Chapter 2
Making Nano-Objects

Making nano-objects is a big challenge and the main goal is to manufacture them at low cost, with a good yield, using the simplest and most efficient technology possible. There are two ways to tackle the problem:

1. The *top-down* approach consists in starting from macroscopic materials such as a wafer of silicon. They are "carved" and modified to produce nanoscale objects. Several techniques are used to build pieces of nanometer-size in one or more dimensions: evaporation techniques to manufacture thin films of thickness smaller than 100 nm is one example of this. The most used top-down approach is to extrapolate microtechnology techniques to smaller dimensions. This is what is presently done to manufacture microprocessors with patterns below 100 nm. It should be noted that films with a thickness smaller than 100 nm have been made for a long time by evaporation, molecular beam epitaxy, or similar techniques.
2. The *bottom-up* approach is where atomic and molecular units are assembled to form molecular structures ranging from atomic dimensions to structures in the nanometer size or above. Making macromolecules (polymers) from one or several monomers is an example of the bottom-up approach. Nature uses this route to build up complex structures, but *nature is cleverer* than humans. Erosion is the top-down approach of nature to carve macroscopic objects like rocks, for example. Chemistry and biology are the sciences involved in the bottom-up approach. Furthermore, time and control are essential aspects to be considered in any bottom-up approach used for manufacturing nano-objects.

Figure 2.1 schematically shows the basic difference between the top-down approach and the bottom-up approach.

The present challenge is to merge the *top-down* and *bottom-up approaches* to develop a toolbox allowing the creation of low-cost complex nanoscale structures. Lithography techniques (top-down) can produce nano-objects and their functionalization can be achieved using chemistry or biological sciences (bottom-up).

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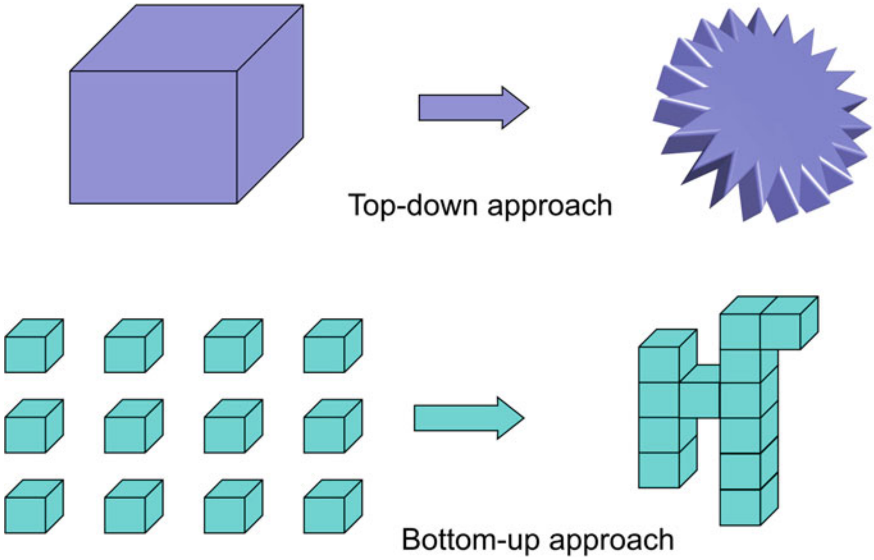

Fig. 2.1 Difference between a *top-down* and a *bottom-up* approach

2.1 The Top-Down Approach

While small systems (cm or mm-size) can be manufactured by precision mechanics with lathes, saws, and sanders, microchips or microsystems are made using planar technology. A disk of silicon or glass, called a *wafer*, is used as a substrate to build up complex microchips or microsystems. Lithography techniques are used to modify the surface of the substrate either by etching or building up new layers.

In microtechnology, lithography is a technique allowing transfer of a pattern to a photosensitive material (called *photoresist* or *resist*) by a selective exposure to light (ultraviolet or X-rays) or particles (electrons or ions). In microelectronics, silicon wafers are mostly used. An image of the pattern is projected, using a reduction lens onto a silicon wafer coated with a thin layer of photoresist, usually deposed by spin coating. Depending upon the nature of the photoresist, the exposed part can become soluble in the developer liquid used after exposure, or it can become insoluble, depending on the method used. An image of the mask pattern is obtained on the wafer after etching by the developer.

The principle of lithography (there are several steps, called *masks levels* in the manufacturing of integrated circuits) is shown in Fig. 2.2. The different stages are schematically displayed. A masking level starts by depositing a thin layer of photoresist (resin) by spin coating (the wafer is made to rotate at high speed while the dissolved photoresist is poured onto the wafer), making in this way a homogeneous thin layer of photoresist (steps 1–2). The pattern of the mask is then projected using a reduction optics system (step-and-repeat exposure) (3). After exposure, the

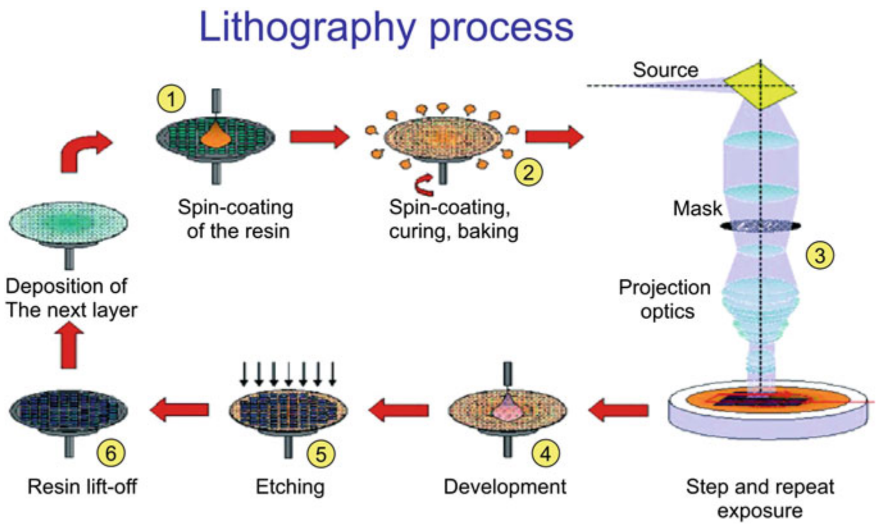

Fig. 2.2 Different stages in a lithography process during one masking level. Clef CEA n° 52. Image courtesy of CEA/LETI (France)

photoresist is developed (4) and the parts of the resin which are removed after development are selectively etched (5). The remaining part of the resin is then lifted-off (6) before deposition of the following layer.

2.1.1 Photoresists

Most lithography techniques used in micro and nanoelectronics are based on planar technology. A photoresist layer is used to image the pattern of a mask in a positive or negative manner (like in photography for negatives or slides) onto the resist. After developing, the positive or negative image of the mask pattern is reproduced onto the resist, which in turn, can be used as a mask for the wafer. The principle of positive or negative resist processes is shown in Fig. 2.3.

Most of the photoresists used in micro and nanoelectronics are based on organic polymers deposited in a very thin layer by spin coating onto the wafer. The resist is chosen in such a way that its solubility in a particular solvent changes after it has been exposed to radiation. (light or electrons, for example). If the change is a higher solubility we have a positive resist. If, on the contrary, the change is a lower solubility we have a negative resist. A good resist should produce steep edges after development in order to make very small, well-defined structures. A small change in the radiation dose must induce a big change in solubility. Many other properties and constraints for the resist are required and they are a key element in micro- and nanosystems manufacturing. The demand is even more stringent for nanotechnologies compared to microtechnologies because a higher accuracy is required.

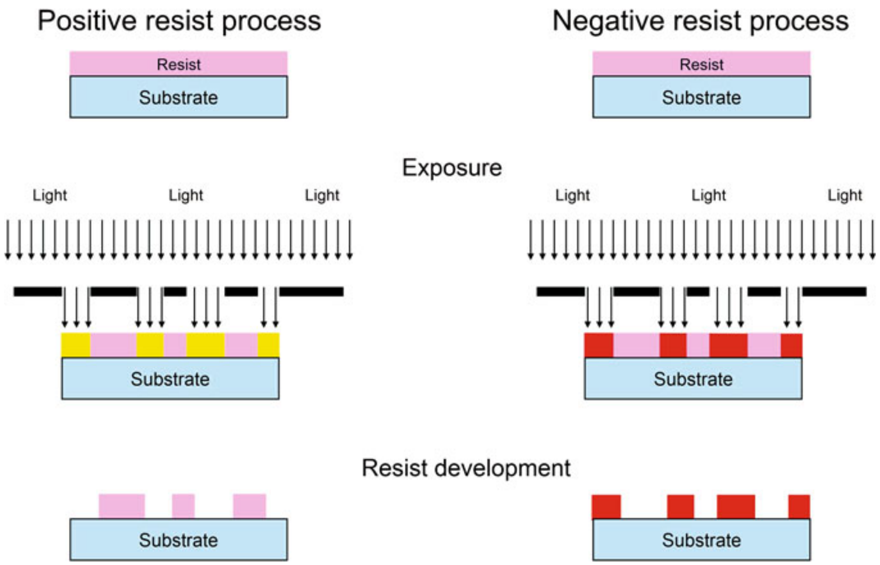

Fig. 2.3 Principle of lithography using a positive and a negative photoresist

Lithography for chips (such as memory chips or microprocessors) demands extremely high-performance processes:

- The spatial resolution is more and more precise; printing lines of 45 or 30 nm are nowadays currently used in the manufacturing of chips. The 22 nm lithography technology is now commercially used, for example, to manufacture the "Sandy Bridge" Intel microprocessors.
- The pattern that has to be transferred onto the wafer is extremely complex. For example, with a 30 nm printing line resolution, assuming that we create square pixels of 100 nm on a surface of 25 mm^2 (square of 5 mm on each side), there would be 2.5 billion of pixels. This is much higher than HD video pixel density (1080p = 1920 $\times$ 1080 pixels) which has "only" 2.07 million pixels. Even the ultra-high video definition format which is under preparation (4320p = 7680 $\times$ 4320 pixels) has only 33.18 million pixels on a much larger area. Any error in one pixel makes the chip nonfunctional and must be rejected in the manufacturing process.
- Integrated circuits are manufactured with successive layers obtained by transferring a pattern to the wafer. The number of mask layers is large, typically between 15 and 25. Each layer must be aligned with respect to the previously patterned layers with an accuracy which is a fraction of the linewidth resolution. This is similar, in principle but not in accuracy, to the way a color picture is produced in a sublimation printer where the three colors (cyan, yellow, and magenta) must be precisely overcoated.

Table 2.1 The number of transistors, the accuracy of the lithographic process, the area and transistor density are shown for different microprocessors which have been put on the market over the last two decades

Year	Microprocessor	Number of transistors (millions)	Process (nm)	Area (mm^2)	Density (millions of transistors/cm^2)
1993	AMD 486	1.2	350	35	3.4
1995	AMD K6 III	9	250	78	11.5
1998	AMD Athlon	37	180	120	30.8
2003	AMD Opteron	100	130	193	51.8
2005	AMD Dual Core Opteron	233	90	199	117.1
2009	AMD Six-core Opteron 2400	904	45	377	239.8

As an illustration of the progress in making micro- and nanoscale objects, Table 2.1 shows the evolution of the density of transistors among different generations of microprocessors and the accuracy of the printing line. In parallel, the cost of a transistor has dramatically reduced.

Light sources used in lithography processes correspond to given wavelengths. Above 100 nm processes, the g-line (436 nm) and the i-line (365 nm) of mercury lamps have been used. To have smaller wavelength, excimer laser are utilized (KrF at 248 nm and ArF at 193 nm). To go down to smaller dimensions, extreme ultraviolet lithography (EUVL) uses light of very short wavelength (13.5 nm) allowing manufacturing features for the 32 nm process. Because conventional optics no longer works, mirrors and reflective masks are required to image patterns on the silicon wafers.

In order to increase the resolution, new techniques are developed such as immersion lithography where the air gap between the final lens of the optical device is replaced by a liquid with a refractive index greater than one (Fig. 2.4). The gain in resolution is equal to the refractive index.

2.1.2 e-Beam Lithography

Electron beam (*e*-beam) lithography uses a beam of electrons to pattern a resist deposited on a substrate. Depending upon the nature of the resist, the irradiated zones can be etched or not etched after chemical treatment. The main quality of *e*-beam lithography is that a resolution of a few nanometers can be routinely obtained. No mask is required during the irradiation, which is performed in raster mode: the electron beam scans point-by-point the substrate area to form the pattern.

One drawback of *e*-beam lithography is that it takes a long time to expose the whole substrate because this is done point-by-point. Light (UV or X-rays) illuminates

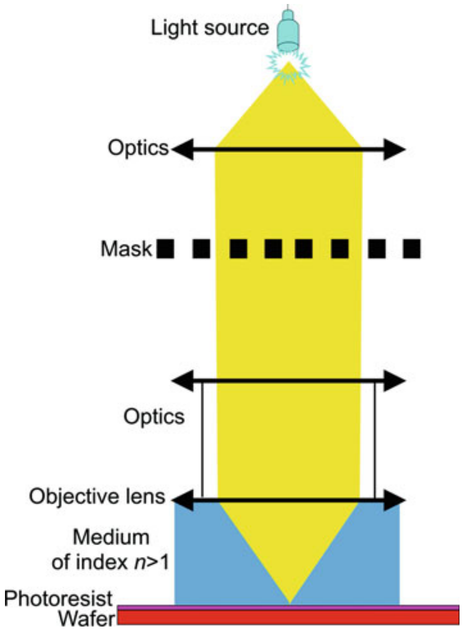

Fig. 2.4 Principle of immersion lithography

the whole substrate at once allowing to proceed much more swiftly. Because of this extremely slow speed, *e*-beam lithography is mostly used in research and development laboratories or for low-volume production of semiconductors.

2.1.3 Block Copolymer Nanolithography

A homopolymer is made by polymerization of a single type of monomer. A copolymer is a polymer obtained by polymerization of two or more different monomers. A block copolymer consists of two or more subunits of homopolymer (blocks) linked by covalent bonds. Block copolymers are used to manufacture nanoscale periodic structures. During solidification, phase separation takes place and distinct periodic nanostructures are formed. Depending upon the relative volume structure, spherical, cylindrical, lamellar, or more complex periodic structures can be made. In the case of lamellar structures, for example, lamellae can be oriented parallel or perpendicular to the surface with a period ranging between 10 and 100 nm. More generally, directed block copolymer self-assembly allows making periodic nanostructures with long- range order such as high density nodes or pores arrays. This technology is relevant for magnetic data storage, semiconductor devices, nanophotonics, etc. Nanoparticle-block copolymers self-assembly allows fabrication of ordered mesostructures with characteristic lengths in the range of 2–50 nm.

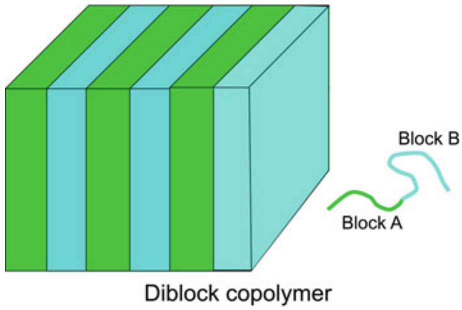

Fig. 2.5 Schematic illustration of a diblock polymer

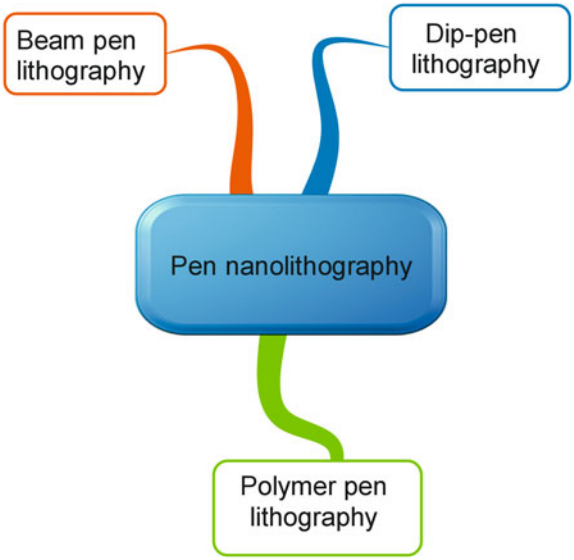

Fig. 2.6 Different pen nanolithography techniques

An illustration of the type of structure (diblock polymer) which can be obtained is shown in Fig. 2.5.

2.1.4 Pen Nanolithography

There are three main types of pen nanolithography (Fig. 2.6).

Dip-pen nanolithography uses the tip of an atomic force microscope (AFM) coated with a chemical or biological compound to pattern the surface of a substrate with accuracy below 100 nm. The tip of the cantilever of the AFM acts as a "pen," the chemical or biological compound as an "ink," and the surface of the substrate as a "paper." One-dimensional and two-dimensional arrays of cantilevers increase the speed of patterning. For example, two-dimensional arrays of 55,000 tips can make 88 million dots in 5 min. Today, dip-pen arrays with more than a million tips have been made. Different inks can be deposited in the patterning process.

Dip-pen nanolithography allows manipulating individually single biological structures like viruses or cells. The aim in the near future is to develop high-resolution dip-pen nanolithography of high throughput with the ability of multiplexed deposition on a substrate.

Polymer pen lithography combines the principles of dip-pen nanolithography and contact printing to pattern large areas (larger than several square centimeters). An array of inked elastomeric tips is used to print features with dimensions between about 90 nm up to 10 μm. The interesting thing is that it is not necessary to reink again the tip after each printing.

Beam-pen lithography uses a polymer pen array coated with a thin layer of gold. UV light entering the polymer tip in the backside of the pen is channeled through a nanometer-size aperture. This method allows pushing the lateral resolution of features that are produced to below the diffraction limit. For example, using 400 nm wavelength, it has been possible to make 100 nm features. The advantage of this method is a high throughput.

2.2 On-Wire Lithography

Several powerful methods exist to make zero-dimensional systems (e.g., nanoparticles and nanodots). Many studies are today devoted to one-dimensional systems (e.g., nanowires and nanorods). The diameter, length, and composition of these one-dimensional systems can be controlled on demand. On-wire lithography is a novel method allowing synthesis of segmented structures and introducing changes by post-chemical treatment; for example gaps in one-dimensional systems. Segmented structures with disks or gaps can be synthesized with disks having different properties than the initial material of the nanowire and gaps can be filled, by subsequent chemical treatment, with organic or biological molecules, so giving the system new functionalities.

Usually, nanowires and nanorods are synthesized by several methods such as vapor–liquid–solid growth and specific nanolithography techniques. However, there is a demand to make more complex objects, based on one-dimensional systems, providing new functions. This requires being able to make segments of different chemical compositions, to coat them with specific metals or molecules to dope them chemically, and so on.

The principle of on-wire lithography is the following (see Fig. 2.7). Multilayered nanowires are made in a porous alumina template (which is a thick disk with cylindrical holes) by electrodeposition. Different plating solutions are used so that segments of different metals can be made. The length of the segments is controlled by the amount of electrical charge delivered during electrodeposition. After dissolving the template, nanowires are released and put onto the substrate. A thin layer of silica or metal can be deposited by plasma-enhanced chemical vapor deposition. Afterward, the substrate is immersed in ethanol and sonicated, which releases the nanowires.

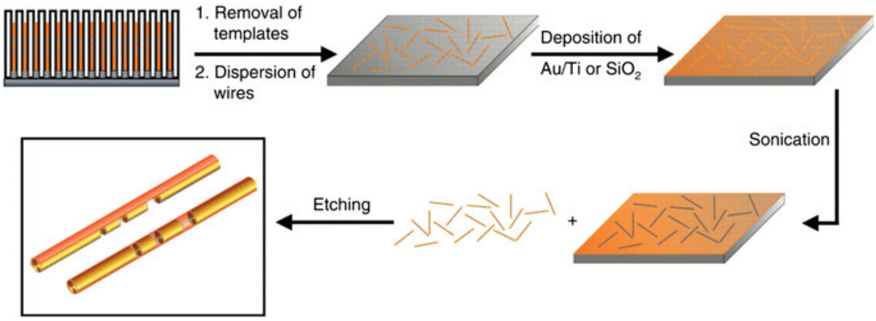

Fig. 2.7 Principle of on-wire lithography. Science, 2005. Courtesy of C.A Mirkin

Some of the segments can be removed by wet-etching, for example, for creating gaps in the nanowire.

Several applications of the objects produced in this way are photonic devices, plasmon guides, electrical devices, and chemical and biological sensors. Based on the synthesis of nanowires by electrochemical deposition within a template and wet chemical etching, the advantage of the on-wire lithography technique is that it can be easily controlled and implemented. It has a high throughput and does not require expensive equipment. Nanowires with gaps as small as 2.5 nm can be obtained for example.

2.2.1 Nanoimprint Lithography

Nanoimprint lithography is a low-cost process with high throughput and moderately high resolution allowing production of nanometer scale patterns. It is able to make 25 nm feature size over large areas. It can also be used on nonflat surfaces. Several applications of nanoimprinting are possible such as nanowires, silicon nanodots, or nanophotodetectors. The principle of thermal nanoimprinting is shown in Fig. 2.8. In the first step, a mold (stamp (1)) with nanostructures is pressed into a thin film of a resist cast on a substrate (2). This step is made easier by heating the resist above the so-called glass transition temperature, i.e., the temperature above which the resist becomes thermoplastic (it behaves like a viscous liquid, the viscosity decreasing as the temperature increases). An image of the mold is impressed onto the resist (3). In the second step, this image is made more precise using an anisotropic etching process to remove the residual resist present in the compressed area. Silicon oxide or silicon can be used as mold materials and the pattern is made by *e*-beam lithography, for instance. The resist can be PMMA (poly-methyl-methacrylate) which has a glass transition temperature at about 105 °C. This technique is based on the thermoplastic behavior of the resist and is sometimes referred as thermoplastic nanoimprint. There is another close technique known as photo nanoimprint lithography where a curable liquid resist is used. This is a polymer material with chemical additives which becomes hard under irradiation (curing), for example using

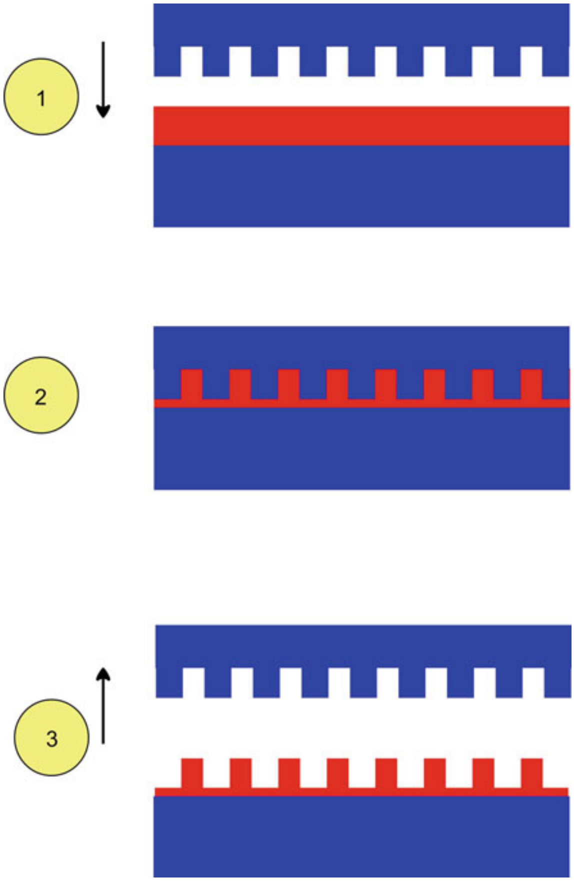

Fig. 2.8 Principle of thermal nanoimprint lithography

UV light. This occurs because there is cross-linking between the polymers chains of the curable liquid under irradiation. In this process, the mold is pressed onto the substrate where a thin layer of curable liquid is deposited. The resist is cured with UV light which necessitates that the mold is made out of a material transparent to the wavelength used.

2.3 Nanochemistry

It is possible to make nanoscale building blocks using synthetic chemistry. This is the essence of nanochemistry. These blocks can have different size, shape, structure, composition, functionality, etc. More complex architectures can be built from these blocks to get new functions and properties. To make nanostructures from single molecules or molecular units, they have to be assembled in more complex structures by means of specific interactions. Supramolecular chemistry is the way to do that.

The research in this area was pushed in particular by Cram et al., who were awarded the chemistry Nobel Prize in 1987 for their contribution to this subject. Supramolecular chemistry is the area of chemistry where chemical systems are made from single molecules, chemical subunits, or components, using weak forces like intermolecular forces, ionic or hydrogen bonds, or metal–ligand interactions. Covalent bonding can also be used, provided it does not affect the structure of the elementary units used. Self-assembly is the driving force to create complex structures from elementary elements. It can be spontaneous or directed self-assembly using templates. When self-assembly of molecules and materials are directed by templates, additives are used that can be involved in co-assembly or they can guide the assembly during a lithographic process.

The process of self-assembly can be reproduced at several scales leading to hierarchical systems with different building rules at different length scales. From the elementary component (molecules or other subunits), the different steps generate more and more complex structures of different sizes. Biological structures are used to build hierarchical structures at different length scales and this is also now being achieved for artificial materials. New properties can appear, unknown at the single component level because collective properties come into play. Organic chemistry is interesting to produce elementary components of a structure because a large variety of molecules with different shapes and functionalities can be synthesized.

2.4 Langmuir–Blodgett Films

Langmuir–Blodgett films are made of one or more monolayers of an organic material deposited onto the surface of water. The principle of fabrication is schematically shown in Fig. 2.9. The monolayer is made by putting the organic molecules onto the water surface in such a way that they are not closely packed. A sliding barrier is used to make a closely packed layer. The process is followed by measuring the surface pressure. The organic molecules which are used have generally a hydrophilic head (a polar group) and a hydrophobic tail. They are often a fatty acid. A substrate, dipped into the water, is moved up and a monolayer deposits onto its surface. The process is monitored by checking the surface pressure and moving the sliding barrier.

One or more monolayers can be deposited in this way onto the substrate. Figure 2.10 shows an example of several monolayers fabricated by the Langmuir–Blodgett technique on a hydrophilic substrate. The construction is done head-to-head and tail-to-tail.

The Langmuir–Blodgett technique is interesting for preparing highly organized thin films. One can have a homogeneous deposition of a thin film over large surfaces, typically several cm^2, with precise control. Multilayers from two to hundreds of monolayers can be fabricated. The choice of the substrate and the nature of the molecules makes the method very flexible. For example in Fig. 2.11, where a hydrophilic substrate is used, we have a tail–head construction. Using a hydrophilic substrate it is possible to produce tail-to-head or tail-to-tail structures (Fig. 2.10).

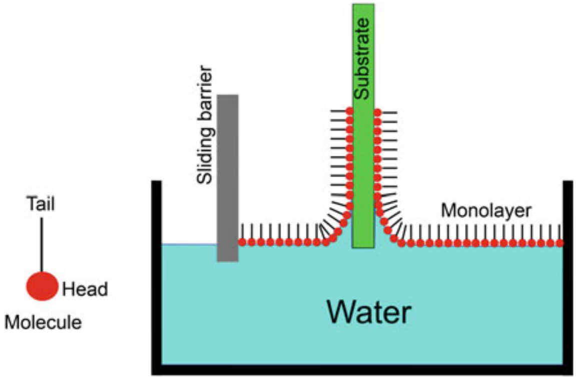

Fig. 2.9 Principle of the preparation of Langmuir–Blodgett films

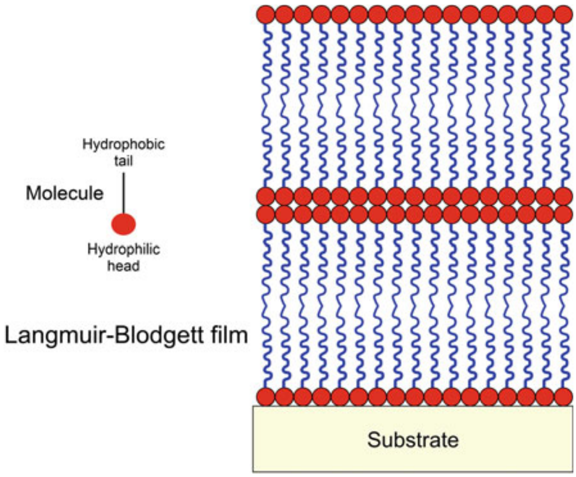

Fig. 2.10 Schematic drawing of multilayers obtained with the Langmuir–Blodgett technique on a specific substrate

With a hydrophobic substrate one can make head-to-tail deposition with the tail located onto the substrate.

2.5 Self-assembled Monolayers

The self-assembled monolayer (SAM) technique encompasses methods in which amphiphilic molecules, i.e., with a hydrophilic head and a hydrophobic tail self-assemble onto the surface of a two-dimensional metal or semiconductor, or on the curved surface of nanoparticles. Self-assembly takes place because there is chemisorption of the hydrophilic head of the molecules onto the substrate surface. After some time, ranging from minutes to hours, a semicrystalline or crystalline structure is formed on the surface of the substrate. This process was first developed with a long chain of alkanethiolates that could assemble on gold surfaces. A schematic representation of a self-assembled monolayer is shown in Fig. 2.12. The head is

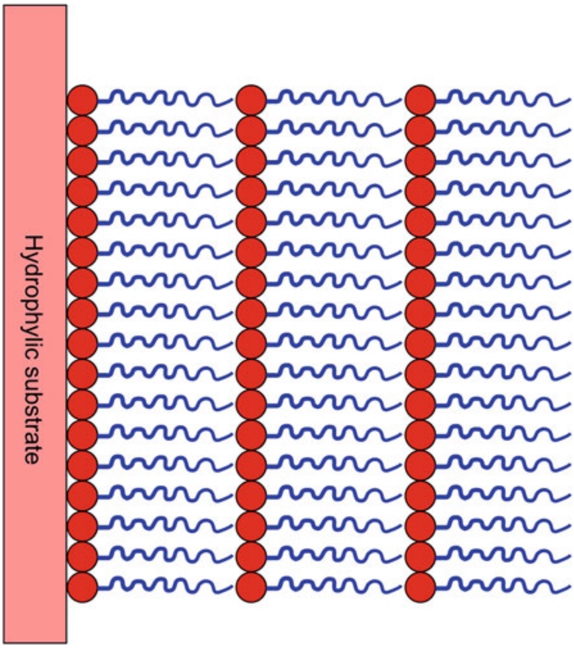

Fig. 2.11 Schematic drawing of a tail-to-head structure of three monolayers made by the Langmuir-Blodgett method on a hydrophilic surface

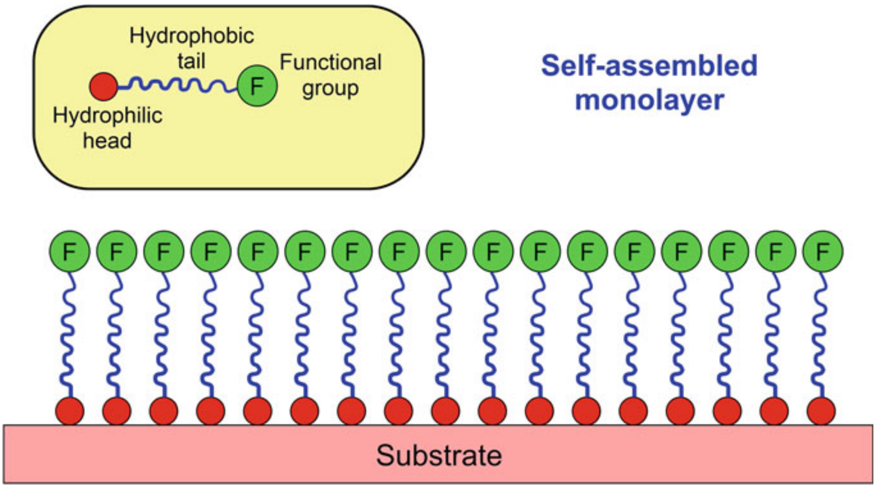

Fig. 2.12 Representation of a self-assembled monolayer

hydrophilic and is connected to an alkyl chain that can eventually be functionalized to tailor the interfacial properties of the SAM.

2.6 Conclusion

There are basically two approaches to manufacture nano-objects:

- The *top-down* approach where nano-objects are built starting from macroscopic objects using different tools and techniques to remove or add material. Lithography techniques are now sophisticated enough to work at the nanoscale and are extensively used to do that. Adding material can be done by various techniques such as evaporation or chemical vapor deposition. Using a scanning tunneling microscope to build nano-objects starting from elementary building blocks can eventually be classified in this category.
- The *bottom-up* approach starts from molecules which are synthesized on demand and self-assembled to form the nano-object. The building blocks, which can be molecules, can be functionalized and their geometry controlled.

Hybrid approaches combining the top-down and bottom-up approach offer more possibilities and flexibility.

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