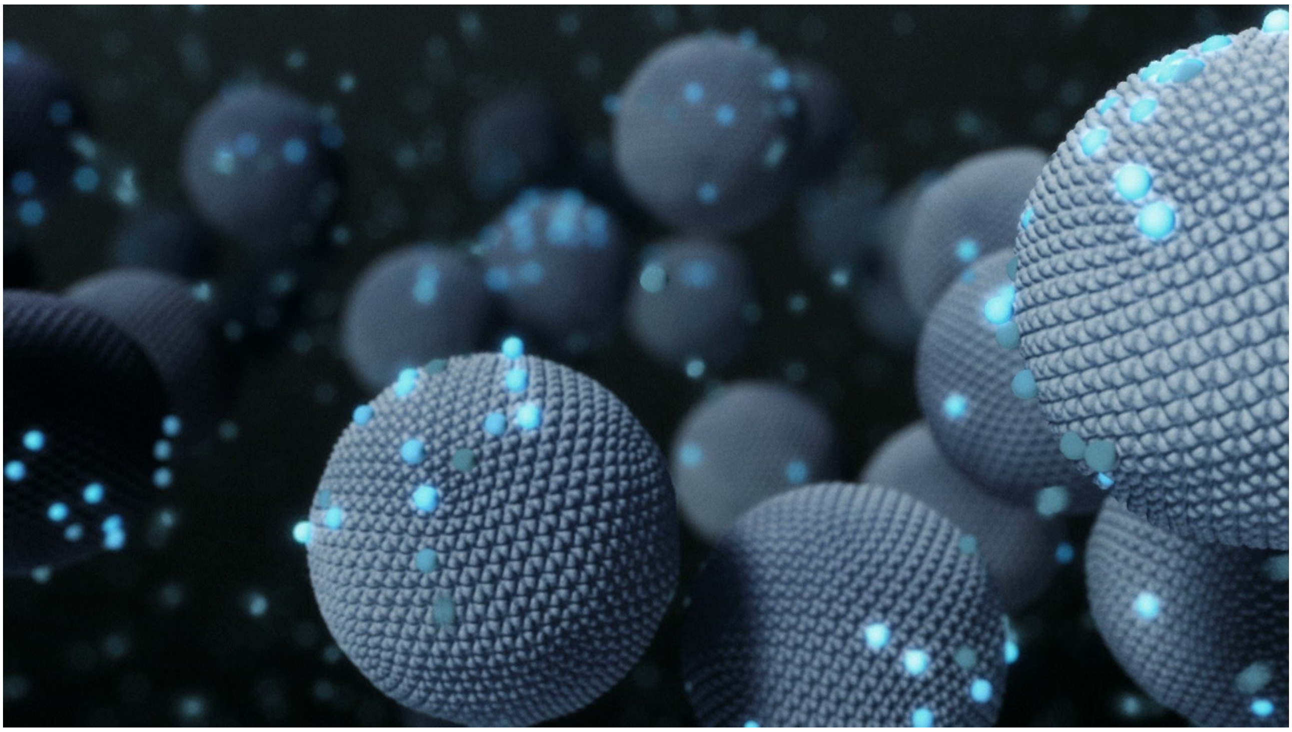
Nanotechnology Fabrication Methods.



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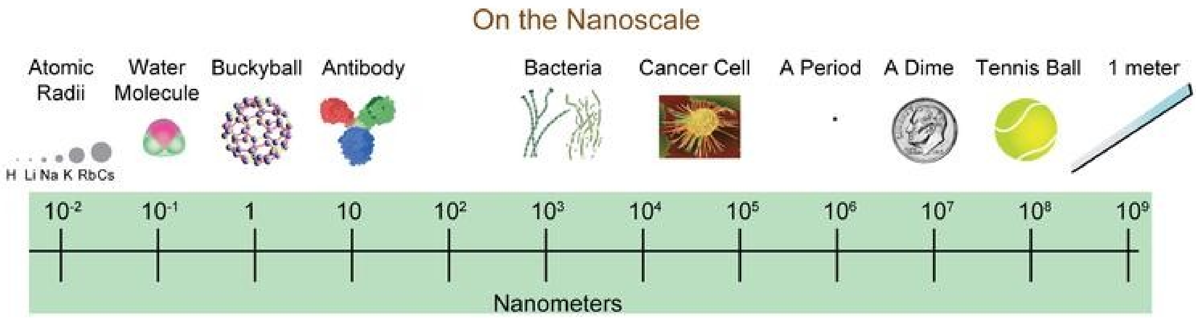
Summary:

1. Introduction to Nanotechnology:

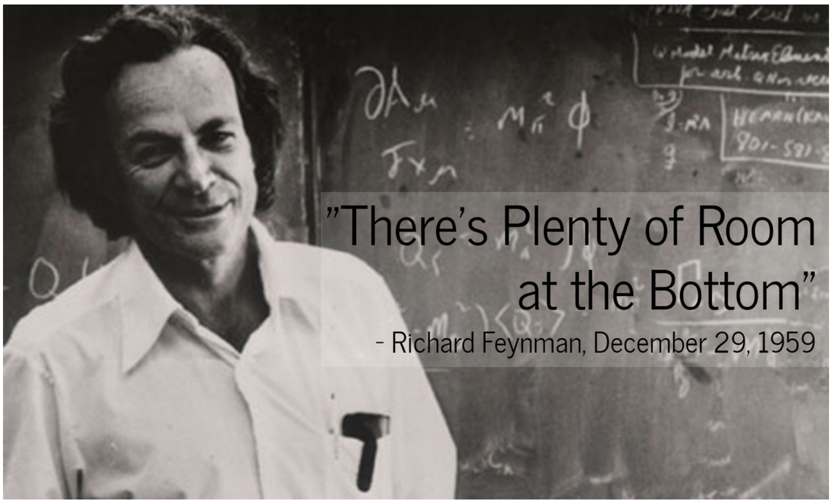
Nanotechnology involves the design, creation, handling and study of all technologies and sciences, that are applied to a nanoscale level. This means extremely little measures, nano measures, at a scale of $1 \cdot 10^{-9}$ meters. Nanotechnology scale goes from 1 nm to 100's of nm, this involves so many different possibilities, from the manipulation of simple atoms, or molecules, to the manipulation of virus, bacteria or cells.



Picture 1 : Nanoscale.

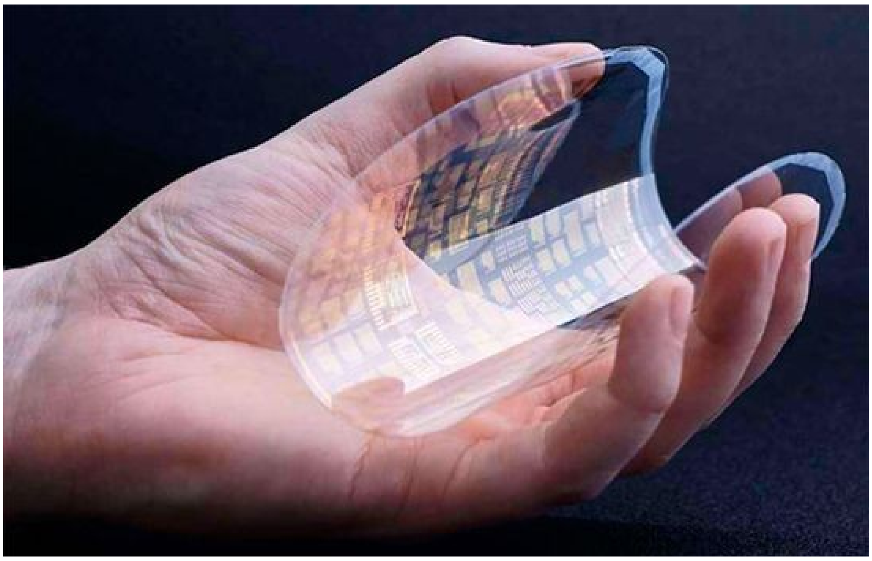
The concept of Nanotechnology was first appointed, in 1959, during a conference of the future of the technology, in the California Institute of Technology (CaItech), by Professor Richard Feynman. The suggestive title of the conference, "*There is plenty of room at the bottom.*", was just the beginning of what we know as nanotechnology nowadays.

Even the concept, and all the ideas of Feynman were there, it was not until a few decades later, in 1981, when thanks to the creation of the scanning tunnelling microscope, by Gerd Binnig and Heinrich Rohrer, the world will be able of see and handle single atoms and molecules as explained by Feynman.



Picture 2 : Richard Feynman.

The nanotechnology materials, or nanomaterials, open a new door to what we know about the behaviour of matter. Several phenomena become pronounced as the size of the system decreases, statistical mechanical effects or quantum effects. Materials reduced to nanoscale can show different properties compared to macroscale, enabling unique applications.

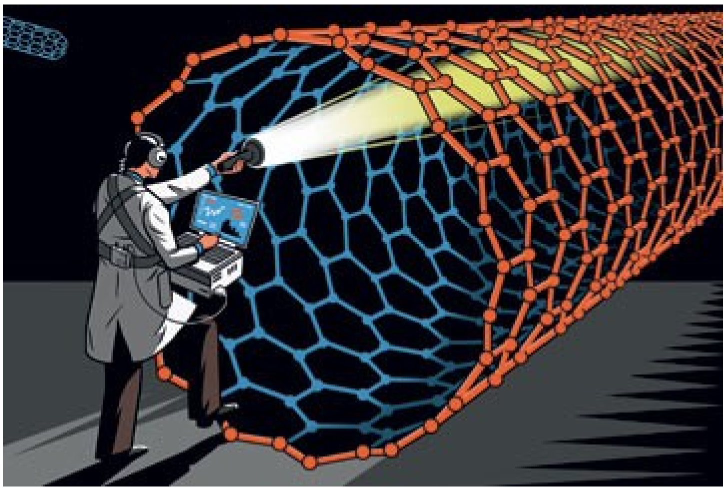


Picture 3 : Nanomaterials.

All this reasons inspired the nano-science community to develop nanotechnology fabrication methods, to manufacture this materials in a more “industrial” way.

2. Nanotechnology Fabrication Methods:

Even nanotechnology is a recent technology, there are many manufacturing methods and tools, used for the fabrication of nanomaterials, including nanostructured surfaces, nanoparticles, etc.



Picture 4 : Nanotechnology, a recent technology.

Nanotechnology fabrication methods can be usually subdivided into two groups: top-down methods and bottom-up methods. On one hand we have the top-down methods, nanomaterials are derived from a bulk substrate and obtained by removing material, until the desired nanomaterial is obtained, this category includes the printing methods. On the other hand, bottom-up methods are just the opposite, the nanomaterial is obtained starting from the atomic or molecular level and gradually assembling it, until the desired structure is formed.

Picture 5 : Moai - Representation of Top-down methods.

Picture 6 : Lego Moai - Representation of Bottom-up methods.

In both methods is important to have a good control of the fabrication conditions, such as presence of dust, control of the electron beam, etc.

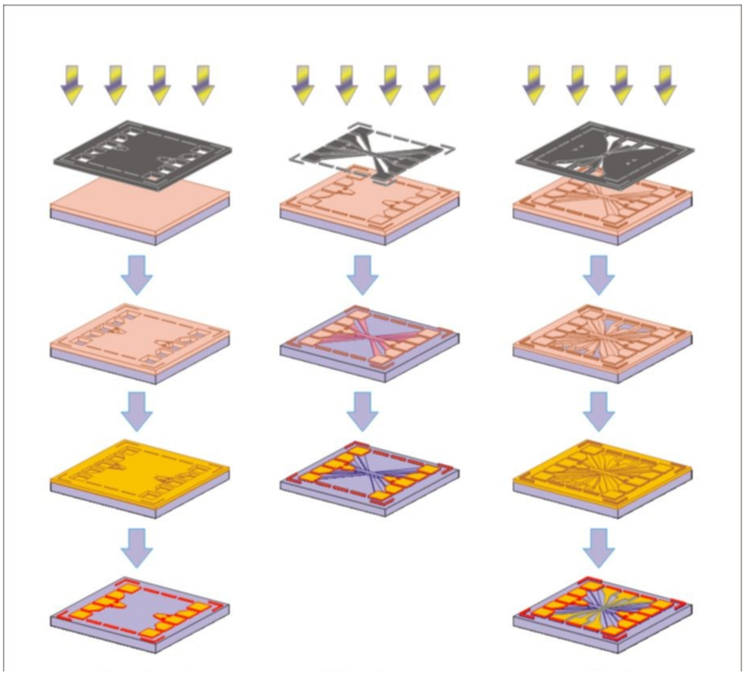
2.1. Top-down Methods:

The main idea of Top-down methods derived from the fabrication methods used in the semiconductor industry to fabricate elements for computer chips.

These methods, called lithography, removes layers of material, from a precursor material, selectively using a light or electron beam, and thanks to the advances of the lithography fabrication methods, has been possible to reduce the size of electronic devices.

- **Conventional Lithography:**

The main idea of lithography is to transfer an image from a mask to a receiving substrate. The lithographic process consists of three steps. Coating a substrate with a sensitive polymer layer, called resist, exposing this resist to light or electron beams and develop the resist image with, commonly, a chemical substance, called developer, which reveals a positive or negative image on the substrate.



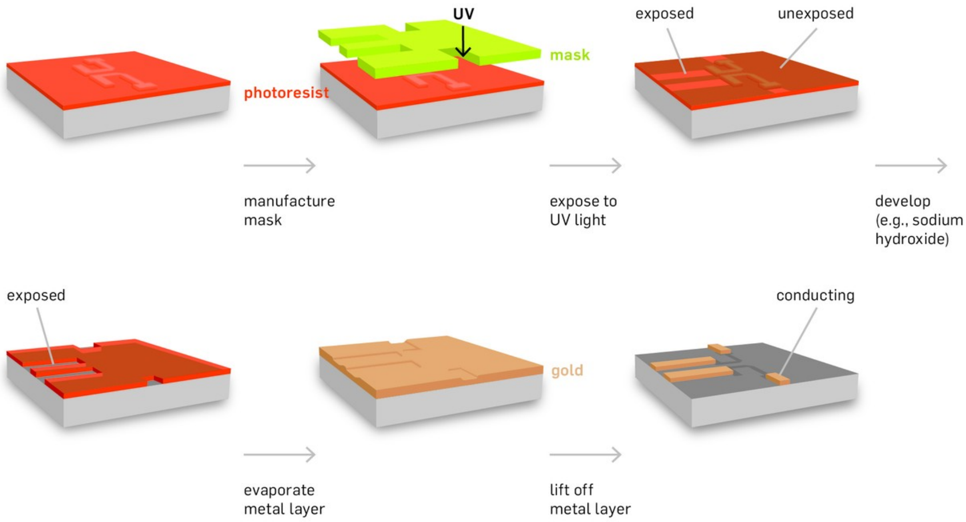
Picture 7 : Lithography Process.

The next step is to transfer the pattern from the resist to the underlying substrate, through a number of transfer techniques, such as chemical etching and dry plasma etching. This techniques can be divided in two groups, methods that use a physical mask, where the resist is irradiated through the mask which is in contact with the resist (mask lithography). The other group of methods use a software mask, a scanning beam irradiates the surface of the resist sequentially through a controlled program, where the mask pattern is defined (scanning lithography).

Speed is the main difference between mask and scanning lithography, whereas mask lithography is a fast technique, scanning lithography is slow. We also have to take in account the resolution, scanning lithography has a better resolution, which entails expensive equipment.

- **Photolithography:**

Photolithography uses light, UV, deep UV, extreme UV or X ray, which exposes a layer of radiation sensitive polymer though a mask. The mask is usually an optically flat glass plate which contains the desired pattern, made of an absorber metal.



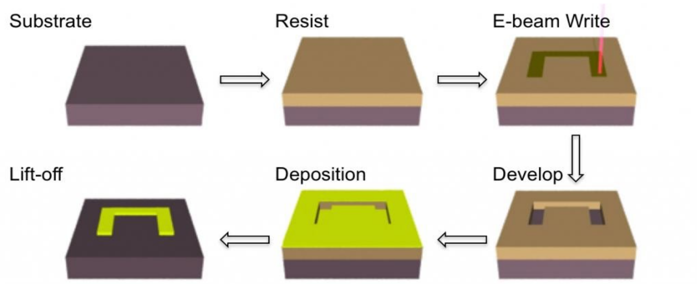
Picture 8 : Photolithography Process.

The image on the mask can be replicated as it is, placing the mask in contact with the resist (contact mode photolithography) or reduced, projecting the image of the mask using an optical system (projection mode photolithography).

The resolution of contact mode is near 0,6 µm, using UV light, for more resolution we need to use projection mode or go to next-generation photolithography, using extreme UV or X ray, but this technologies use very expensive equipment.

- **Scanning lithography:**

Scanning lithography uses energetic particles, such as electrons and ions, to pattern appropriate resist films of nanometre resolution. The most commonly know is using electrons, e-beam lithography.



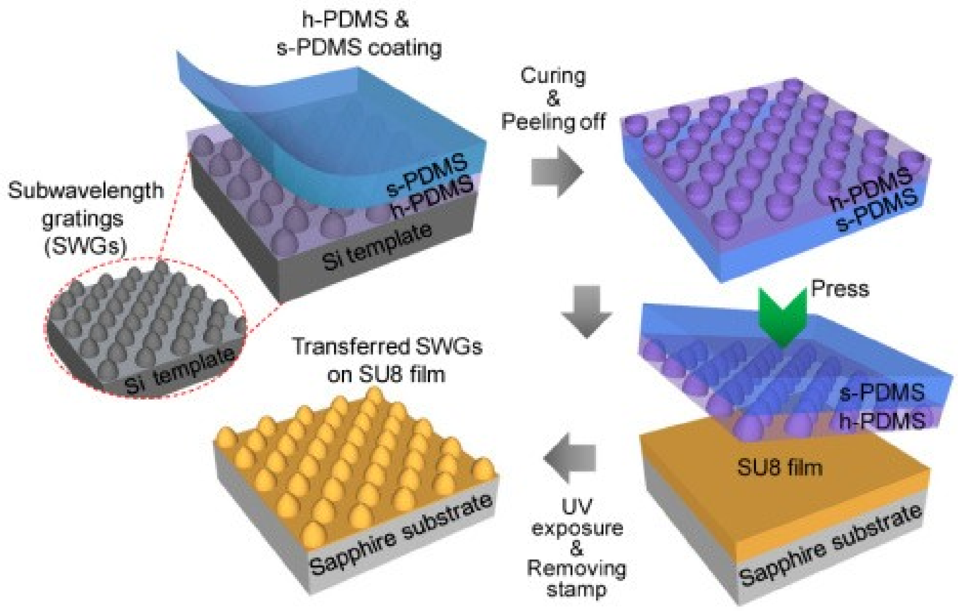
Picture 9 : Scanning Lithography (e-beam).

In an e-beam lithography process, a beam of electrons scans across the surface of an electron-sensitive resist film, such as polymethil methacrylate, that polymer is used as the mask. Then we applied the same process as the photolithography, using UV light we replicate the image of the mask in the resist.

The process is the same for focused ion beam lithography, and resolution in both techniques is higher than photolithography, near 50 nm, the main disadvantage is that both are serial techniques, that involves a very slow process.

- **Soft lithography:**

In soft lithography we use a soft mould prepared previously by casting a liquid polymer precursor against a rigid master. These methods have been developed specifically for making large-scale nanostructures with equipment that is easier to use and cheaper.



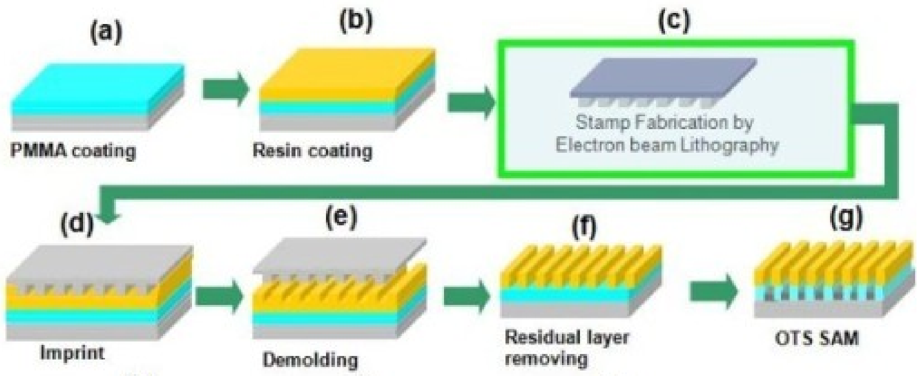
Picture 10 : Soft Lithography.

The mould is usually made of polymers such as polymides or polydimethylsiloxane, which is a non toxic polymer, so it can be used safely with biological materials. This is a big advantage in devices that aim to integrate nanostructures with biological systems. The master is normally fabricated via a conventional lithographic method.

- **Nano-imprint lithography:**

The main concept of nano-imprint lithography is to use a hard master with a 3D nanostructure to mould another material, which assumes its reverse 3D structure.

Since the master has a fine nanostructure, to be successful the process must be done under pressure, also we must place a coating on the master to avoid adhesion to the mould. The mould after this must be heated, above its Tg temperature, in order to be soft enough to completely enter the fine master nanostructure.



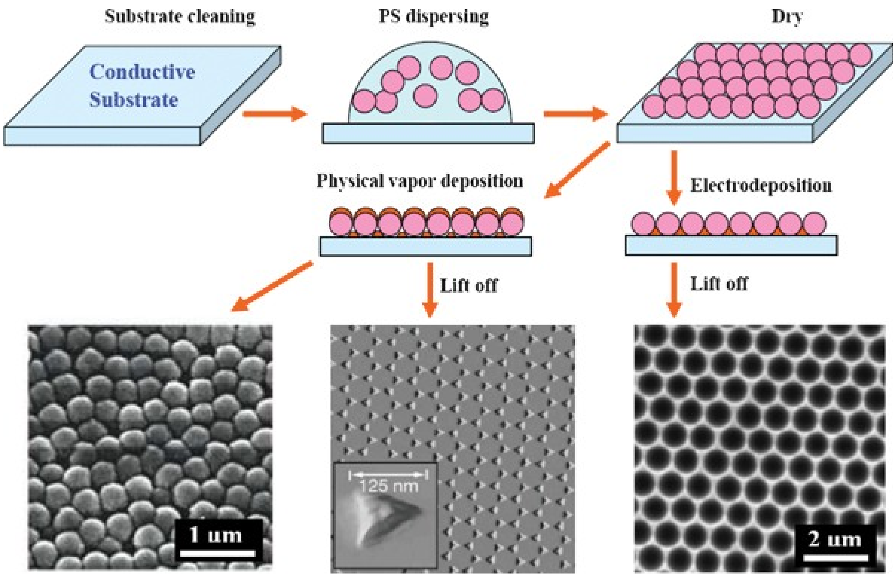
Picture 11 : Nano-imprint Lythography.

The method is the equivalent of embossing at the nanoscale, and it is required specialised equipment to be done.

- **Nanosphere lithography:**

In the nanosphere lithography an ensemble of nanospheres ordered on a surface are used as a mask. The nanospheres are dispersed in a liquid, known as colloid, depending on the surface properties and the type of media used in the colloid, the nanospheres will self-assemble in an ordered pattern.

There will be an empty space between the nanospheres, which is regularly repeated in the entire surface, this space is usually employed to crate relatively flat nanopatterns on the surface. The nanosphere patter is used as a mask, and a material such as gold or silver is sputtered on it, after removing the nanospheres a regular pattern of dots is left.

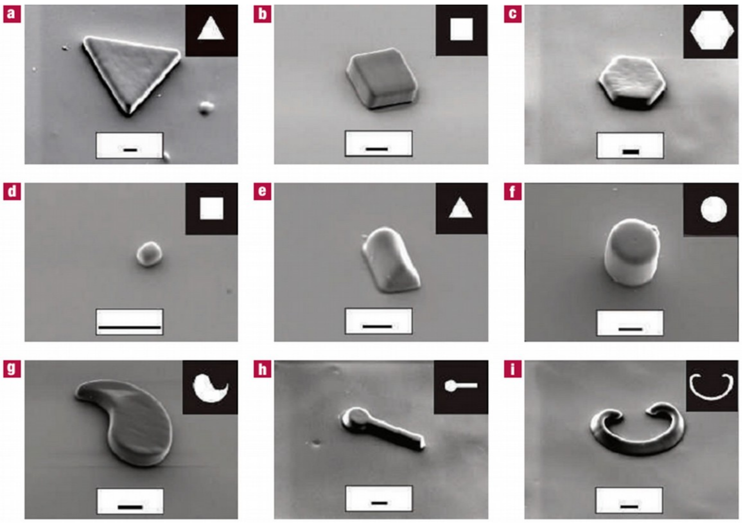


Picture 12 : Nanosphere Lithography.

Nowadays nanosphere lithography has evolved into a method that allows the fabrication of very complex structures as carbon nanotubes, arrays of nanostructures and 3D structures with small holes.

- **Colloidal lithography:**

Colloidal lithography is similar to nanosphere lithography, we use a colloid as a mask for the fabrication on nanostructures on surfaces but in this method we use electrostatic forces to obtain short-range ordered arrays of nanospheres on the surface.



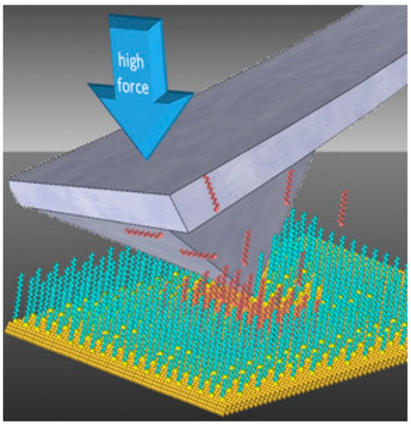
Picture 13 : Colloidal Lithography.

The interesting of this method is that there are plenty of nanostructures that can be formed: holes, cones, rings, "sandwiches" of different materials.

- **Scanning probe lithography:**

Scanning probe lithography uses small tips to image surfaces with atomic resolution in a pattern.

We have two different methods, SPL (Scanning probe lithography) which uses the tip of an AFM to selectively remove certain areas on a surface and on the other hand, DPN (Dip-Pen nanolithography) which also uses an AFM tip to deposit material on a surface with nanometre resolution.

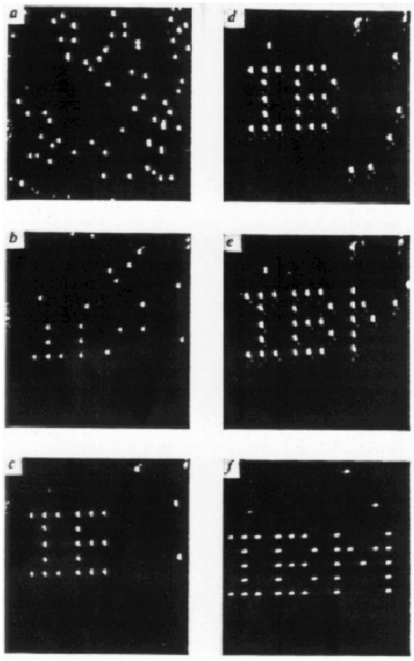


Picture 14 : Scanning Probe Lithography.

The main advantages of this techniques are the high resolution and the ability to generate complex patterns with arbitrary geometries, but the main limitation is the speed, because they are serial techniques as e-beam lithography.

- **Writing "atom-by-atom":**

Scanning tunnelling microscope can be used for more than visualise atoms, it can be use to carefully move atoms on a surface using the tip of the STM, and it was demonstrated when IBM write the company logo with atoms in 1999.



Picture 15 : IBM Writing atom by atom.

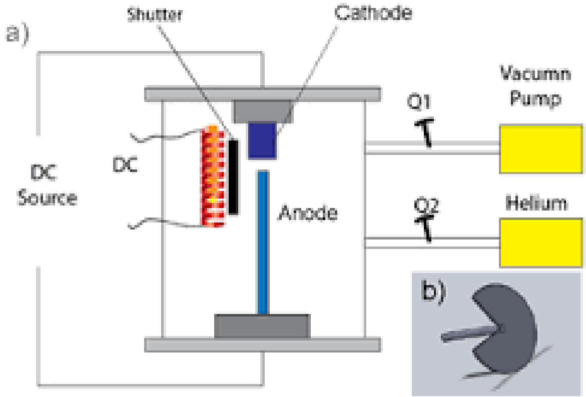
This capacity has great potential for the future generation of data storage devices, and it allows building a material atom by atom independently. This opens the door to new materials with completely new properties. This process is still very slow because we have to manually move the atoms, one at a time.

2.2. Bottom-up Methods:

Bottom-up methods can be divided into two groups, gas-phase methods and liquid phase methods. In both cases the nanomaterial is fabricated through a controlled fabrication route that starts from the single atom or molecule.

- **Plasma arcing:**

Plasma arcing is the most common method for fabricating nanotubes. In this method we use a plasma, which is an ionised gas. Then we applied a potential difference between two electrodes and the gas between ionises. The electrode (anode) vaporises as electrons are taken from it, for instance, a carbon electrode is used to produce the carbon nanotubes.



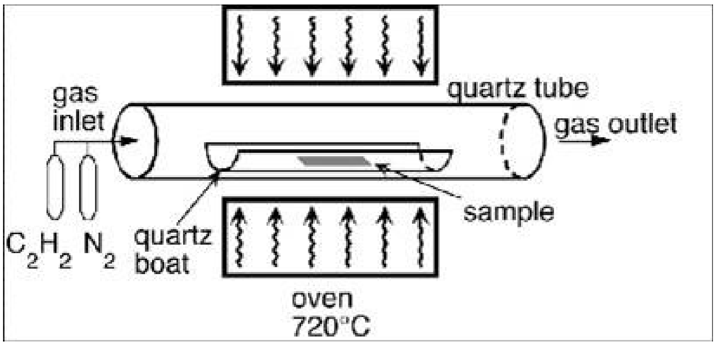
Picture 16 : Plasma Arcing.

This electrode is consumed during the reaction producing carbon cations, these positively changed ions pass to the other electrode, to pick up electrons and are deposited to form the nanotubes.

This method is also used to deposit nanolayers on surfaces, but it must be 1 nm thick to be considered as a nanomaterial.

- **Chemical vapour deposition:**

To be able of making a good Chemical vapour deposition, the material to be deposited is first heated to its gas form and then allowed to deposit as a solid on a surface.



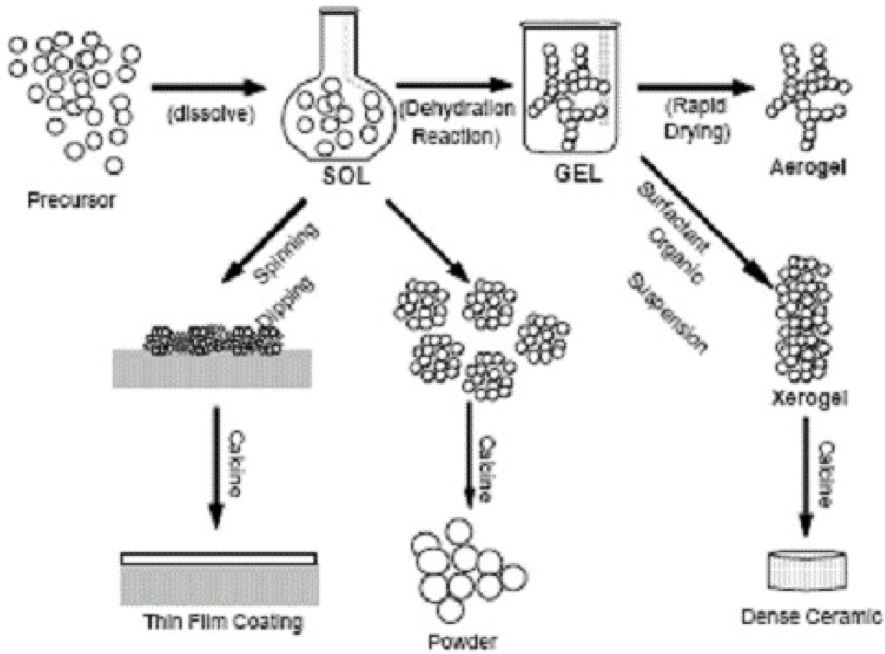
Picture 17 : Chemical Vapour Deposition.

Its usually done under vacuum, and the deposition can be direct or through a chemical reaction so that the material deposited is different from the one heated. Is often used to deposit a material on a flat surface.

- **Sol-gel synthesis:**

Sol-gel synthesis is performed in the liquid phase, and can be use for fabricating nanoparticles as well as nanostructured surfaces or 3D materials.

The sol is a colloid, a chemical mixture where the particles of one substance are suspended in the mixture. The first phase of the process is the synthesis of the colloid, this colloidal suspension evolves forming networks to a process called gelation, forming a network in a continuous liquid phase.

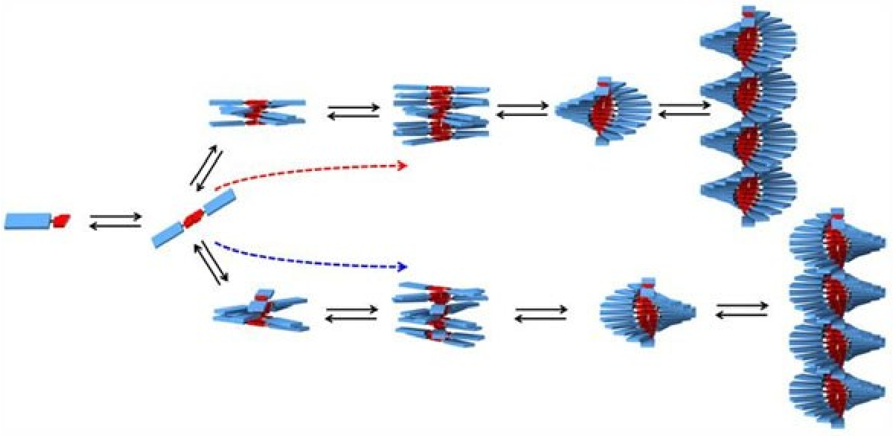


Picture 18 : Sol-Gel Synthesis.

The first phase is the hydrolysis reaction, using a catalyst, it can be a base or an acid. After hydrolysis the sol starts to condense and polymerise, and depending on some conditions such as pH, can reach dimensions of a few nanometres. Then the particles agglomerate, and a network starts to form throughout the liquid medium, which forms a gel.

- **Molecular self-assembly:**

Self-assembly is how all natural materials, organic and inorganic are produced. In natural biological processes, molecules self-assemble to create complex structures with nanoscale precision.



Picture 19 : Self Assembly.

In self-assembly sub units spontaneously organise and aggregate into stable structures. This process is guided by information that is coded into the characteristics of the sub units and the final structure is reached by equilibrating to the form of the lowest free energy.

3. Conclusions:

Even nanotechnology is recent in history, this is one of its main advantages, we have lots of ways to improve methods of fabrication, or even discover different ways of manufacturing nanomaterials.

We are just starting knowing how to deal with the nano world, and the possibilities are amazing, the properties of the materials can be modified and adjusted to our desires, and maybe in some years this technology becomes cheaper and more accessible to work with so we can advance more in the study of nanomaterials.

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