Microscopes: first **eyes**, now also **tools**

The nanosciences and nanotechnology owe their emergence to the recent spectacular advances made in techniques of observation and manipulation. Three main types of microscopy are widely used, in particular at the CEA. They are local probe microscopy, first developed in the 80s, the much older transmission electron microscopy (about 1930) and scanning electron microscopy (about 1965). Today local probe microscopy uses a large family of instruments that have revolutionized our knowledge of solid surfaces and now make it possible to build nano-objects atom by atom. Conventional electron microscopy has also made great advances and now provides a wealth of surface and volume information.


Artechnique/CEA

Transmission electron microscope (TEM) (400 kV JEOL) at CEA/Grenoble. This instrument is currently equipped with a high-resolution CDD camera and can be used to visualize defects in crystalline structures. Twenty years ago, with its resolution of 0.17 nm it was one of the most powerful microscopes in the world.

Nanometric materials have a very long history. The craftsmen of Ancient Rome used gold powder to colour glass, and glazes containing metal **nanoparticles** to decorate pottery. However, these applications were derived from empirical knowledge. By contrast, the nanotechnology era is characterized by the controlled, systematic use of nanoparticles and nanocomponents. This became possible only when tools became available to manipulate and observe individual nano-objects, and monitor their movements (Box F). What really opened up the nanoworld and revealed its exciting possibilities was the invention of *local probe microscopy* and in particular **tunnel-effect** scanning tunnelling microscopy (STM) in the1980s (Box G).

The revolution of local probe microscopy

Thanks to local probe microscopy, it is now possible to visualize individual **atoms** and **molecules** deposited on a surface (see *Local probe microscopy: contact and manipulation*). Of course, visualizing them does not mean seeing them with your bare eyes; "groping in the dark" would be a more accurate way to describe the technique. But local probe microscopy is not just a method for examining materials; it can also be used to act on those materials. It lends us not only eyes but also hands. A local probe microscope can be used to pluck an atom from a surface and reposition it somewhere else. Organic molecules can be gently moved into their correct positions in a more complex assembly. We now at last have a tool to build nano-objects from their elementary building blocks, atoms and molecules. This **bottom-up** approach starts with elementary components and assembles them into nano-objects. In academic research local probe microscopes are extremely powerful tools with which it is possible to manipulate individual nano-objects and study some of their properties (depending on the type of manipulator tip used). For technological applications, these instruments are simple, rapid, robust and cost-effective tools for characterizing nano-assemblies. For example, the atomic force microscope (AFM) can be used to rapidly determine the type of **nanostructures** (wires or boxes) obtained according to germanium growth parameters (Figure 1). Unfortunately, these microscopy techniques still have two important limitations: they study only the properties of surfaces, and as tools for fabrication they are relatively slow. However, conventional electron microscopy may help to overcome these limits.

F How do we see or "feel" the nanoworld?

To find something out about an object we have to approach it in some way and obtain information from it. The methods we can use may be grouped into three families: (i) methods that study a signal that is naturally or artificially emitted by an object, (ii) methods that send a signal to it and study the signal it re-emits, and (iii) methods that use direct contact with the object to measure a force of interaction between it and a probe.

Detecting signals emitted by the object

We can see the stars without having to interact with them. Large structures can naturally emit signals that are strong enough to be detected far away. The emissions from nano-objects are generally so weak they are smothered by the signals of neighbouring objects. There are two ways to get round this: we can (i) isolate the nano-object to make sure the emitted signal really originates there and nowhere else (e.g., isolation of atoms with a laser beam or of certain nanostructures on etched nanodots to study their luminescence), or (ii) position the detector close to the object. However, most nano-objects are not radioactive or naturally phosphorescent, and so they have to be stimulated in some way to emit a signal. *The Tomographic Atom Probe* is a powerful technique that analyses a particular signal (for more details see http://www.cameca.fr/html/tap_technique.html). A short, intense electric pulse is used to strip **atoms**, layer by layer, from an object that has been shaped to a fine point. The atomic mass of the stripped atoms can be determined by mass spectrometry, and the three-dimensional atomic structure can be reconstructed layer by layer. Unfortunately, this method requires a conducting object and a perfect radius of curvature, and not all nano-objects can be given this shape. In **scanning tunnelling microscopy (STM)**, a very fine point is brought near the surface of the object and strips **electrons** locally.

Using a probe signal

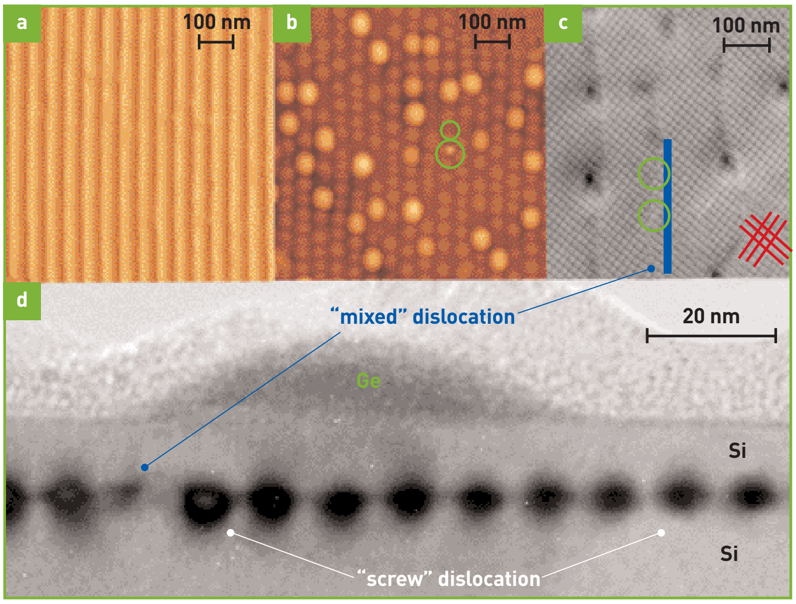
This is the "classical" approach used by all **conventional microscopy**. A probe is brought to the object and the re-emission (reflection or transmission) of the incident signal is used to characterize the object. Depending on the type of probe used (visible light, X-rays, electrons, ions, ultrasound), we have **optical, Raman, X-ray, electron, ion or acoustic microscopy**. Here, the **resolution** attained by the method is determined by the wavelength associated with the probe signal. A strong interaction between the probe and the object is necessary to obtain an image of a small lone object.

Pseudocontact or interaction force

This is the "groping in the dark" method. A probe is brought near the object until a force of interaction, or "pseudocontact" is established. The information is obtained by scanning the surface of the object and observing how the force acting on the probe varies. To obtain highly local spatial information the contact probe must be very small. This method generally yields information only about the surface, but it is a fascinating technique and one of the few that can manipulate atoms *individually*! *Atomic force* microscopy (**AFM**) and *magnetic force* microscopy (**MFM**) belong to this family.

The development of transmission electron microscopy

The transmission electron microscope (TEM) was the first instrument to give, from the 1970s onwards, direct images of atomic structures, *i.e.*, images showing the arrangement of atoms in a material. However, the technique was relatively cumbersome(1). A complete set of lenses had to be aligned (see *Conventional electron microscopy: scanning and transmission*), the sample had to be thinned down to obtain ultrathin areas (less than 40 nm thick), and simulations had to be run to interpret the experimental images correctly. In addition, these high-resolution images can be obtained only on certain types of material - **crystals** - viewed in certain directions, and the images in fact represent only a projection of the atomic structure. But despite its limitations, the technique has provided, and is still providing, valuable information on the atomic organization of nanostructures. It enabled Sumio Iijima to discover carbon nanotubes in 1991(2). Variations in atomic struc-



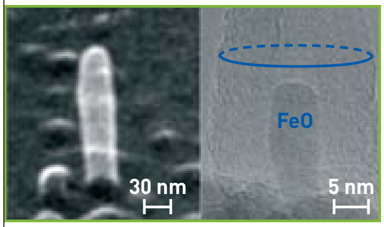
CEA/DRFMC/V. Poydenot

Figure 1.
Germanium nanostructures deposited on special "twist-bonded" silicon substrates. AFM images a) and b): depending on the growth parameters, germanium wires or islands are obtained. TEM image c) (top view): Ge boxes and deliberately buried linear defects ("mixed" and "screw" dislocations) are visible simultaneously. TEM image d) (edge view): the edge of the island is clearly visible vertically above a "mixed" dislocation.

(1) The electron microscopy laboratory at CEA/Grenoble was the pioneering French laboratory in high resolution electron microscopy in 1975-1990.

(2) S. Iijima *Nature*, 354, 56 (1991), http://www.onera.fr/conferences/nanotubes/trans01.htm for a presentation in French, or Lijima's own site: http://www.labs.nec.co.jp/Eng/innovative/E1/01.html

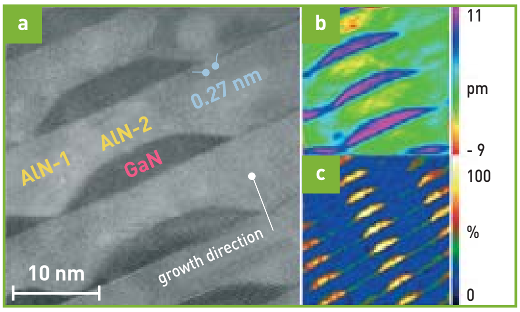
ture can be detected inside nano-objects. For example, Figure 2 shows the anchoring of a carbon nanotube on a reduced iron oxide catalyst. Distortions inside nanostructures can also be measured by numerical analysis of the images. (Figure 3).



CEA/DRFMC/M. Delaunay

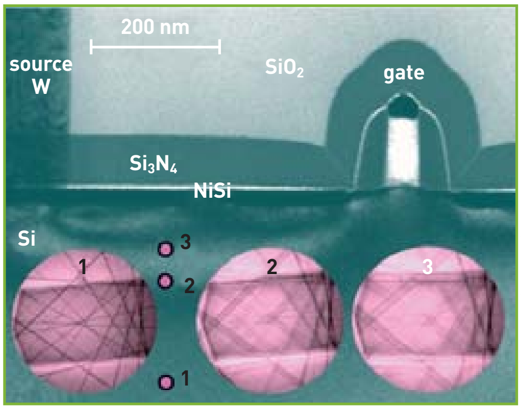
Figure 2.
Growth of multiwall carbon nanotubes on iron oxide catalysts deposited on Si. a) scanning microscope image, b) high-resolution electron microscope image (recorded on a 400 kV JEOL instrument). This nanotube has formed around the oxide catalyst. The distance between layers is 0.34 nm.

But electron microscopy is not restricted to high resolution microscopy. Since the first electron microscope was made in 1931 by Ernst Ruska, many techniques have been developed, and the electronic microscope offers many possibilities. These include: detection of linear defects in crystal structures (Figure 1), local diffraction (Figure 4), local chemical analysis by either direct imaging or scanning (Figures 5 and 6), and measurement of magnetic and electrical fields by electronic holography. Until recently, each of these techniques needed specific equipment and was optimized on different microscopes. The use of computers now makes them all much simpler to use and also makes it possible to set them up on a single microscope. This multipurpose instrumentation forms the basis of the new microscope ordered in January 2005 by CEA/Grenoble (Box 1). But the contribution of information technology to microscopy does not end there. First, computer-processing can yield a complete series of images of the same object, and be used to reconstruct the structure of a nano-object in three dimensions: 3D mapping already has near-nanometre resolution. Second, the real-time analysis of stored images permits better alignment of the microscope lenses, allowing complex lens systems to be devised. Spherical aberration correctors[(3)], which appeared in 1997, will be revolutionizing electron microscopy through the new possibilities they offer: better resolution, obviously, but also more space



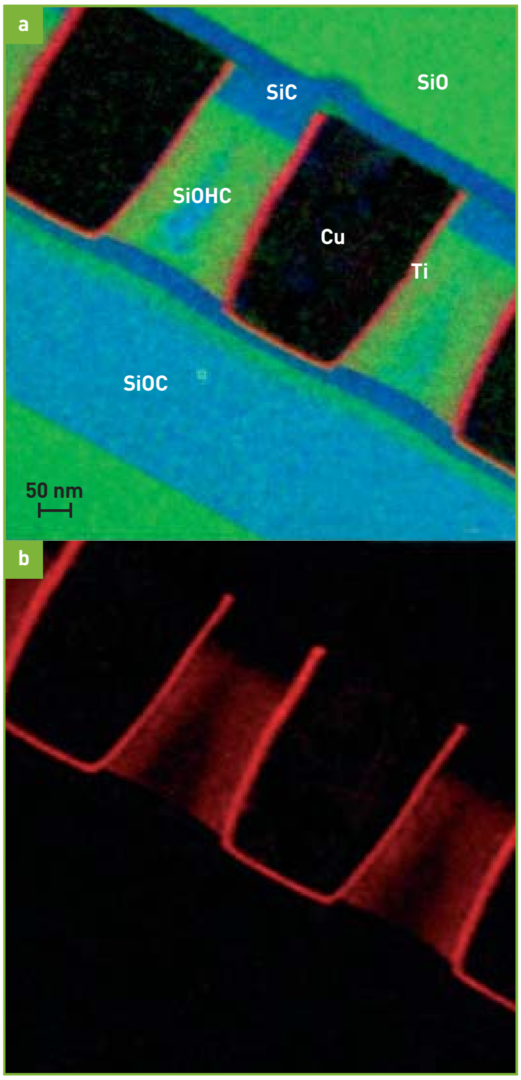
CEA/DRMFC/J.-L. Rouvière & E. Sarigiannidou

Figure 3.
Gallium nitride (GaN) quantum boxes, edge view.
a) high-resolution image recorded with a 400 kV TEM at CEA Grenoble. Each white point represents a doublet of atomic columns (one of Ga or Al, and one of N). The distance between doublets is about 0.27 nm.
b) Variation Δc of the distance between the atomic planes (0002) perpendicular to the growth axis: mapping is performed by high-resolution numerical analysis.
The image clearly shows that the AlN located above the GaN boxes (AlN-2) has a lattice parameter 7 pm smaller than the reference region AlN-1: the GaN thus strains this region. On the chemical image c) of the same sample (Ga threshold), taken with a 300 kV TEM, the layer of AlN has a homogeneous colour and shows no traces of Ga.



Collaboration CEA/Grenoble/Alliance R. Pantel & L. Clément

Figure 4.
Image obtained by local electron diffraction on a 200 kV TECNAI TEM operating in STEM mode. Diffraction diagrams are plotted at different points of the sample (beam diameter approx. 1 nm), three of which (coloured images) have been superimposed onto the general image of the transistor. By studying these images, the distortions of the silicon substrate can be measured to 10^{-3} nm.



CEA-Leti/J.-P. Barnes, D. Lafond

Figure 5.
Chemical image of interconnections in an integrated circuit recorded at CEA-Leti on a 200 kV JEOL TEM.
a) Superimposition of maps of Ti, O and C, and b) Map of Ti. This image shows the diffusion of Ti out of the thin film of TiN (thickness 8 nm) in the low-k SiOC region.

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(3) Haider *et al.*, Nature, 392 (768)1998, *P. E. Batson, N. Dellby, O. L. Krivanek Nature* 418, 617 (2002).

The future corrected holographic microscope + STEM at CEA/Grenoble

1

In January 2005, CEA/Grenoble ordered a 300 kV "holographic microscope" from FEI(1) which is to be equipped with a spherical aberration corrector for the condenser lenses. In scanning mode (STEM, for scanning transmission electron microscopy), this transmission electron microscope (TEM) should have a resolution approaching 0.1nm.
This microscope will be installed early in 2006 in the new Minatec buildings. A microscopy facility will also be set up, combining the microscope equipment of three laboratories at CEA/Grenoble (pure research at DRFMC (Department of Fundamental Research on Condensed Matter) and applied research in microelectronics (Leti: Electronics and Information Technology Laboratory) and metallurgy and new energy sources (Liten: Innovation Laboratory for New Energy Technologies and nanomaterials)).
Its detectors (2048 x 2048 pixel CCD camera, Gatan-Tridiem post-column spectrometer and X-ray detector) and equipment (aberration corrector for the condenser, Lorentz lens and STEM module), will make this new microscope one of the most technically advanced in the world. It will allow several measurements to be made on the same object. The adjoining figures illustrate some of the exceptional possibilities this new facility will offer: visualization of atomic columns of dopants (Figure E1), visualization of electric potentials (Figures E2 and E3) and visualization of magnetic potentials (Figure E4). A special effort will be devoted to electron holography, a technique invented in 1948 by the 1971 Nobel prizewinner Gabor, but not yet highly developed in France. Holography makes it possible to address directly both the amplitude and phase of the wave function of the electron (Figure E2), whereas until now most experiments have measured either the amplitude or the phase. In electron microscopy, the most widely used holographic technique uses interference between the incident beam that travels past the object (reference wave) and the beam that travels through the object (the wave function to be determined). The two beams are superimposed by means of a beam deflector, the Möllenstedt biprism, which is a very fine wire (about one micron in diameter) held at an electric potential of tens or even hundreds of volts.

D. A. Muller

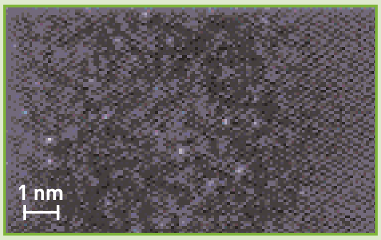

Figure E1.
Visualization of single atoms (Sb dopant) in Si columns. Each white point represents two columns of about 20 silicon atoms. The brightest columns contain one, two or three dopant atoms (Sb). Image recorded with a 200kV JEOL TEM operating in STEM mode by D.A. Muller, *Nature*, vol. 416, 826 (2002).

Rau

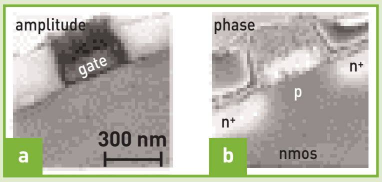

Figure E2.
Dopant mapping in an integrated circuit by electron holography. Image recorded with a Philips CM200 transmission microscope equipped with a holographic biprism (with permission from Rau *et al. Phys. Rev. Lett*. 82, 2640-2643 (1999); fig.1; © 2005 American Physical Society).

McCartney, Arizona State University, Tempe

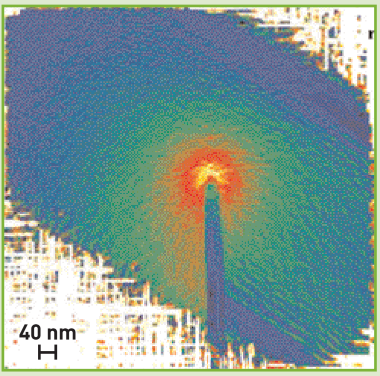

Figure E3.
Electric field gradient mapping around multiwall carbon nanotubes. A field of 1.22 V/nm is measured at the top of the nanotube when it is held at an electric potential of 120 V. It is essentially the tip that emits electrons (with permission from Cunings *et al., Phys. Rev. Letters* 88, 056804 (2002); Fig. 1 ; © 2005 American Physical Society).

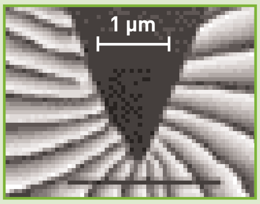

Figure E4.
Magnetic field mapping around a tip point in a magnetic force microscope (MFM). The image is obtained by electron holography in a transmission electron microscope. It is the fine magnetic layer at the MFM tip surface (black) that generates the visualized magnetic field. (G. Matteucci, B.G. Frost, F.F. Medina; *Ultramicroscopy* 99 (2004) 95; © 2005 Elsevier).

(1) Set up in 1971 to market crystals for electron guns, the American company FEI merged in 1997 with the Dutch microscope builder Philips Electron Optics.

around the sample(4). This space gain is going to facilitate in situ studies during growth and can turn the electron microscope into a true nanolaboratory, where nano-objects will be observed directly with very high resolution during their growth or during the application of external forces, whether mechanical, magnetic or electric. We can see this happening already: using an environmental electron scanning microscope, where the object is immersed at high temperature in a gaseous atmosphere, it has been possible to observe the growth of carbon nanotubes in real time(5). A local probe microscope can

CEA/DRFMC/P. Bayle-Guillemaud

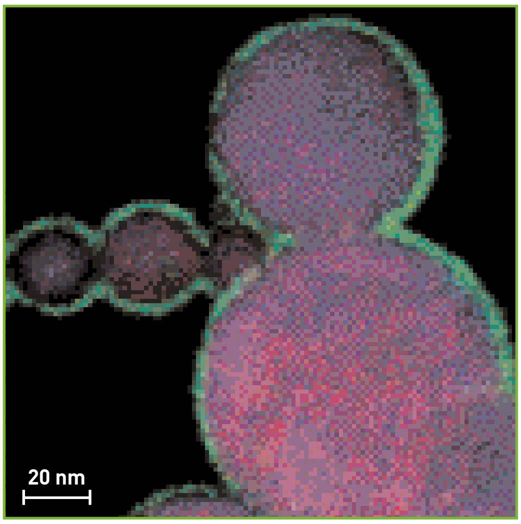

Figure 6.
Chemical mapping of small magnetic particles of FeNi reconstructed from three chemical images (O = green, Ni = red, Fe = blue) obtained with a JEOL 300 kV TEM equipped with a GIF spectrometer. The oxide layer appears clearly at the surface.

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(4) See the American TEAM project (http://ncem.lbl.gov/team3.htm).

(5) R. Sharma, Z. Iqbal: *Applied Physics Letters* (2004) Volume 84 p. 990 *In situ* observations of carbon nanotube formation using environmental transmission electron microscopy.

Artechnique/CEA

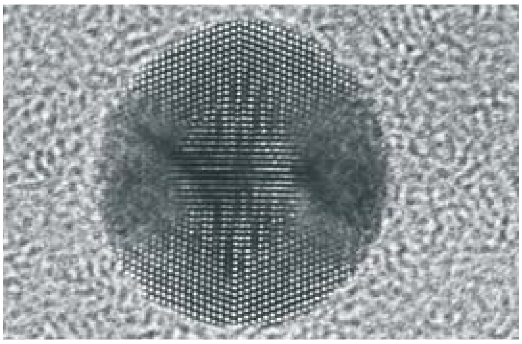
Installation of a *focused ion beam* (FIB) at CEA-Leti, Grenoble. The two ion beams are used both to weld and to cut samples over distances of a few nanometres.

be introduced into the microscope column(6) to act, electrically or mechanically, on an individual object, which is simultaneously “imaged” by the electron microscope (Box 1).

Thus electron microscopy has proved to be one of the few techniques that can provide a nanometre-scale three-dimensional analysis of all the characteristics of a nano-object: structure, chemistry, magnetic field, electric field, growth. As nano-objects are generally small enough to be electron-transparent with no preparation needed(7), the only limitation of the technique will be the capacity of the nano-object to resist damage by the electron beam throughout the duration of the observation period. With all these innovations, electron microscopy can be expected to remain a relatively cumbersome and costly technique compared with local probe microscopy, though less so than **synchrotron radiation** equipment. Initially not all laboratories will be able to afford instruments equipped with all the technological innovations. Specialized centres will have to be set up to serve as host structures and to develop the possibilities of the new instruments. CEA/Grenoble is hoping to set up such a centre based on the new microscope it is due to receive at the end of 2005.

Advantages of scanning electron microscopy

Scanning electron microscopy (SEM) does not reach the resolution attainable with transmission microscopy (TEM or STEM) or scanning tunnelling microscopy (STM). However, this technique possesses many advantages, and in many ways (*e.g.*, cost, convenience, operating principle, possibility of building nano-objects, non-deterioration of the object) is a good compromise between transmission microscopy and local probe microscopy. It is the preferred tool in the *top-down* approach (developing macroscopic devices that work down to the scale of atoms and molecules). Since the first instrument was commercialized in 1965, the resolution of scanning microscopes has continuously progressed to reach 1 nm today, and even 0.4 nm on a prototype equipped with a spherical aberration corrector. At present the scanning electron microscope is a very efficient tool for the rapid visualization of the presence, shape and arrangement of nano-objects (Figure 2). The magnification of the microscope can be adjusted very rapidly to go from a general view of the object (usually of the order of a centimetre) to an image containing details at near-nanometre scale. Most importantly, when equipped in a variety of ways, the scanning microscope can become the central controlling "eye" in a "nanofactory" for the fabrication of nano-objects A beam of **ions**, or focused ion beam (FIB), can be readily combined with the electron beam of a scanning microscope to produce a device called a dual-beam or cross-beam microscope, depending on the instrument maker. With a beam of gallium ions, a FIB instrument can act as a scalpel to shape motifs at a scale slightly greater than a nanometre(8). This tool is just beginning to appear in French laboratories (Box 2). Micromanipulators, very similar to local probe microscopes, can be added to handle the structures by welding or manipulation. In addition, a small local tuyere can be brought close to the ion beam impact area. This tuyere releases a gas, *e.g.*, an organometallic compound, which is cracked locally by the ion beam. In this way welds or local metal deposits can be made (currently 20-40 nanometres). This opens the way to growing nano-objects in an electron beam. In addition, the electron beam may be used to cure resins with a resolution of a few nanometres: this is very high performance **lithography** in terms of resolution. In sum, although it does not operate at atomic or molecular levels, scanning microscopy is an essential tool in the fabrication of nanostructures, because it uses the simplest and best microscope that rapidly links the macroscopic to the nanoscopic.



CEA/DRFMC/J.-M. Pénisson

High-resolution image (obtained with a 400 kV microscope) of a palladium catalyst (Pd) deposited on a membrane of amorphous carbon. The icosahedral particle has a diameter of 10 nm. Each white point represents a column of about 10 atoms precisely aligned in the direction of the incident electron beam. The different levels of contrast correspond to different facets of the particle.

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(6) http://www.gatan.com/holders/stm_holder.htm

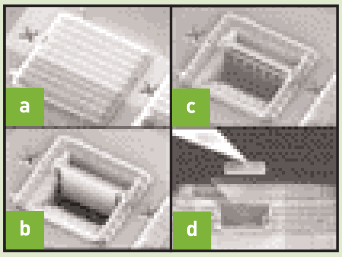
(7) The thinning down of objects can generate defects in the prepared surface.

(8) The FIB can also be used to form images. The resolution of this ion microscope is slightly less than 10 nm.

The FIB, a nanometre-scale scalpel

2

These images show the extraction of a strip containing an integrated circuit transistor. All this sample preparation is carried out in a FEI dual-beam FIB. The transistor will later be examined under a transmission electron microscope (TEM).
a) The transistor is marked by two crosses and protected by a metal deposit.
b) The ion beam removes material around the transistor to leave a strip 20 microns in length which is held only by two top contacts.
c) The strip is thinned down to about 100 nm: the structure of the transistors appears.
d) A fine metal dot moved by a nanometric manipulator is welded to the upper part of the strip. By gently pulling the dot, the two top contacts are snapped, and the strip is extracted from the integrated circuit before being welded onto a TEM grid. A similar FIB has been in operation since January 2005 at CEA/Grenoble.



CEA

Important developments are still possible

This overview shows that researchers can now obtain images of a nano-object with a resolution of less than a nanometre. Ever since they were first invented, these microscopy techniques have been constantly improved, and important developments are still possible. Clearly, none of them taken singly will be sufficient to solve all the problems that researchers and development engineers will meet, and it is important to keep on exploring all the possibilities offered by the different instruments. There are other types of microscopy (atom probe, acoustic, X-ray, Raman, etc. - see Box F), but these techniques do not yet offer the resolution necessary to observe individual nanostructures. A combination of all these microscopy techniques may prove necessary to solve certain specific problems. In addition, the imaging or study of the properties of an individual object is certainly not sufficient if large numbers of objects have to be fabricated and made to operate in parallel. It is therefore also important to develop techniques that can accurately measure average properties of a set of objects. The article *Observing the growth of nanostructures* illustrates the utility of collective characterization techniques.

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CEA Grenoble Centre

Conventional electron microscopy: scanning and transmission

Developed more than fifty years ago, conventional electron microscopy has seen considerable technical progress and has made a fundamental contribution to the nanosciences. It is now many years since transmission electron microscopy reached atomic resolution, *i.e.*, about two tenths of a nanometre. Scanning microscopy is an extremely flexible tool, but its resolution is no finer than about a nanometre. Scanning transmission microscopy is a choice method for visualizing interfaces, chemical composition and structures in three dimensions

Transmission microscopy

A transmission electron microscope (TEM) works in much the same way as a traditional optical microscope. The first optical microscope was made in Holland in about 1605, and the first TEM in Germany by Ernst Ruska in 1931. A probe beam is directed onto the sample, travels through it, and is then detected. A system of lenses is used to focus the beam onto the sample (condenser system). Another set of lenses (main lens + projectors) modifies the exit beam to form a magnified image of the object. But there the analogy ends. In an optical microscope, the probe beam is a beam of **photons**, the lenses are made polished glass, and the **resolution** is usually limited to a few tenths of a micron. In an electron microscope the probe beam is a stream of **electrons**, the focusing lenses are coils producing a magnetic field that deviates the electrons, and the resolution can reach a tenth of a **nanometre**. To obtain this resolution, the electrons are accelerated by an electric potential of a few hundred kilovolts, and travel through the sample before detection. In a conventional transmission microscope, the image is formed globally in a single exposure, because the electron beam is very wide and irradiates the whole of the object being visualized.

Scanning microscopy

In a scanning microscope, a raster image is built by scanning the object with a narrow electron probe. At every position of the probe beam a signal is recorded by one or more detectors, and software or an acquisition board maps the signals that are detected. The concept of the scanning microscope appeared very early on, as soon as the first transmission microscopes came into use in the 1930s. However, it was not until the mid-1960s that electronic systems were able to direct the electron beam and build up an image point by point. Historically, this concept gave birth to two different instruments: the classical scanning electron microscope (SEM), and the scanning transmission electron microscope (STEM). We can note that a similar scanning system is used in the local probe microscope, and in particular in the scanning tunnelling microscope (STM). In an SEM, the detectors (secondary electron detectors, back-scattered electron detectors, re-emitted X-ray detectors) are positioned *in front of* the object, and we essentially examine the surface of the objects. In an STEM, the electrons travel through the sample and the detector or detectors (annular detectors, central detector or electron spectrometer) are positioned *behind* the sample.

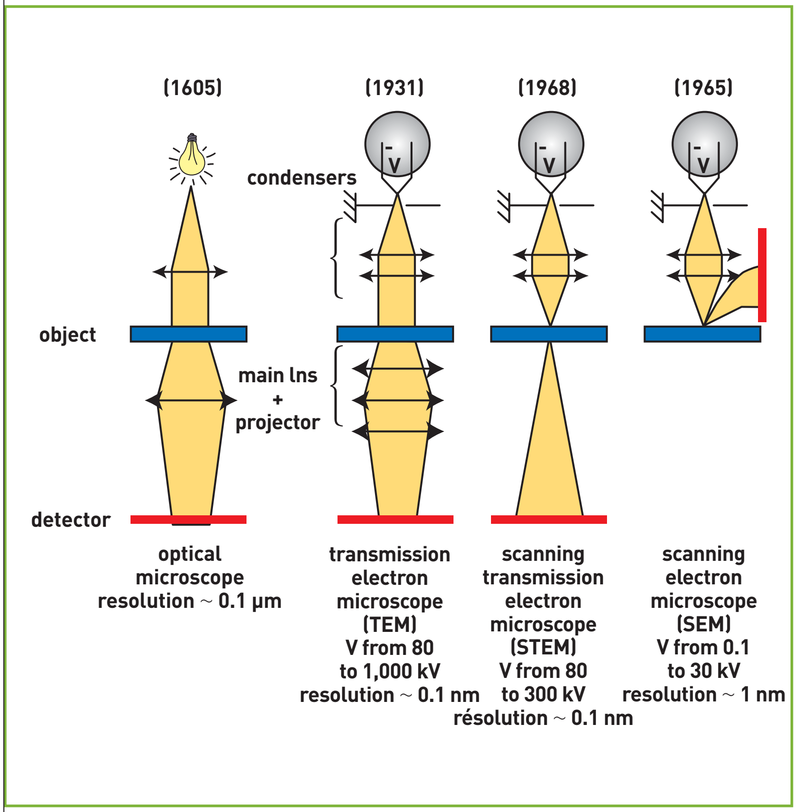


Figure 1.
The different operating modes of electron microscopes.
The position of the main detectors that serve to form the image is shown in red. STEMs and TEMs can also have detectors fitted on the beam source side of the sample.

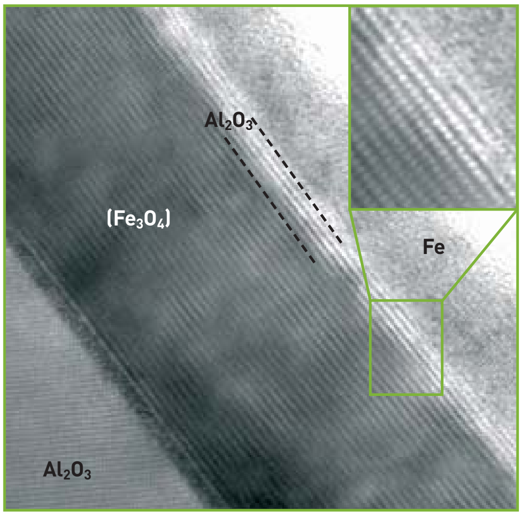
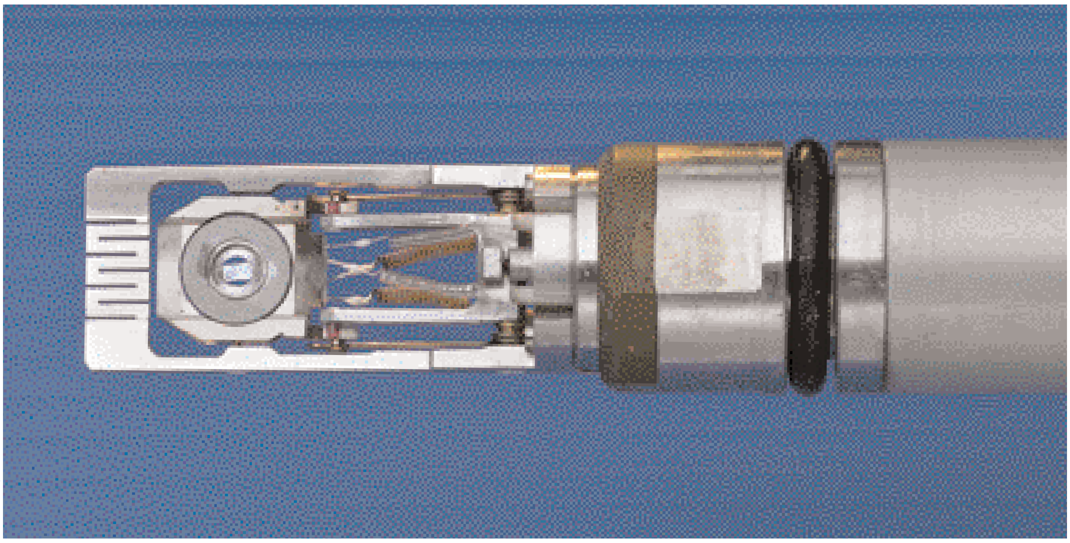


Figure 2.
Image obtained by transmission electron microscopy of a multilayer sample made up of a sapphire substrate (single-crystal alumina Al_2O_3), a 15 nm layer of iron oxide (Fe_3O_4), a thin insulating barrier of crystallized alumina (1.5 nm) and a layer of iron (3 nm).
The crystalline structure appears as fine pale lines with modulated intensity.
Each spot making up these lines corresponds to the projection of an atomic row perpendicular to the image plane.
This stacking is done to study the transport of spin-polarized electrons through the thin alumina layer.
(A. Bataille, J. B. Moussy, S. Gota, F. Paumier, M.J. Guittet, M. Gautier-Soyer and P. Bayle-Guillemaud).

Transmission microscopes (TEM and STEM) are thus used to study the three-dimensional structure of objects. To be electron-transparent the objects have to be relatively thin (10 nm to 300 nm depending on the microscopy technique used). Whereas conventional objects have to be thinned down, **nanostructures** can be examined directly if they are laid on a thin substrate, *e.g.*, a porous carbon membrane, or if they can be positioned so that their support lies outside the beam.

The electric potential V at which the emitting tip is held depends on the type of microscope. The electrons must have sufficient energy to travel through the sample: TEMs and STEMs therefore use higher acceleration voltages V than SEMs. STEMs that focus all the energy of the electron beam on a single point generally use an acceleration voltage lower than that used in classical TEMs. But the boundaries between these different types of microscope are becoming more and more blurred. A TEM can be very easily converted into a STEM by adding a scanning module, and the resolution of a TEM/STEM is currently almost the same as that of a dedicated STEM. A SEM can be fitted with a STEM module without reaching the resolution of a dedicated STEM.

Because the electrons interact strongly with matter, the microscope column, where the electrons are travelling, is generally under a hard vacuum. However, this condition can be relaxed near the object by using differential apertures. There are scanning and transmission microscopes - called environmental microscopes - in which the object is immersed in a low-pressure gaseous atmosphere, and where the growth of nano-objects can be observed in real time.



Artechnique/CEA

Close-up view of a sample, a silicon slab 3 mm long, placed on the heated sample holder (800 °C) of a transmission electron microscope (TEM) (JEOL 300 kV).

Expected evolution

The current trends include computer-controlled operation and alignment of the microscopes, improved lens optics using aberration correctors and monochromators, and lower acceleration voltages to reduce radiation damage caused by the electron beam.
More and more detectors (spectrometer, annular detector, CCD cameras, etc.) and accessories (scanning modules, biprism for holography, heated or cooled sample holder, or one equipped with a local probe, environmental cell, etc.), are being fitted to microscopes, gradually turning them into veritable nano-laboratories.

> **Jean-Luc Rouvière**
Materials Science Division
CEA Grenoble Centre

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.

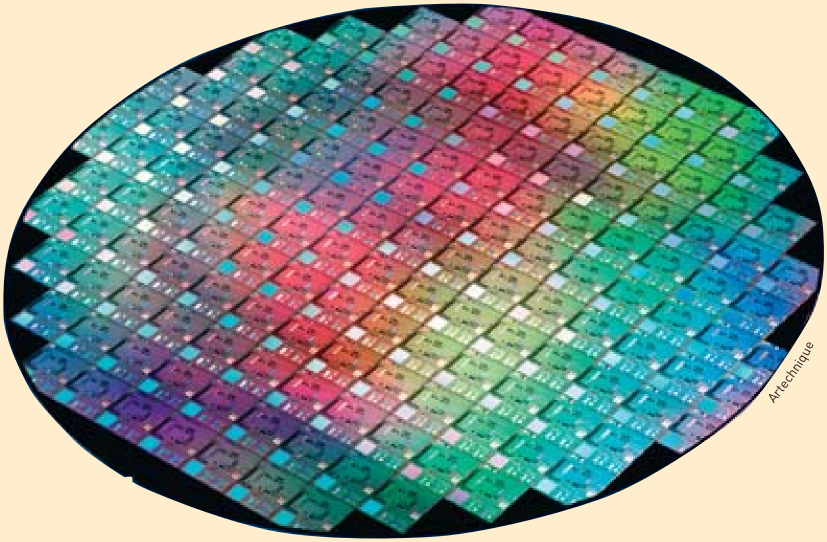
Another advantage of juxtaposing the two is that it provides a good illustration of the two main ways of developing nanoscale systems or objects: ***top-down*** and ***bottom-up***. In fact, there are two ways into the nanoworld: molecular manufacturing, involving the control of single atoms and the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

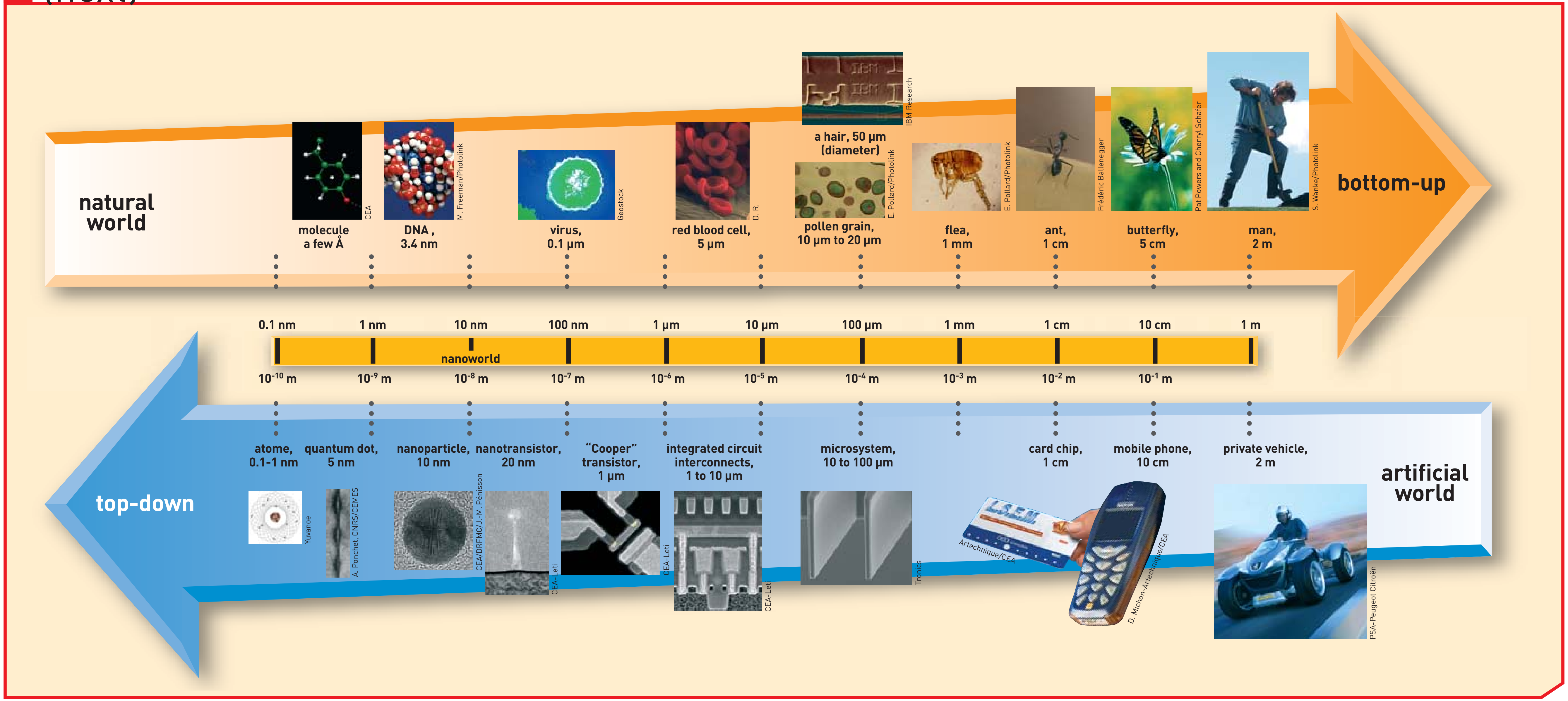
The **nanosciences** can be defined as the body of research into the physical, chemical or biological properties of nano-objects, how to manufacture them, and how they self-assemble by auto-organisazation.

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.



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

* 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.



natural world

bottom-up

molecule
a few Å
CEA

DNA ,
3.4 nm
M. Freeman/Photolink

virus,
0.1 µm
Geostock

red blood cell,
5 µm
D. R.

a hair, 50 µm
(diameter)
IBM Research

pollen grain,
10 µm to 20 µm
E. Pollard/Photolink

flea,
1 mm
E. Pollard/Photolink

ant,
1 cm
Frédéric Ballenegger

butterfly,
5 cm
Pat Powers and Cherryl Schafer

man,
2 m
S. Wanke/Photolink

top-down

atome,
0.1-1 nm
Yuvanoe

quantum dot,
5 nm
A. Ponchet, CNRS/CEMES

nanoparticle,
10 nm
CEA/DRFMC/J.-M. Pénisson

nanotransistor,
20 nm
CEA-Leti

"Cooper"
transistor,
1 µm
CEA-Leti

integrated circuit
interconnects,
1 to 10 µm
CEA-Leti

microsystem,
10 to 100 µm
Tronics

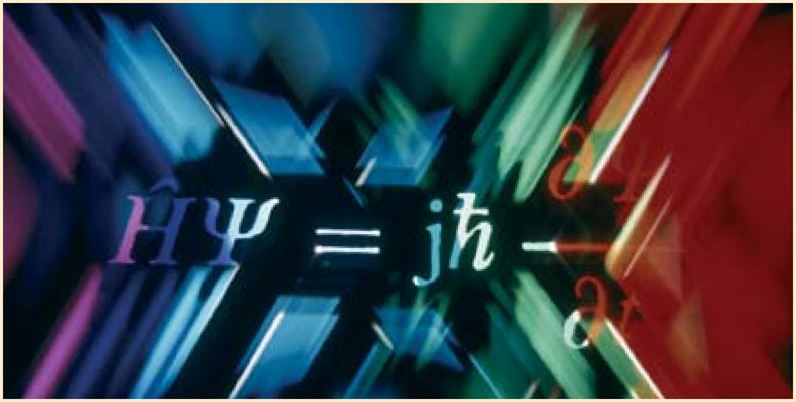
card chip,
1 cm
Artechnique/CEA

mobile phone,
10 cm
D. Michon-Artechnique/CEA

private vehicle,
2 m
PSA-Peugeot Citroën

artificial world

B A guide to quantum physics



D. Sarraute/CEA

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

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 constant (symbolized as h) which has a value of 6.626 x 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.

B (next)

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 entanglement*, 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.

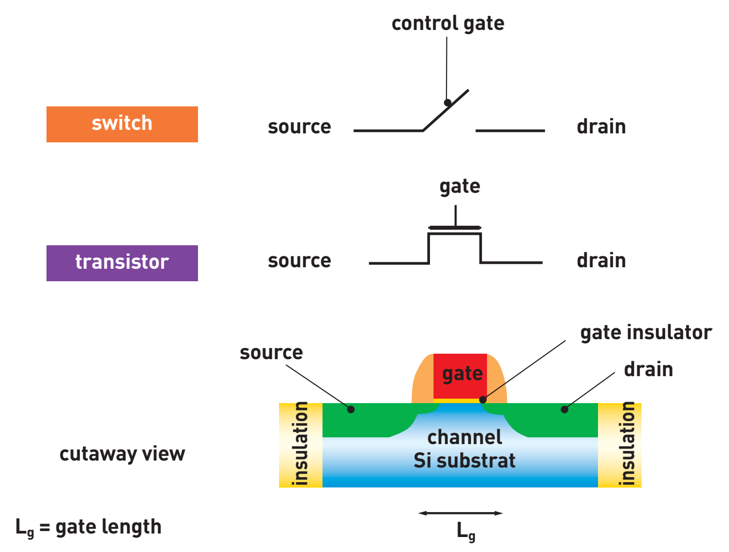


Figure.
A MOS transistor is a switching device for controlling the passage of an electric current from the source (S) to the drain (D) via a gate (G) that is electrically insulated from the conducting channel. The silicon substrate is marked B for Bulk.

The transistor, a name derived from *trans*fer and re*sistor*, 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

D (next)

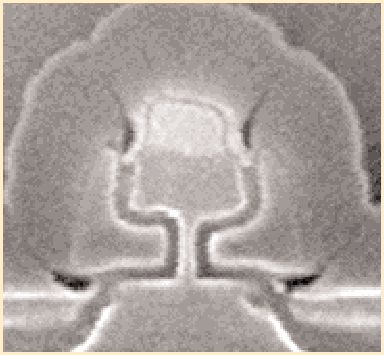
separated by a thin layer of inversely-doped semiconductor. By assembling two semiconductors of opposite types (a p-n junction), the current can be made to pass through in only one direction. Bipolar transistors, whether n-p-n type or p-n-p type, are all basically current amplifier controlled by a gate 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!

Lucent Technologies Inc./Bell Labs

The very first transistor.



STMicroelectronics

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

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(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

Artechnique

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

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.

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".

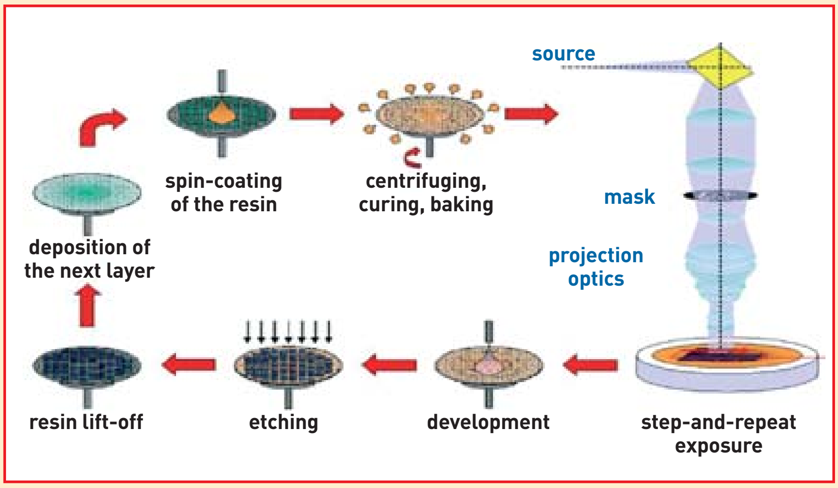

Figure. The various phases in the lithography process are designed to carve features out of the layers of conducting or insulating materials making up an integrated circuit. The sequences of the operation are laying of a photoresist, then projecting the pattern on a mask using a reduction optics system,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