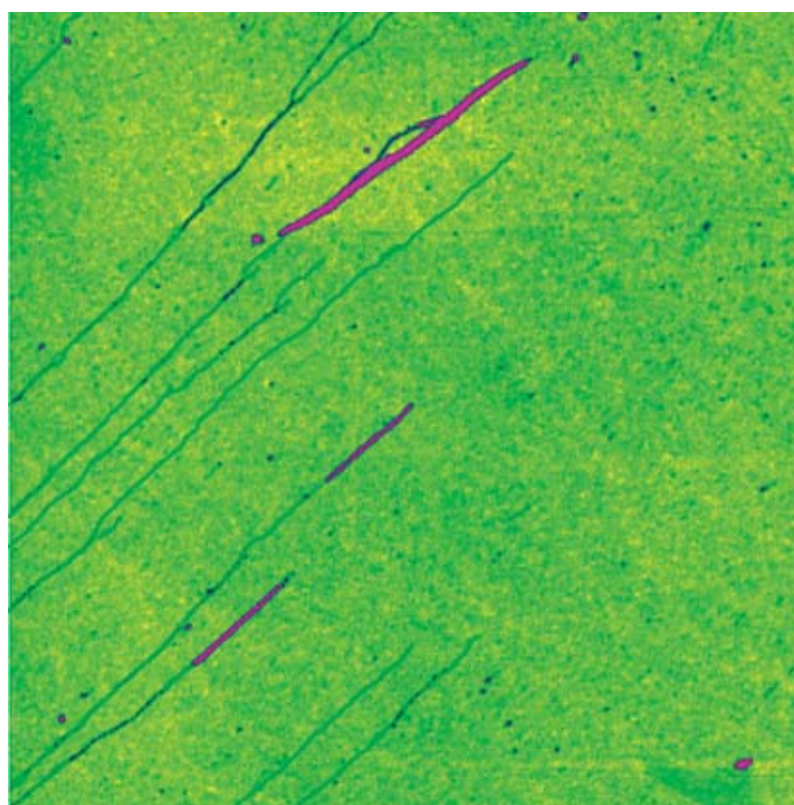
For nano-objects not to remain mere laboratory curiosities, they have to be assembled and built into optimally-engineered devices. The purpose of molecular electronics is to design and build electronic circuits using functionalized molecules, carbon nanotubes or nanowires as components. Living organisms are both a source of inspiration and a vast domain for nanotechnology applications. Chemists use DNA or viruses as templates to assemble nano-objects and build structures. Because they can be equipped with a wide range of functions that lend them novel properties, carbon nan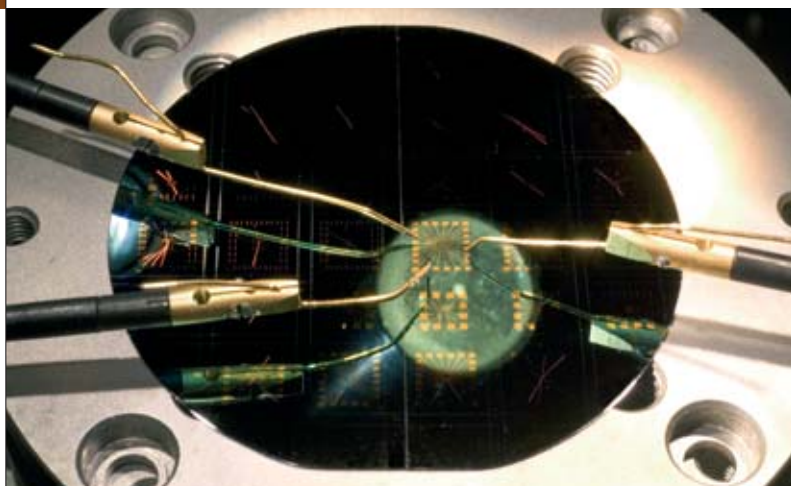otubes, nanowires, and metallic and semiconductor nanoparticles make, among other things, excellent detectors of biomolecules. In addition, the ability of biomolecules to bind and self-organize on the surface of carbon nanotubes can be used in many exciting applications, in particular to devise drug vectors. Also, hybrid materials based on nanoparticles obtained by the sol-gel technique can find applications in optics. A new generation of hybrid nanomaterials with a hierarchical organization is being studied and is opening up promising perspectives.

CEA/LEM/L. Goux Capes, A. Filoramo and J.-P. Bourgoin

Carbon nanotubes (pink) linked to DNA strands (black). The carbon nanotubes are aligned by combing the DNA strands.

Molecular electronics, a domain at the crossroads of chemistry, physics and engineering

Beyond the conventional development of current silicon-based information technology, new perspectives are opening up for the integration of molecular nano-objects synthesized by chemical means. The interfacing of totally different materials, the standardization of integration processes and an improved understanding of molecular electronics are the new challenges that must be met to overcome the inherent limitations of current CMOS electronics as regards production costs and energy consumption that are expected to be reached in the next fifteen years.

Electrical measurements under point contacts in nanocomponents.
Using micromanipulators, gold points set up an electrical contact with nanoelectrodes via 100 x 100 micron gold squares. These squares are connected by finer and finer gold motifs to electronic nanocomponents constructed at the centre of the motif (the characteristic size of the nanocomponent is one hundred thousand times smaller than the size of the motif itself).

Molecular electronics, defined here as the scientific domain that is concerned with developing electronic devices and **circuits** based on nano-objects such as (bio)molecules, **aggregates**, **nanowires** and **carbon nanotubes** (see *The building blocks of tomorrow's materials*), is enjoying a boom in interest among many scientists and the commitment of several major industrial players (IBM, HP, Infineon, Philips, NEC, **Intel**, Samsung). This current enthusiasm is due to the domain's unusual position at the frontiers of knowledge and as a potential reservoir of innovation for micro- and nanoelectronics. Molecular electronics has only been truly accessible to experimentation for a few years now, and it promises to offer a complement, or even a possible alternative, to all-**silicon** data processing, which scientists predict will reach its ultimate development limits in 10 to 15 years. It is hoped that molecular electronics will introduce low-cost manufacturing methods based on compo-

nent **self-assembly**. It should offer possibilities for improved management of complexity in ultradense circuits, lower computation energy costs, and novel functions, based on electromechanical systems, for example.

This emergent scientific domain, which is essentially multidisciplinary, is located at the intersection with chemistry, which synthesizes nano-objects, physics, which studies their properties, and engineering, which permits their implementation. This broad base lends the domain an appeal and is also an asset. It explains why many actors at the CEA working in different scientific areas are involved, from the Materials Science Division (DSM) to the Technological Research Division (DRT).

Molecular electronics is highly complex. Here we shall attempt to clarify this complexity by describing the basic building blocks that are used, how these can be interconnected to build components, and the methods employed to assemble these components into circuits with different architectural features.

The building blocks: choice, wealth, complexity

The nano-objects mainly used as the basic building blocks of molecular electronics are **molecules**, nanowires and carbon nanotubes.

Made by chemists, *molecules* can be adapted to the target application, and can be synthesized to specifications in large quantities. They present discrete electronic energy levels, which produce observable **quantum** effects. They can be bistable, or even multistable, *i.e.*, they can possess two or more stable states at a given temperature, which is of fundamental importance for the engineering of devices. Lastly, they display an excellent aptitude for self-assembly, especially as regards biomolecules that can serve as **templates** to guide the assembly of other objects. However, they are very sensitive to their environment, with poor heat-resistance and limited **electron conductivity**.

Nanowires and carbon nanotubes are **nanometric** in diametre and micrometric in length. According to their structure, they possess **semiconductor** or metallic properties. They are robust and withstand heat treatment. They show limited self-assembly properties, essentially defined by the molecules that can be **adsorbed** on their outer surface.

Very promising first components

In the last few years remarkable experimental developments have led to the construction of several types of devices.

Molecular components
Since the first theoretical proposals for molecular **diodes**[1] made by Ari Aviram and Mark A. Ratner in 1974, the problem of experimentally connecting
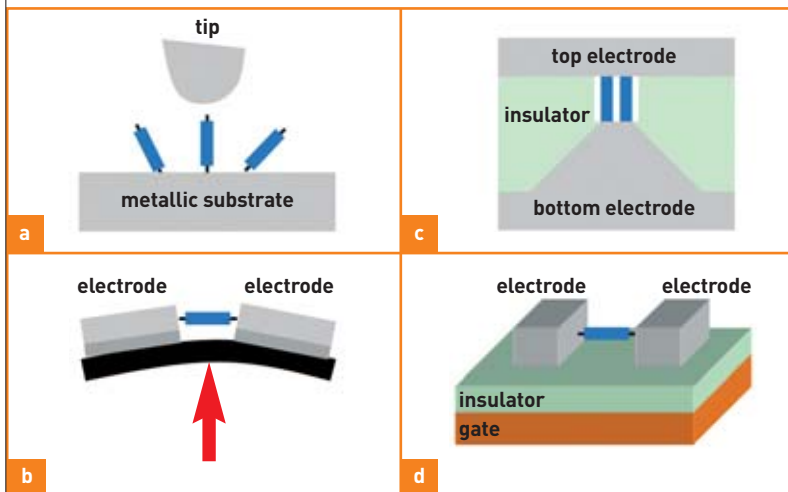

Figure 1.
Different experimental techniques to connect one or more molecules:
a, tunnelling microscopy; b, break junction technique; c, nanopores; d, planar nanogaps.

(1) Molecular diode: a molecule that displays a current rectifying effect due to the presence of a good electron *donor* part and good electron *acceptor* part linked by a saturated **covalent** chain, the current travelling preferentially from the donor to the acceptor.
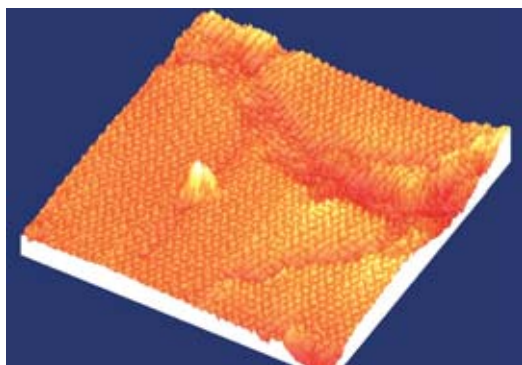
Self-assembled monomolecular layer of dodecanethiol on a single gold crystal viewed by tunnelling microscopy. Each "bump" in the relief corresponds to a molecule of dodecanethiol. The bright protuberance is a molecule of bisselenolterthiophene inserted in the monolayer. Although its geometrical dimension is comparable to that of dodecanethiol, it seems to rise out of the layer as tunnelling microscopy shows its greater ability to conduct electricity.

up a single molecule had long remained unsolved. Today, several experiments have shown that it is possible to prepare metal-molecule-metal, and even metal-**atom**-metal junctions. We can cite the use of the **tunnelling** microscope (see *Local probe microscopy: contact and manipulation*), the break junction technique pioneered by the CEA, planar nanogaps, and "vertical" geometries of the "nanopore" or "crossbar" type, although these last two bring into play several hundred molecules (Figure 1).

These experiments have been conducted to address two complementary themes. First, it was necessary to understand the nature of the charge transport in a molecule; whether it is coherent, the molecule acting as a sort of electron waveguide, or *incoherent*, the **electron** hopping onto and interacting with the molecule. Pioneering experiments conducted by the groups of Mark A. Reed at Yale University, Paul S. Weiss at Pennsylvania State University, Ronald G. Reifenberger and Supriyo Datta at Purdue University in the US, Christian Joachim at the Center for the Materials Design and Structural Studies (Cemes: Centre d'élaboration de matériaux et d'études structurales/**CNRS**), the group of the Solid State, Atoms and Molecules Research Department (CEA/Drecam: Département de recherche sur l'état condensé, les atomes et les molécules) at Saclay and the teams of Hongkun Park at Harvard University and Paul L. McEuen at Cornell University in the US have shown that the transport involves molecular orbitals[2]. Thus the understanding of the transport mechanism leads on logically to the study of the links between molecular structure and transport properties. It is clear that the future of molecular electronics will be strongly determined by the thorough control of the organic-inorganic interface. Researchers at Drecam have shown, for example, that simply replacing an atom of sulphur

by an atom of selenium at the molecule metal contact point is enough to change the conductivity of a metal-molecule-metal junction by more than one order of magnitude.

Figure 2 shows an example of current-voltage characteristics measured on a molecule of bisthiolterthiophene by the break junction technique (Figure 1) at the Drecam. A gold nanowire suspended between two metal pads is stretched and broken by gradually twisting the supporting substrate. The distance between the two gold surfaces thus created can then be adjusted to within a picometre (1 pm = 10^{-12} m). It is therefore possible to adsorb molecules on these free surfaces, and then re-close the junction until one of them makes a contact between the two parts of the wire. These nanometric connectors make it possible to study the behaviour of one or several molecules subjected to an electric voltage. More recently, the construction of planar nanogaps (Figure 1), in particular by the groups of Hongkun Park and Paul L. McEuen, has made it possible to add a third control **electrode** to influence, **electrostatically**, the transport within a molecule connected across two electrodes. These nanogaps 1 to 3 nm in width are obtained by the controlled breakage of a tiny nanofabricated metal wire. These experiments, conducted at very low temperature, show that it is possible to make a single-electron molecular transistor.
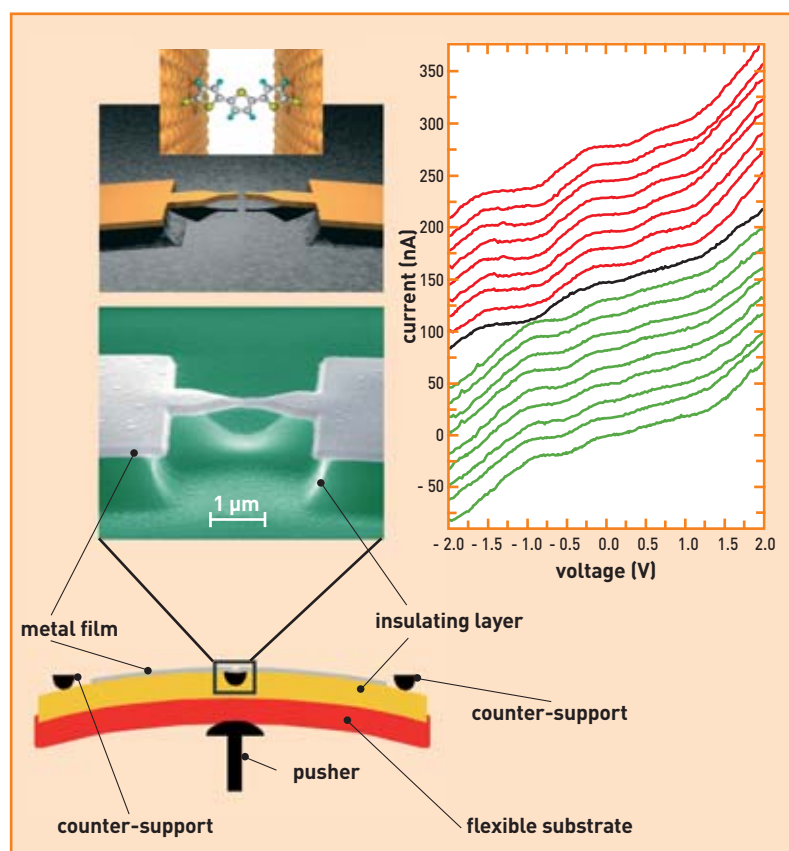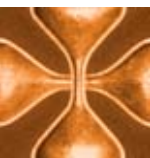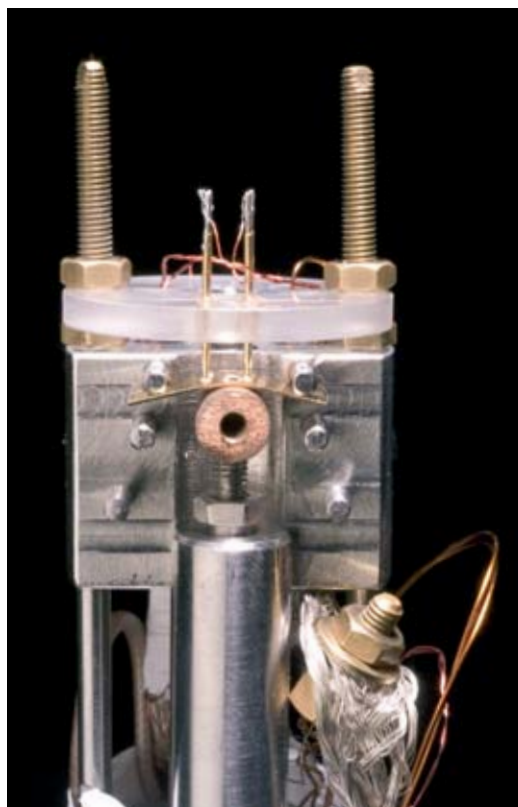

Figure 2.
The break junction technique and an application for the measurement of the current-voltage characteristics of the molecule of bisthiolterthiophene shown. The curves are offset for clarity. Their high number shows the stability of the measurement and the "humps", which correspond to the contribution of the molecular orbitals, signal the molecular transport process. The red curves are obtained after reducing the space between the two gold electrodes to a little less than 0.4 Å (from C. KERGUERIS *et al.*, *Phys. Rev. B – Condensed Matter*, 59, 12505, 1999).

(2) Molecular orbital: the orbital resulting from the overlap of the atomic orbitals of two linked atoms. It possesses two energy levels each of which can hold at most two electrons, one *binding*, which is more stable that the original atomic orbitals, and one *antibinding*, which is less stable.

A. Gonin/CEA

The next objective will be to use these components to perform molecular data processing. The transistors described above are remarkable tools for the study of fundamental physics, but like most of the other single-molecule components made to date, they cannot yet be exploited for this purpose. These components are intrinsically highly sensitive to the immediate environment of the molecule. The current approach instead favours devices that use several thousand molecules, such as nanopores (Figure 1) developed by the Yale group, the "crossbar" devices of the James R. Heath (UCLA) - Stan Williams (HP) team, or components based on surface-grafted **por-**

phyrins developed by CEA/Grenoble. In all three cases, the most clear-cut application is the development of memories.

Components based on carbon nanotubes and nanowires

Just as for molecular devices, practically all the components are currently available for electronic devices based on carbon nanotubes or nanowires. In the last five years the pioneering work of the teams of Cees Dekker at the University of Delft in the Netherlands, Phaedon Avouris at IBM's T.J. Watson Center, Paul L. McEuen at Berkeley, Hongjie Dai at Stanford and Charles M. Lieber at Harvard (USA) for example, has helped to develop a new domain that promises wide-ranging applications. The nano-objects that are used, in particular carbon nanotubes, present quite remarkable electrical and thermal conduction properties and robustness, and yet can be manipulated like molecules.

The current scale of these devices is greater than that of molecular components, typically 1-10 nm in width by 5-500 nm in length. The nano-objects used in them support either a **coherent** quantum transport (**ballistic** transport), or specific tunnel transfer effects, resonant or non-resonant, such as the **Coulomb blockade** mechanism.

Impelled by groups at IBM, Delft and Stanford/Cornell, the development of transistors based on high-performance carbon nanotubes has been extremely rapid (about four years, starting from nothing). It is noteworthy that these transistors, which can be prepared like *p* or *n* **transistors**, perform extremely well and better, for comparable geometry, than "good" silicon **MOSFETs**. Their characteristics come close to a **transconductance** of 6,000 **S/m** or 12 μS/nanotube, an effective **charge carrier** mobility of 3,000 cm²/V·s or a subthreshold slope, which is a measure of the energy necessary to switch the transistor from "off" to "on" mode, of less than 70 mV/decade.

It is important to note that these transistors do not function exactly like MOSFETs, but like **Schottky**
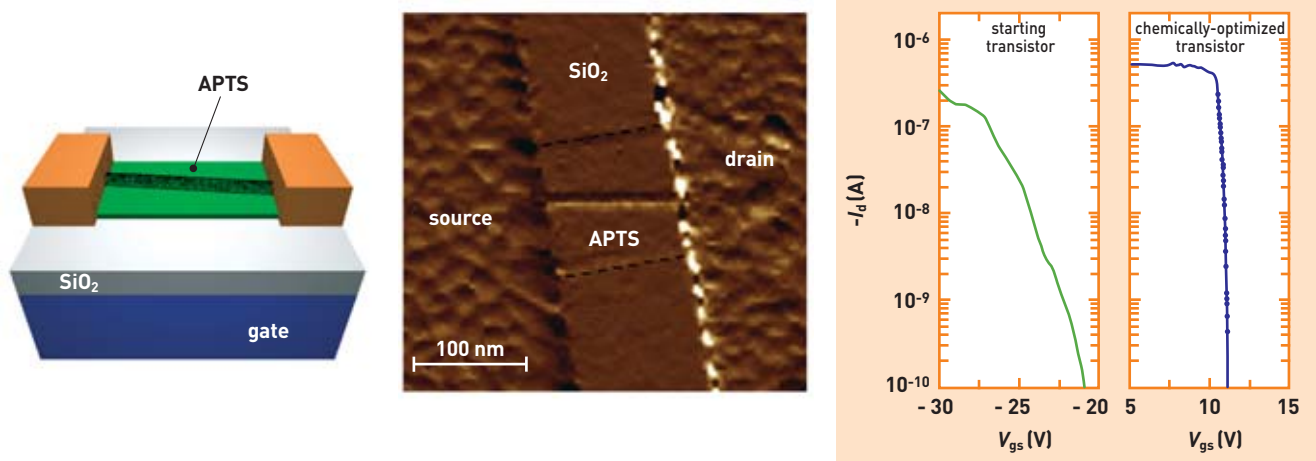
Figure 3.
Centre, atomic force microscope image of a transistor based on carbon nanotubes self-assembled on a monomolecular layer of amino-propyl-triethoxy-silane (APTS) that serves as a molecular glue. Left, diagram of the structure. Right, optimization by the chemical route (using trifluoro-acetic acid, TFA) of the performance of a transistor based on carbon nanotubes. The current in the nanotube (I_d, drain current) is modulated by the voltage applied to the gate (V_{gs}, gate-source voltage). After optimization, the transition between on and off modes is much sharper (from S. AUVRAY *et al.*, *Nanoletters* , 5, p. 451, 2005).

Electromechanical component formed by a carbon nanotube suspended between two gold electrodes.
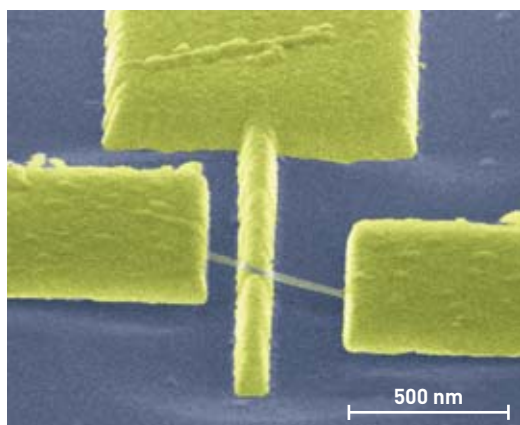
CEA/LEM/R. Lefèvre, M. Goffman et J.-P. Bourgoin

barrier transistors: the **gate** modulates the injection efficiency of **source** carriers into the **channel** and not the density of channel carriers. This feature was understood and demonstrated only in the last three years, and the first developments for the optimization of these components are only now starting to appear; for example, the improvement of the geometries of transistors (optimization of the insulator and the gate or contact geometry) by the Stanford and IBM groups, *n*-type "doping"[3] demonstrated by these same research teams, along with *p*-type doping by Drecam (Figure 3). These transistors can be combined to produce simple circuits such as **logic gates** or oscillators[4].

Besides transistors based on nanotubes, other types of components using carbon nanotubes or nanowires have also been developed: resistors, diodes, resonant diodes, switches, single-electron transistors, and electromechanical devices. The latter are especially promising for applications as high frequency oscillators or resonators, or as force sensors. In parallel with the improved performance of these components, it is now clear that the future of this domain is directly conditioned by the development of techniques to achieve the controlled positioning of these devices[5].

Components assembled in circuits

Here we focus essentially on circuits based on carbon nanotubes or nanowires. The self-assembly of these nano-objects to form circuits is the most promising route today. The intrinsic properties of the nano-objects can be harnessed to manipulate nano-objects without being held back by the limits of **lithography** techniques (Box E, *Lithography, the key to miniaturization*). Self-assembly also promises reduced manufacturing costs. This last point is important given that
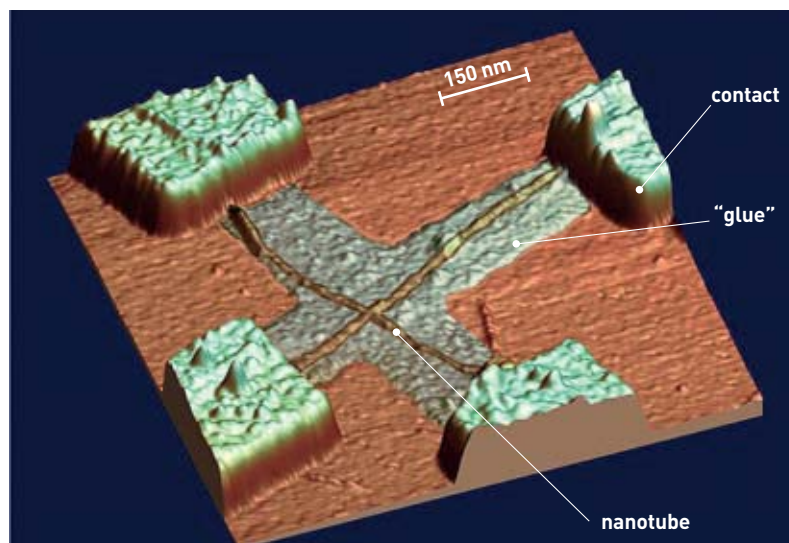
(3) This is not doping in the strict sense, but an optimization of performance by improving the efficiency of injection through the source Schottky barrier.

(4) Oscillator: a system that varies periodically with time, *e.g.* sinusoidally (sinus or cosinus).

(5) Carbon nanotube-based electronics has to solve a second major problem: the separation of semiconductor and metallic nanotubes. Several promising studies are in progress in France, Europe and the US.

the price of a semiconductor manufacturing unit is predicted to exceed 50 billion dollars in 2008.

At the joint CEA-Motorola molecular electronics laboratory at the Drecam, CEA/Saclay, a method developed in 2002 has made it possible to position carbon nanotubes on a surface in a controlled manner. The surface is first of all chemically **functionalized** by a monomolecular layer at the locations where the nanotubes are to be deposited. It is then dipped in a solution of nanotubes that self-assemble at the functionalized sites. Other techniques are based on combing, i.e., lining up the nanotubes using a solvent flow that aligns them like tree trunks in the current of a river, or in a field produced by an alternating current. A special place will be given to methods based on the localized growth of carbon nanotubes and nanowires. They involve the use of a growth **catalyst**, the localization and size of which directly condition the position and diameter of the nanotube or nanowire. These techniques are developing rapidly, and will without doubt be most important in the future, once the size and localization of the objects can be accurately controlled. The CEA's Innovation Laboratory for New Energy Technologies and Nanomaterials (Liten: Laboratoire d'innovation pour les technologies des énergies nouvelles et les nanomatériaux) is currently working in this field, with

Crossover of two carbon nanotubes deposited on silica, illustrating the production of nanotube circuits by self-assembly. The grey strips are molecular glue to allow positioning of the nanotubes (joint work by CEA and Motorola).

CEA/LEM/E. Valentin and S. Auvray

the development of a reactor for the synthesis of carbon nanotubes on 200 mm substrates compatible with the standards of microelectronics.

These positioning methods, once they are validated for application on an industrial scale, will allow the continuous mass production of components containing carbon nanotubes as interconnecting wires or active elements. For the longer term, we note that self-assembly methods, which *circumvent lithography*, are being studied in research laboratories by combining the advantages of biomolecules (self-assembly, specific recognition) and carbon nanotubes (electronic properties).

Developing specific architecture

Several types of elementary molecular components have thus recently been developed. The next step is

obviously to determine how these components can be used to build circuits with specific architectures. Two types of architecture are possible: hybrid and integrated.

Hybrid architecture is conceptually the simpler of the two, being more similar to the current **CMOS** device and so easier to interface with it. Elementary components are to be interconnected by metal wires. This applies, for example, to transistors based on carbon nanotubes used for the fabrication of logic gates and small circuits, diode-transistor type logic, or circuits using single-electron components. Today this type of architecture can be laboratory-tested. This category also includes programmable architecture based on arrays of nanowires, with switches inserted at crossing points. The great advantage of programmable architecture is its ability to tolerate imperfections during fabrication. This technology can present a clear advantage in terms of production costs, because it uses self-assembly and parallel fabrication techniques. However, it has two major drawbacks for large-scale use with extreme miniaturization, which CMOS technology will also ultimately come up against, unless some radically new approach to computation is found. First, when elementary components are assembled closer than about 10 nm, loss of individual identity occurs, and interference arises between different pathways leading from one point to another in the circuit, particularly if the circuitry is regular as in crossbar arrays. Second, even assuming perfect switching operation, *i.e.*, when each switch requires an energy of 17.3 **meV** at ambient temperature[6], a circuit assembling components operating at 10 GHz with a density of about 10^{12} cm^{-2} will require a power of several tens of W/cm^2, which approaches the upper technical limit for energy dissipation.

Integrated molecular electronics, in which the Cemes laboratory in Toulouse is a pioneer, consists in using several functions incorporated in a molecule to perform a calculation. Only the result of that calculation will be transmitted to the macroscopic environment. This approach can theoretically overcome the drawbacks of hybrid architecture. However, the technical difficulties involved in implementing this architecture are still considerable, and so this must be considered as a long-term solution. Note that it should be possible to couple the integrated molecular electronics approach with quantum computation. The first theoretical work is in progress on this possibility.

Perspectives

The remarkable boom in molecular electronics is essentially based today on strong fundamental research coupled with relatively modest technological resources. It promises a development pattern at two distinct timescales: hybridization of CMOS and molecular electronics within 8-10 years, and the development of purely molecular data-processing solutions in 20 years. The functions that can be envisaged include memories and processors, associated with new computation approaches. It is also likely that the real-world interface functions (sensors, transducers, electromechanical actuators, etc.) will be directly integrated with processor and memory functions within complex systems, in more sophisticated versions of the current *systems-on-chips*.

> **Jean-Philippe Bourgoin*** and **Stephan Roche****
Materials Science Division
*CEA Saclay Centre
**CEA Grenoble Centre

(6) Equal to kTLn2, where k is the Boltzmann constant ($k = 1.38 \cdot 10^{-23}$ J/K) and T is the temperature.

A silicon **wafer** is placed in the metal evaporator to deposit a fine layer of gold. Certain parts of the wafer are protected by a resin that is then dissolved away, taking with it the metal layer. This is termed *lift-off*. After this step only the unprotected parts are metallized to build the desired structure.
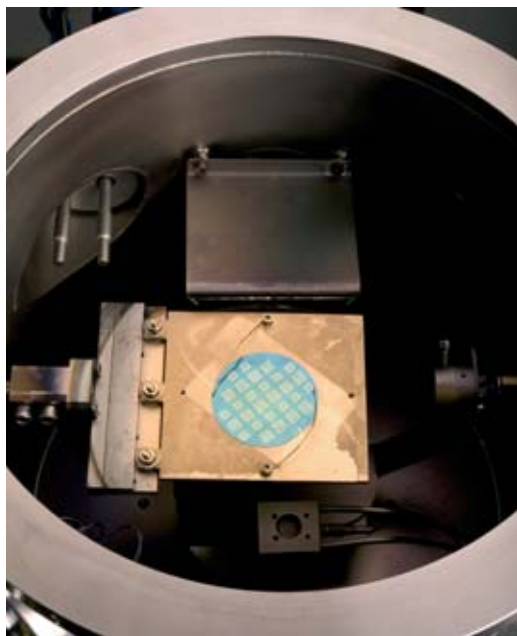
A. Gonin/CEA

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
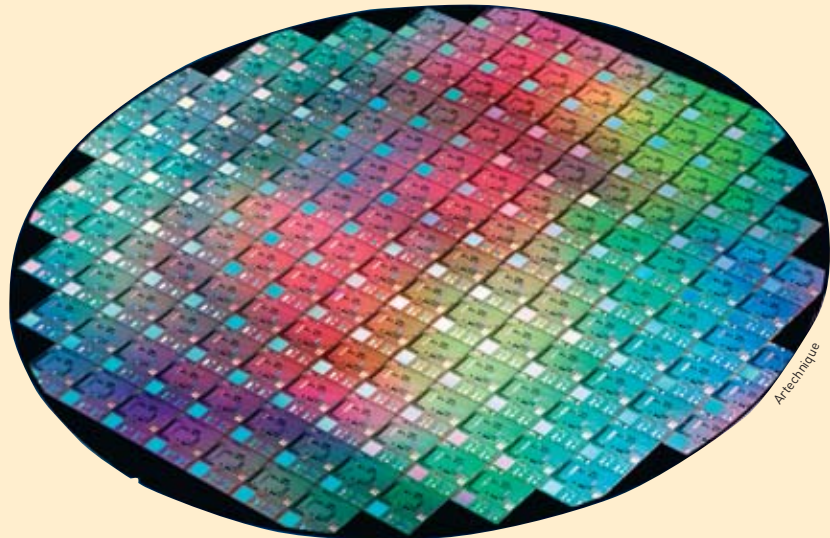
have to take on or use certain physical phenomena, particularly from **quantum** physics, that operate when working at the nanoscale.

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.

A (next)

natural world

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

bottom-up

| 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

top-down

artificial world

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-**
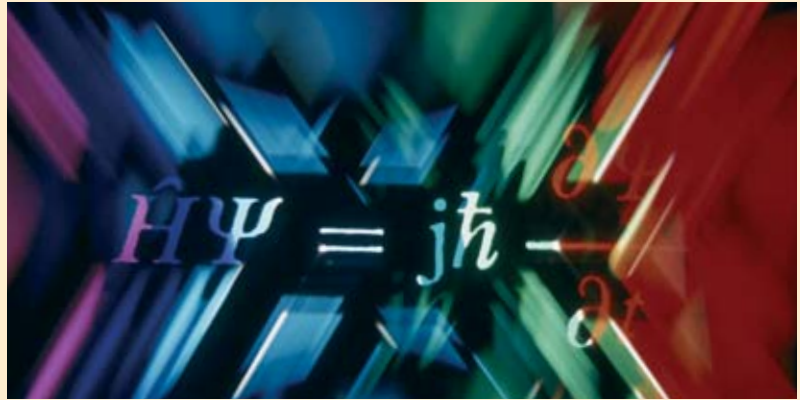
An "artist's impression" of the Schrödinger equation.

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 $5 \cdot 10^{-11}$ 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
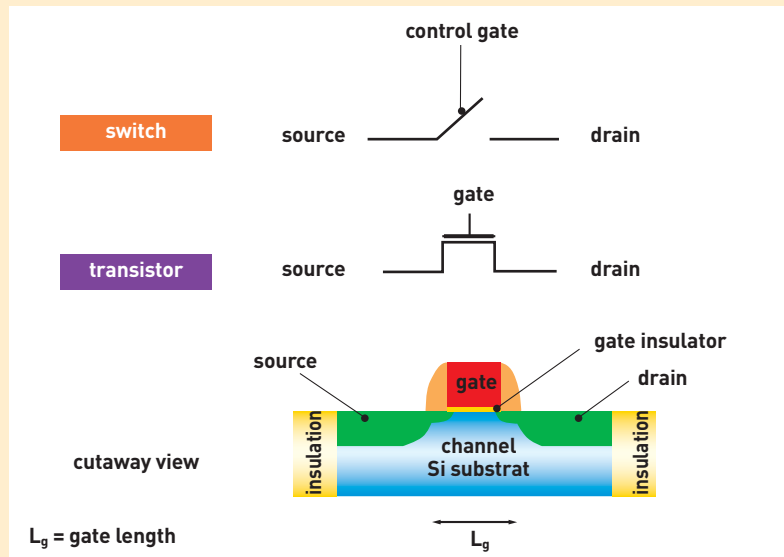

Figure.
A MOS transistor is a switching device for controlling the passage of an electric current from the source (S) to the drain (D) via a gate (G) that is electrically insulated from the conducting channel. The silicon substrate is marked B for Bulk.

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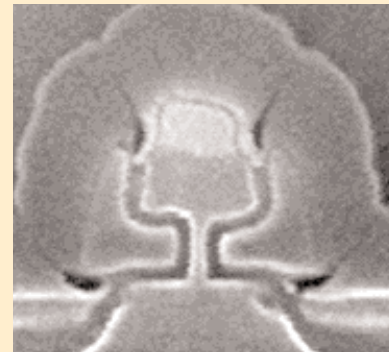
8 nanometre transistor developed by the Crolles2 Alliance bringing together STMicroelectronics, Philips and Freescale Semiconductor.

(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).

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).

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".
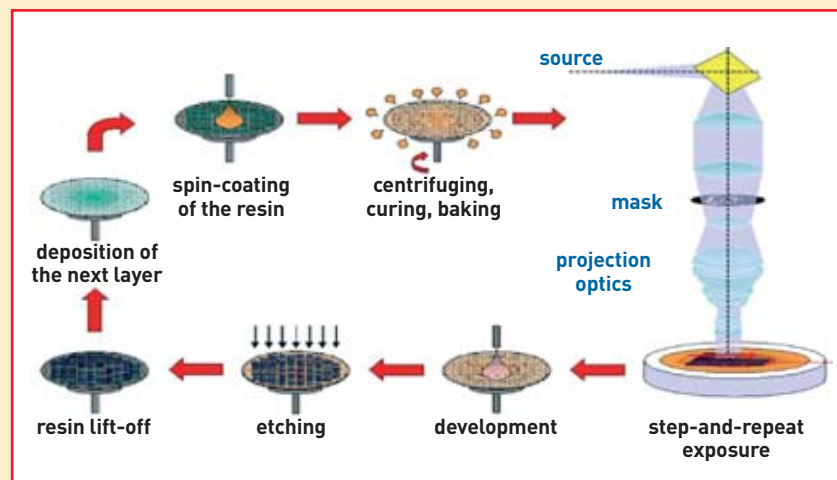

Figure. The various phases in the lithography process are designed to carve features out of the layers of conducting or insulating materials making up an integrated circuit. The sequences of the operation are laying of a photoresist, then projecting the pattern on a mask using a reduction optics system, 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.