NANOPARTICLE TECHNOLOGIES AND THEIR APPLICATIONS

CHAPTER 2: FABRICATION METHODS FOR NANOPARTICLES AND NANOSTRUCTURES

1. Background

This chapter explains some processes used for the manufacture of nanomaterials; nanomaterials are those materials which have at least one dimension at nanoscale level (1-100 nm). These include nanoparticles, nonporous materials, nanostructured surfaces, etc. The nanomaterials fabrication can be subdivided into two groups: bottom-up methods and top-down methods (Biswas et al., 2012). In the latter case, a bulk substrate is used to derive nanomaterials and desired nanomaterial is obtained by progressive removal of material. Top-down methods can be directly explained by the example of carving a statue from a large block of marble. This category also includes printing methods. The opposite is the case with the Bottom-up methods: the nanomaterials like nano coating are obtained starting from molecular or atomic precursors and progressively assembling it to form the desired structure. This method can be explained by building with the bricks.

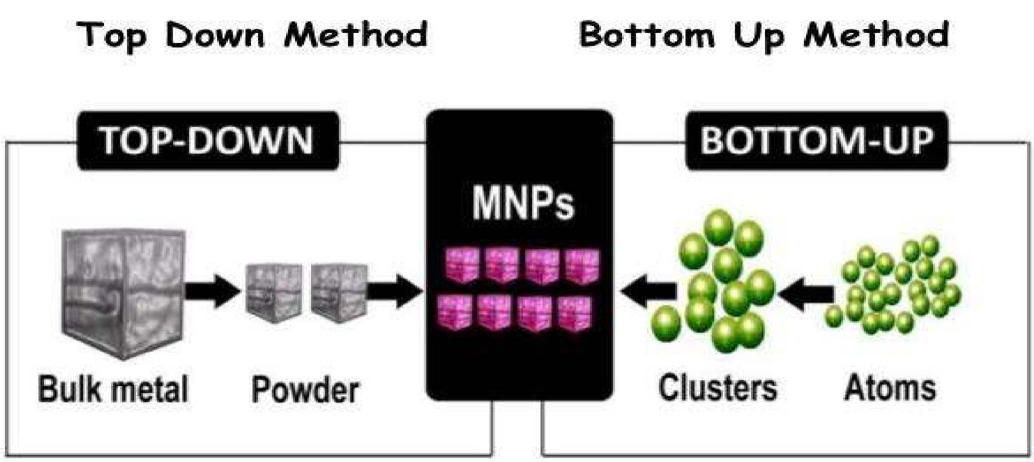

Fig. 13. Schematic of nanofabrication methods (Top-Down and Bottom-Up)
[Source: https://www.slideshare.net/NIKETPOWAR/introduction-of-nanotechnology]

In both above mentioned methods, two conditions are essential: Control of the environment conditions (e.g. contaminants, dust, etc.) and control of production conditions (e.g. electron beam energy, etc.). Due to these reasons, nanotechnology demands highly sophisticated fabrication and characterization tools most of the time operated in clean room environment in a vacuum (Zhao et al., 1997).

2. Top-Down Approach

Various top-down methods derived from semiconductor industry (to fabricate various components of computer chips i.e. integrated circuits) are being used in nanotechnologies. The collective name for these methods is lithography and use electrons or light to remove selective micron scale material from the precursor (Chung et al., 2005). In past years, a lot of research focuses on reducing the size and integrating more functions of the electronic devices, which has been made possible because of the advances in lithographic fabrications processes. In these days, it is possible to make single structure below 100 nm, e.g. transistors in a recent generation are about 45 nm. Hence, the nanostructure is continuously fabricated in the semiconductor industry. Lithographic processes that are capable of making nanoscale structures are reviewed in the coming section. There are various methods to make nanoscale features, here most common methods are discussed.

2.1. Conventional Lithography

Lithography includes a series of fabrication techniques that share the principle of transferring an image from a mask to a receiving substrate. A typical lithographic process consists of three successive steps:

i. Coating a substrate (Si wafer or glass) with a sensitive polymer layer (called a resist).

ii. Exposing the resist to the light, electrons or ion beams.

iii. Developing the resist image with a suitable chemical (developer), which reveals a positive or negative image on the substrate depending on the type of resist used (i.e. positive tone or negative tone resist).

In conventional micro-fabrication used in the semiconductor industry, the next step after lithography is pattern transfer from the resist to the underlying substrate. This is achieved through some transfer techniques, such as chemical etching and dry plasma etching (Stoykovich & Nealey, 2006). Lithographic methods can be widely divided into two main groups which are illustrated below:

i. Use of physical mask in the methods, where the mask which is in proximity with the resist surface through which resist is exposed. The methods in combined are called mask lithography. In mask lithography processes, photolithography is mostly used.

ii. Use of software mask in the methods, where the surface of the resist is irritated by a scanning beam sequentially, through a computer measured program in which mask pattern is defined. Collectively these methods are called scanning lithography.

The primary difference between scanning and mask lithography is speed: where scanning lithography is a slow technique, mask lithography is fast, parallel technique. Resolution is also another main difference which in general is lower for mask lithography. More active radiation sources are used to get a higher resolution which causes higher equipment cost. A typical schematic of a conventional lithographic method is shown in Fig.14.

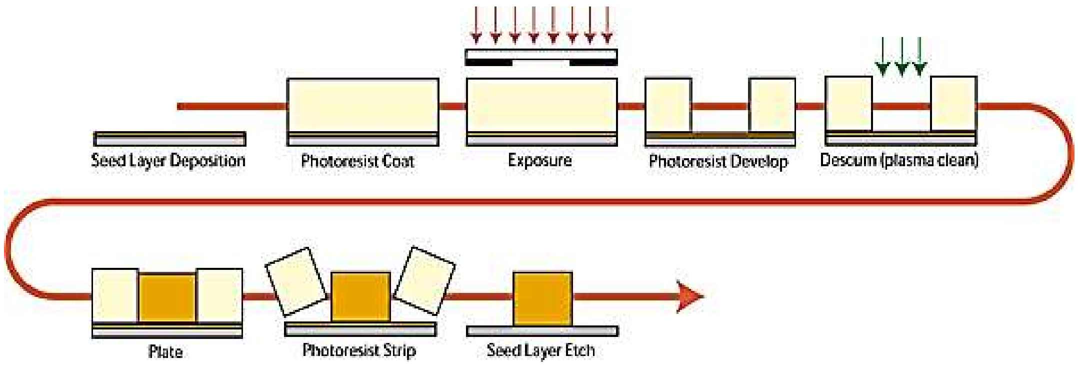

Fig. 14. Schematic of a conventional lithographic technique

[Source: http://replisaurus.siteo.com/en/pag8-ECPR-Method.html]

2.2. Photolithography

Light (X-ray, UV, extreme-UV or deep-UV) is used in photolithography to irradiate a photoresist (radiation sensitive polymer) through a mask. Depending on the light used the mask is quartz optically flat glass plate in which desired pattern is contained: dark areas on a background of UV-transparent. Placing the mask in contact with the resist the image of the mask can be simulated as it is (contact photolithography) or reduced by a factor of 5 or 10 and through an optical system it is projected to the resist layer (projection photolithography). Steps involved in a typical photolithographic method are illustrated in Fig.15.

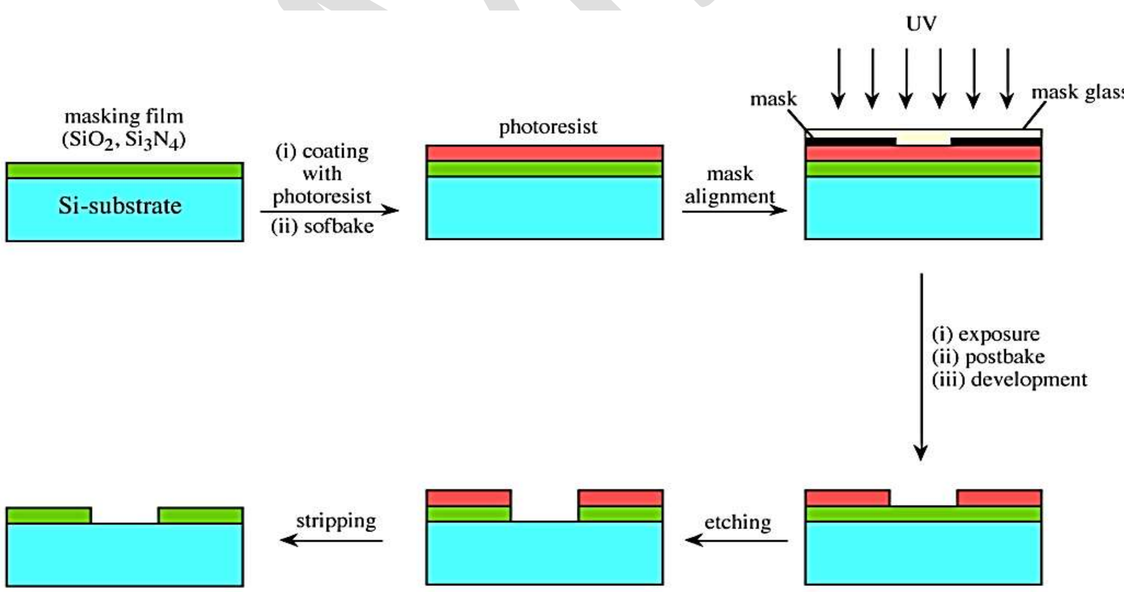

Fig. 15. Schematic of a typical photolithography technique

[Source: https://cnx.org/contents/0661ebbe - 52fb - 48b1 - a96a 0878fa6270ed @ 4/Optical_Issues_in_Photolithog]

Contact mode photolithography has a resolution of about 05-08 µm when 360-460 nm UV light is used. The gap between the flat substrate and mask cannot be reduced to approximately 1 µm hence higher resolution cannot be achieved even if elaborate vacuum system is used to hold the parts together (Rogers et al., 1998). Projection photolithography is used to produce higher resolution patterns. In these technologies, expensive equipment is used hence their use is limited to particular applications. Needed equipment is available in specialized laboratories only.

2.3. Electron Beam and Ion Beam Lithography

Features with nanometer resolution can be achieved by using energetic particles such as ions and electrons to pattern resist film. The technology is named as electron beam lithography when using electrons and using ions it is called focused ion beam lithography.

A focused beam of electrons is used to scan the surface of the resist film in a typical electron beam lithography process e.g. PMMA (polymethyl methacrylate). E-beam has an advantage of high resolution over photolithography: in the case of e-beam lithography patterns, small features of 50 nm can be generated (Vieu et al., 2000). Scattering of the electrons in the substrate and the resist determine the resolution of this technology. This effect, however, is largely reduced when using ions with higher masses than electrons. The working principle of the ion beam lithography is same as of e-beam lithography but in former case ions such as Be^{++}, Li^{+}, H^{++}, and H^{+}, are used. The resolution of both techniques is higher than photolithography but have a disadvantage: both are slow in the process, both are serial methods so both these are mostly limited to use to produce photomasks in light lithography. Working of a typical SPL is shown in Fig.16.

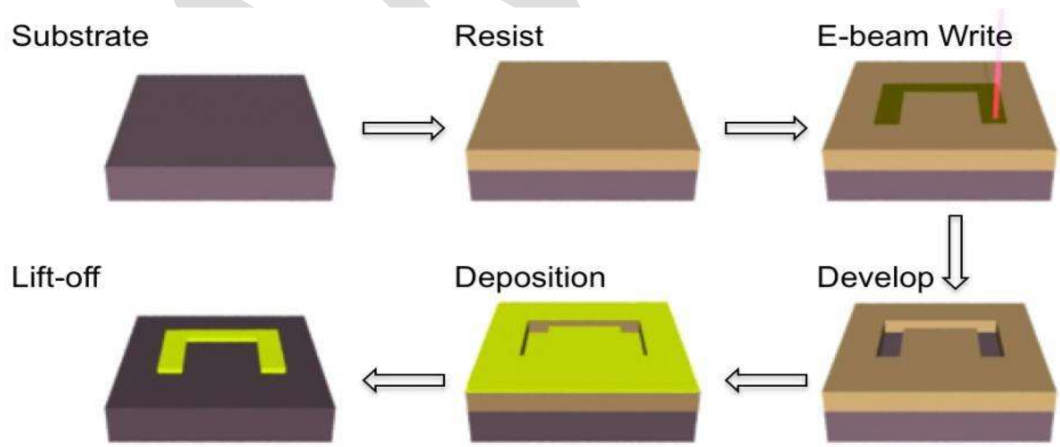

Fig. 16. Fabrication steps in Electron Beam Lithography

[Source: http://www.stoner.leeds.ac.uk/Research/TutFab]

2.4. Soft lithography

Soft lithography involves the use of the flexible molds produced by casting of polymer precursor against a stable master. For making large-scale nano and micro structures, soft lithography is mostly used with equipment that is easier to run compared to the equipment used in conventional lithography (Xia & Whitesides, 1998). Van der Waal's interaction, kinetic factors, and wetting determine the resolution of the soft lithography. This is the main advantage of soft lithography over conventional lithography techniques. Usually, conventional lithography is used to fabricate master. Fig. 17 explains the principle of soft lithography.

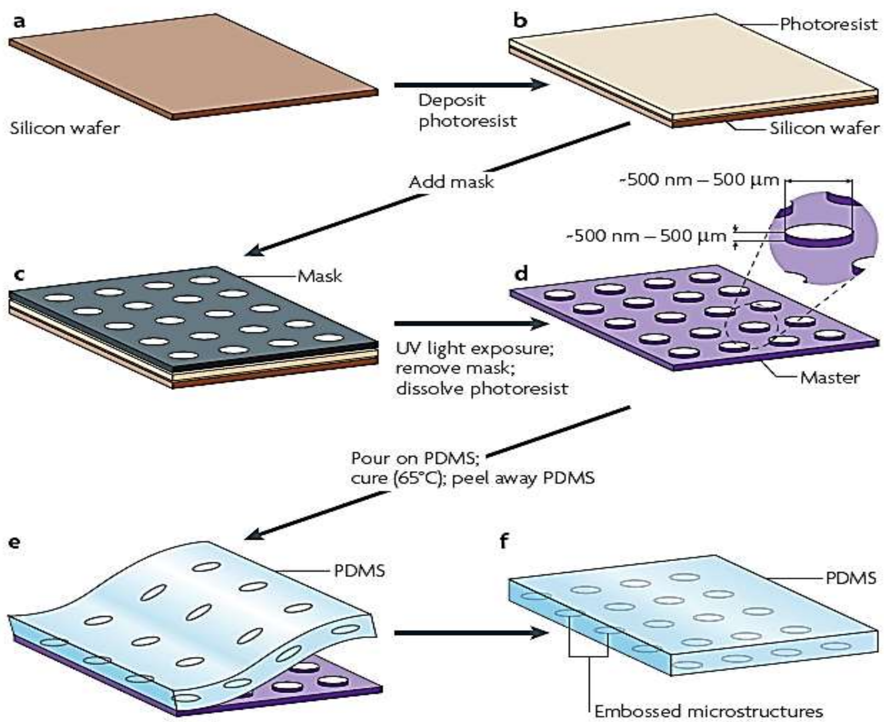

Fig. 17. Steps involved in a typical soft lithographic method (a-f)

[Source: http://www.elveflow.com/microfluidic-tutorials/soft-lithography-reviews-and-tutorials/introduction-in-soft-lithography/introduction-about-soft-lithography-and-polymer-molding-for-microfluidic/]

Some polymers such as polyimides, epoxides, and polyurethanes can be used for molding mostly elastomers poly (dimethylsiloxane) is used. PDMS can be used with biological materials such as living cells as it is non-toxic. This is primary advantage that is used to integrate nanostructures in biological systems. After pouring a liquid PDMS precursor over a master (e.g. silicon master or a photoresist), cross linking is induced by curing and then it is peeled off. The stamp can be used to define constraints in a place where a liquid can be confined, or for the printing of desired material from the stamp to appropriate surface.

2.5. Nanocontact Printing

Lateral dimensions of 500 nm or larger features can be easily made by microcontact printing. The primary challenge till now for microcontact printing has been to attain the capability to micro print with a high resolution whose lateral dimensions are lower than 100 nm (Li et al., 2003). Recently, this has been accomplished by enhancing the stability of PDMS which is highly compressible and soft and has a tendency to collapse or deform. A way to improve stability is to change the chemical formation of a stamp or fix the stiff backplane to the stamp to get harder polymer. This modification has led to the development of print features of as small as 50 nm. The method of printing which uses more difficult stamps is named as non-contact printing (nCP)

2.6. Nano-Imprint Lithography

To use a harder master with three-dimensional nanostructure to mold some material is the principle of nano-imprint lithography which adopts the reverse 3D structure. The process must take place under pressure and avoid catastrophic adhesion a coating must be placed on the master. To soften the mold to fill the master nanostructure completely and efficiently replicated the mold must be heated above its Tg temperature since the master has fine nanostructure the above mentioned steps must be taken care of to achieve nano-imprint lithography (Chou et al., 1996).

2.7. Nanosphere lithography

In nano sphere lithography a collection of nanospheres arranged on the surface is used as a mask (Fig.18). The nanospheres are spread in a liquid i.e. colloid and droplet on the surface are left to dry. Depending on the media used in the liquid e.g. precursor of electrolyte and surface properties e.g. charge the nanosphere will assemble in arranged pattern. In some situations, a crystal in colloidal form is obtained: In a colloidal crystal, each nanoparticle is bounded by six other nanospheres. This regular ordered arrangement can be used to produce ordered and arranged structures on the surface (Hulteen & Van Duyne, 1995).

There will be a space between nanospheres in the conventional ordered arrangement of nano spheres which is repeated over the entire surface. This space in simple methods is used to create two-dimensional nanopatterns on the surface. The materials e.g. silver and gold sputtered on the top, and nano sphere is used as a mask. A regular pattern of dots is left shaped like triangle once the nanosphere is removed but with the concave sides.

The gold dots (patterns) can act as growth sites e.g. growth of ZnO carbon nanotubes (Fan et al., 2006). This results in the regular array of nanowires or nanotubes. Nanospheres lithographic method has now developed into the methods that allow the production of complex arrays of nanostructure including 3D features with little holes in them.

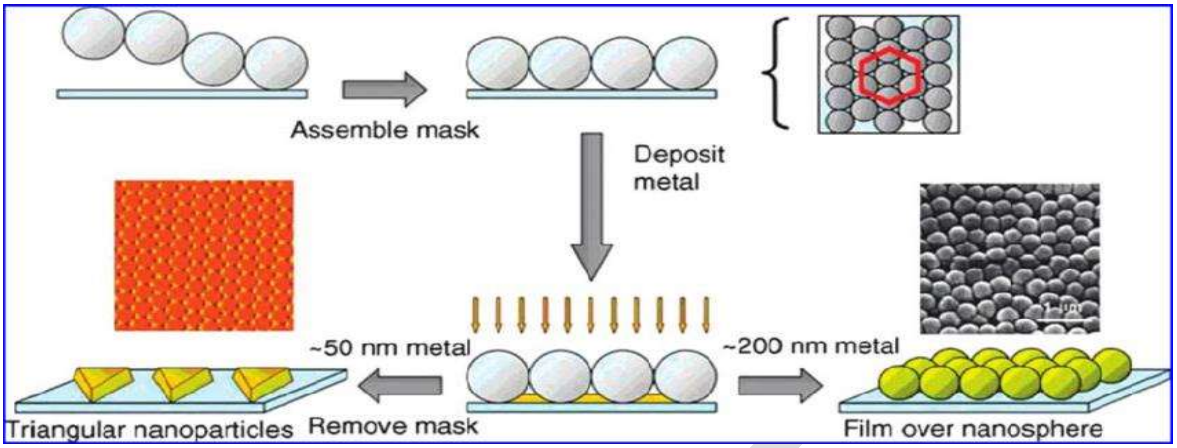

Fig. 18. Illustration of a typical Nanosphere Lithographic method

[Source:https://www.researchgate.net/publication/5621856_Very_High_Density_Sensing_Arrays/figures?lo=1&utm_source=google&utm_medium=organic]

2.8. Colloidal Lithography

The principle of colloidal lithography is same as nano sphere lithography by using liquid colloid as a mask for the production of nanostructures on the surface (Fig.19). A short range ordered array on the surface is obtained by the electrostatic forces in colloidal lithography method. Various processes such as lift-off, etching, etc. can be used to create many nanostructures using the arrays (Yang et al., 2006).

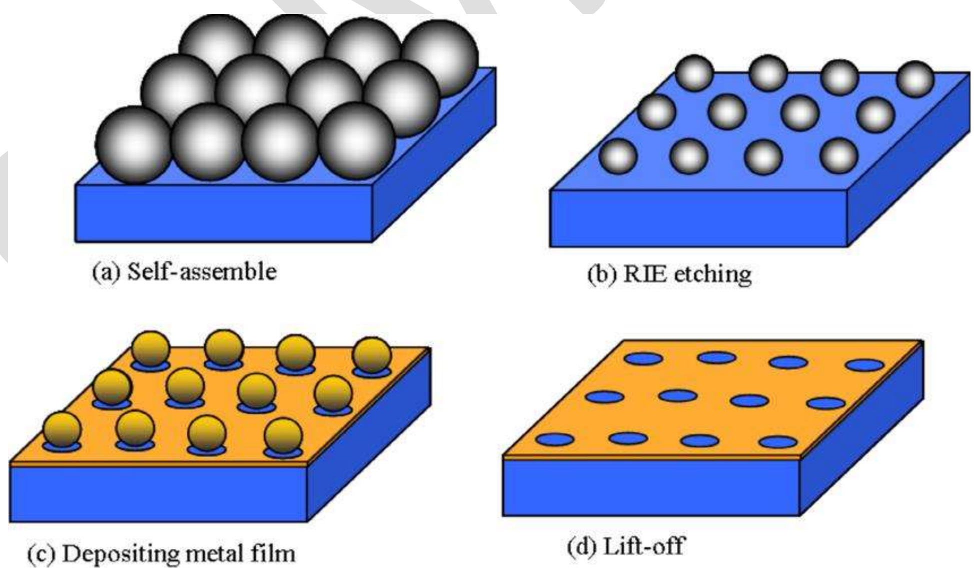

Fig. 19. Fabrication steps (a-d) in Colloidal Lithography

[Source: https://www.researchgate.net/publication/267156262Fabrication_of_nano_metallic_holes_for_color_filters_based_on_a_controllable_selfassembly_of_polystyrene_spheres/figures?lo=1&utm_source=google&utm_medium=organic]

Without discussing the details of the methods, an interesting thing to note is different types nanostructures formed: cones, holes, sandwiches, rings made of various materials, etc. In metals, the nanostructures present a localized surface plasmonic resonance effect which is used for sensing. Therefore, for various sensing applications, these materials are under study.

2.9. Scanning Probe Lithography

Scanning probe microscopy uses small tips of less than 50 nm to image the surface with the resolution of atomic level. That is why this has application in generating nanodevices and nanostructures. Hence they are called scanning probe lithography in which particular area is removed using the tip of an AFM and has similarity with the dip pen nanolithography which deposits the material on the surface using the AFM tip with the of nanometer level (Soh et al., 2013).

Both techniques are direct writing techniques, and their main advantages are the ability to produce patterns with arbitrary geometries both have high resolution. Like ion beam and e-beam lithography, DPN and SPL are serial techniques with the primary limitation of speed.

STM can be used not to just visualize the atoms by writing atom by atom which is a particular feature of STM. About twenty years ago, IBM researchers were able to move an atom on the surface, and they write their company logo with 35 atoms moving on the surface. Letters will be of 1 nm each if one has to write using atoms. With this size of letters, the whole Encyclopedia could be made as the size of the tip of a human hair (10^{-4} m^2). Hence all the books of the world would compact in an A4 size sheet, but it would require very long to write and can only be read by the STM.

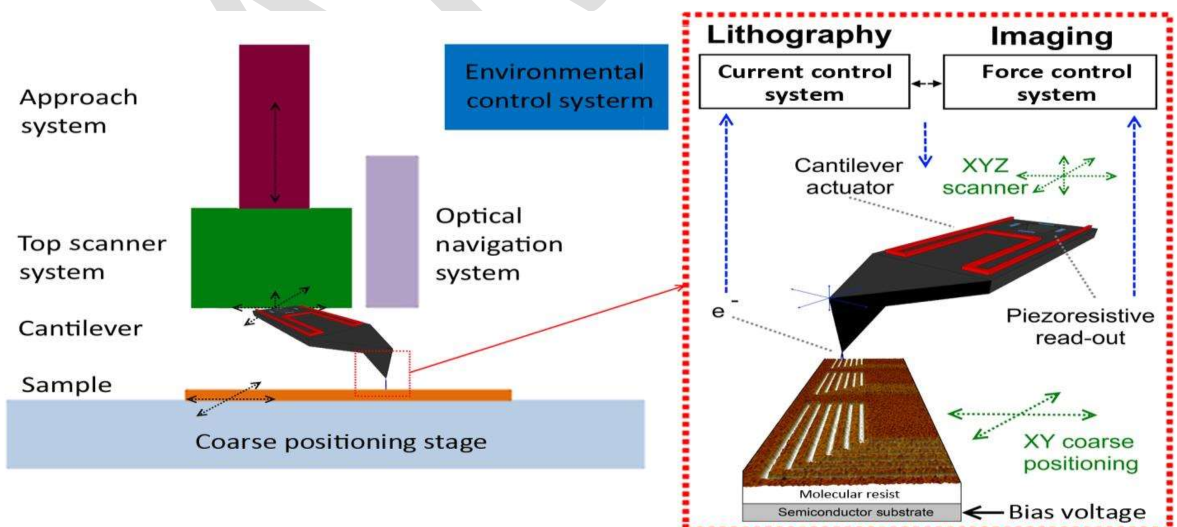

Fig. 20. Typical structure and working principle of the Scanning Probe Lithography

[Source: http://nanolithography.spiedigitallibrary.org/article.aspx?articleid=2330541]

For the future generation of storage devices, the STM's ability to move individual atoms has a very great potential. Nowadays, using a minute bits data is stored on CD-ROMs of semiconductors about 0.1 μm in size. For higher data capacity to achieve the bits written with atoms could be used. The information contained in the nano-CDs with atomic bits is as one million currently used CD-ROMs (Ross et al., 1993).

The material is built atom by atom independent of its physics and chemistry by using STM, as given in Fig.20. This can lead to materials which would have entirely new properties. Since it uses one atom at a time and atoms are moved manually hence this process is prolonged. So we can say that mass production of nano-materials is not possible using this technique.

3. Bottom-up

Bottom-up processes can be divided into the liquid-phase methods and gas-phase methods. In both mentioned methods the fabrication of nanomaterials is through the controlled route of manufacturing starting from the single molecule or atom. Gas-Phase methods normally include chemical vapor deposition and plasma arcing. On the other hand, liquid phase include the most advanced methods such as sol-gel process and elf-assembly of molecules (Shimomura & Sawadaishi, 2001).

3.1. Plasma Arcing

Most common method for the fabrication of nanotubes is plasma arcing. It uses ionized gases which are known as plasma. Between two electrodes the potential difference is applied and gas is fed between these electrodes (Fig.21).

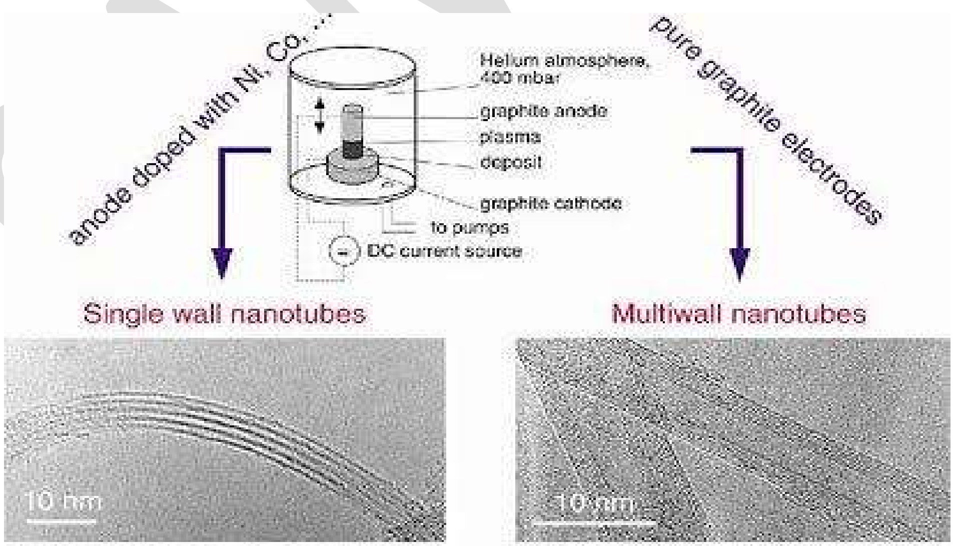

Fig. 21. Schematic of a plasma arcing nanofabrication process

[Source: https://sites.google.com/site/nanomodern/Home/CNT/syncnt/arc-discharge]

The conventional device for the arcing is made of an arc passes from one electrode to other and two electrodes. One electrode (anode) get vaporized as electrons are extracted from it by the applied potential difference. For example, carbon nanotubes are produced by carbon electrodes and are consumed producing cations during the reaction. These cations generated are passed to the other electrode (cathode), they pick up electrons and get deposited to produce nanotubes (Wilson et al., 2002). Deposition of nano layers on the surface instead of fabricating new structure can also be done using plasma arcing. The deposition can be of few atoms depth (at least 1 nm thick to consider a nanomaterial). Hence plasma arcing is opposite to chemical vapor deposition technique

3.2. Chemical Vapor Deposition

The material which is to be deposited on the surface is first heated to gas form, and it is forced to deposit on the solid material surface in chemical vapor deposition. Usually, this method is done under vacuum. The deposition may be direct or by the chemical reaction so that the volatilized atoms are different from that of the deposited atoms/material. If oxygen and carbon are present within the metals, this method can be used to produce nanopowders of carbides and oxides of metals. For pure metals, this approach can also be used to form nanopowders although this is not very easy to create (Park & Sudarshan, 2001).

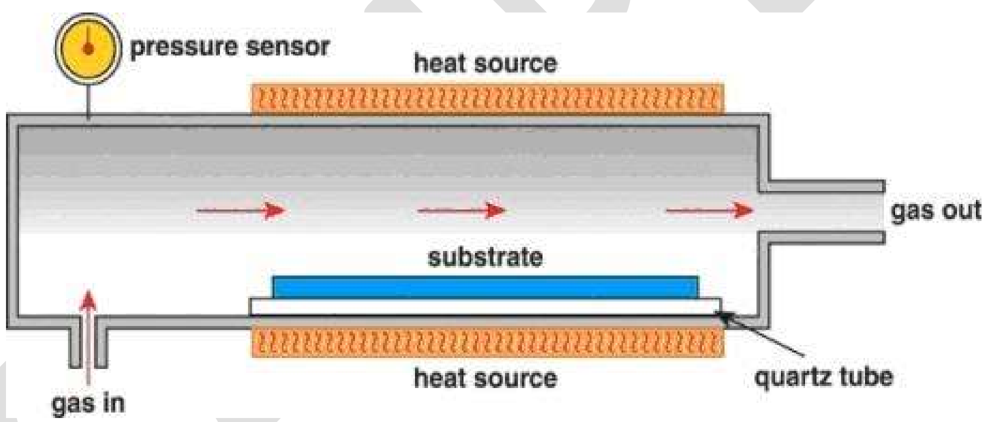

Fig. 22. CVD reactor for synthesis of thin film coatings

[Source: https://www.azonano.com/article.aspx?ArticleID=3432]

Often, on flat surfaces, chemical vapor method is used to deposit materials. The first layer of molecules or atoms can act as a model for the growth of material on the surface when the surface is irradiated to chemical vapor. These nano material structures are usually aligned. A crystallization site may form during the deposition in the depositional axis (perpendicular to the coating surface). The vertical growth of aligned structures starts. Hence it is an example of self-assembly.

3.3. Molecular Beam Epitaxy

In this method, the interaction between the molecular beam and heated crystalline substrate takes place under high vacuum environment to fabricate a single film of crystals (Arthur, 2002). It is possible to build crystal single atomic layer at a time by molecular beam epitaxy. To avoid contaminations during the crystal growth the process of growth is highly controlled. Various analytical techniques are used check the growth of the process and purity of the crystal is ensured. Molecular beam epitaxy is currently used in the semiconductor industry where precise control of the production of crystal layer and dopants control determines the performance of the device e.g. computer chips. Molecular beam epitaxy is used for the fabrication of field effect transistors, laser diodes, light-emitting diodes, read-write heads for computer drives and a lot more (Semond et al., 2001).

3.4. Sol-Gel Synthesis

This method takes place in liquid-phase. For the fabrication of 3D nanostructure nanomaterials and nano structure surfaces nanoparticles, it is beneficial self-assembly process. In a uniform liquid medium, a dispersed solid phase is mixed this colloidal mixture is known as 'sol.' Blood is a good example of naturally occurring sol. As the name gives the idea, a sol-gel method involves the formation of colloidal dispersion (sol) for the evaluation of network, and then afterward gelation of this network provides a liquid-phase called gel (Ko, 1999).

Synthesis of colloid is the first step in sol gel process. Ions of metals are usually the precursors used in this method. Metal alkoxysilanes and alkoxides are mostly used as their reactivity is good with the water (hydrolysis). The most popular used alkoxysilanes are tetraethoxysilane (TEOS) and tetraethoxysilane (TMOS) which make silica gels. Alkoxides such as borates, titanates, and aluminates are used usually mixed with TEOS or TMOS. Moreover, a mutual solvent such as alcohol is used since water and alkoxides are immiscible (Green et al., 1997).

The sol-gel method has four major steps. Firstly, hydrolysis reaction in which –OH group replaces the –OR group. The hydrolysis reaction does not require a catalyst but is faster and complete using a catalyst. In a hydrolysis reaction, the catalysts used are acid (HF or CH_3COOH). Or base (NaOH or NH_3). After hydrolysis, the sol polymerizes after condensation. Hence the growth of particles of dimensions of few nanometers depending on the different conditions such as pH takes place. The polymerization/ condensation reactions are very complex and can involve intermediate products which may include cyclic structure. The particles then join to form agglomeration: a network is formed in the liquid medium forming a thick gel.

The initial conditions of hydrolysis affect the above mentioned four steps and polymerization/ condensation. This condition may be temperature, pH, nature of the catalysts and time of the reaction, etc. Silica gels are commonly made through a sol-gel process. Many other types of gels can be formed. Some such special gels are aluminosilicate gels because of their tubular structure formation. Such type of product is imogolite which has an internal diameter of 1.5 nanometers and an external diameter of 2.5 nanometers. Such types of nanostructure are excellent adsorbents of anions such as sulfate, chlorate, phosphate, and chloride.

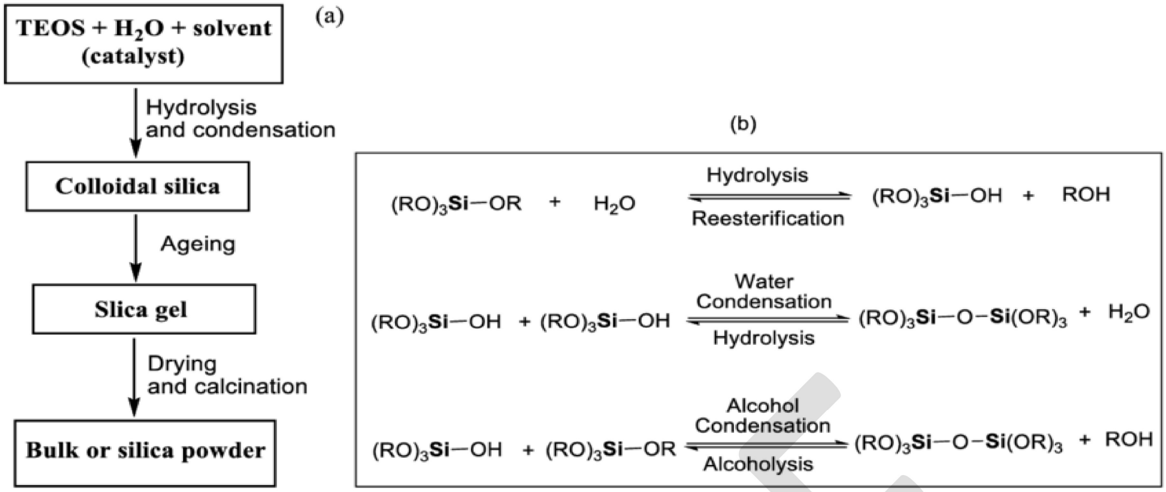

Fig. 23. Flowchart and chemical reactions of a typical Sol-Gel process

[Source: https://www.researchgate.net/publication/309320461_A_short_overview_on_the biomedical applications_of_silica_alumina_and_calcium_phosphate-based_nanostructured_materials]

Hydrofluoric acid can dissolve away the imogolite structure. Hence, template synthesis can be done by these nanostructures: the tube is dissolved away after filling with the atoms leaving the layers of atoms (in a row of 1 nm, 2.5 atoms of gold).

3.4.1. Synthesis of Nanostructured Surfaces by Sol-Gel Method

Fig.23 and Fig.24 explain the sol-gel processes. The gel can be placed over the surface to make the large surface area nanoparticles. Hence, by this way, a higher bulk-area ratio is acquired. Another way could be the formation of an aerogel. These are 3D growing networks of particles with the air or any other gas trapped in the spaces (interstices). Aerogels are categorized by very light weight, being porous and able to withstand 100 times more weight than their own.

A sol-gel method in ordered liquid is a versatile method to form ordered surface nanostructures. LCs are exactly this: they exist in the liquid phase (instead of solid) but have a crystalline structure. Silica nanostructure with controlled shape, ordering and pore size can be made in that way.

Nanostructured metals and oxides can be produced by the above described liquid crystalline casting processes (Wu et al., 1999). Nanostructure catalytic surfaces can be made by this development, such as palladium and platinum surfaces. It is highly beneficial to have a surface where catalytic reaction involves all metal atoms (just surface atoms are not included as in typical solids) since these metals are costly and rare.

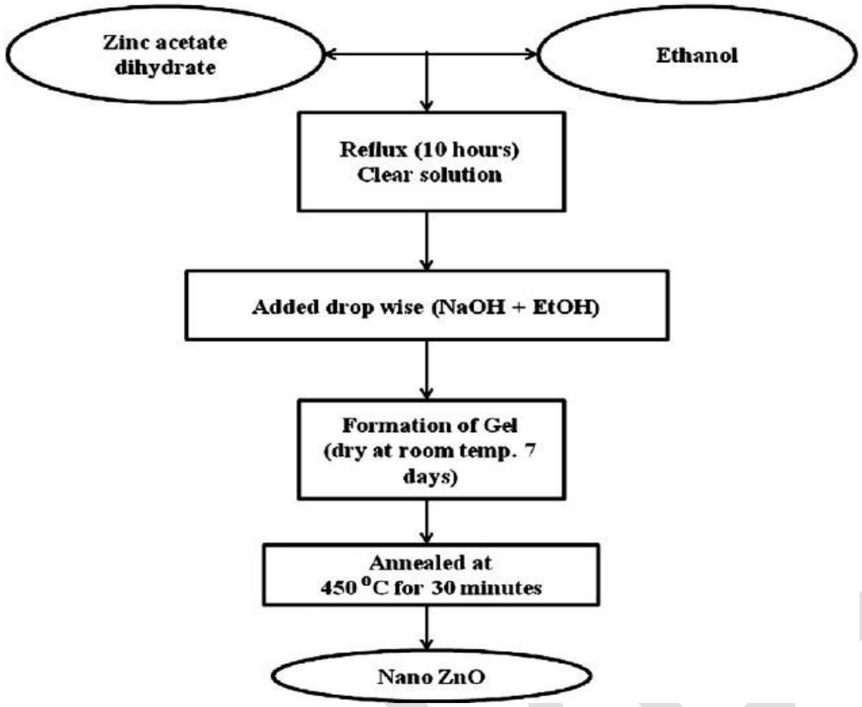

Fig. 24. A flowchart for synthesis of ZnO nanoparticles

[Source: https://www.researchgate.net/publication/257013819_Comparative_study_on photocatalytic activity of_ZnO_prepared_by_different_methods/figures?lo=1&utm_source=google&utm medium=organic]

3.4.2. Functionalized Silica Glass Surfaces

Within the silica glass structure, the sol-gel method allows the integration of bio-organic, inorganic and organic molecules. Because inorganic and organic molecules are prepared at high temperature, they cannot be incorporated into the glass. In sol-gel method, these molecules can be integrated as sol-gel method operates at low temperature (high temperature in some cases). Hence it is possible for example that silica glass can be combined with the enzyme's molecules. The resultant material has the advantage of plastics, and the product can be attracted to other materials which can be made in many ways. The glasses are more stable to chemical attack and heat. Glasses are also transparent, protected in their reactivity and do not leach out in the entrapped molecules.

3.5. Molecular Self-Assembly

Nature inspired fabrication tool is molecular self-assembly method: all inorganic and organic are produced by this self-assembly process. Complex structure with nanoscale size can be created by self-assembly in natural biological processes. For example, the formation of cell membrane from phospholipids and fabrication of DNA helix. Sub-units in self-assembly spontaneously aggregate and organize into the clear and stable structure through interaction which is noncovalent. Information coded into the features of final structure and sub-units is reached by equalizing to a form which is lowest free energy state guides the overall process (Zhang, 2003).

Till now, by the top-down method the devices have been made starting from the bulk material piece and carving down to small particles; now researchers are studying to build material by the bottom-up approach by starting from molecules or atoms to the bulk material which is idea inspired from nature. This fabrication technique is currently advancing and latest research nowadays. Hence instead of using top-down approach i.e. to carve down bulk materials into small pieces which are typical approach for the fabrication of integrated circuits such as microlithography and micromachining. Now the bottom-up approach is a promising approach to build nanostructures by assembling small pieces to larger structures.

It should be noted that tiny objects are now possible to make by this approach. It is still a vision to build devices like integrated electronic circuits through atom by atom assembly by using the computer assisted program, but it is also possible to make small components of IC through atom by atom self-assembly process, for example, a nanowire, etc.

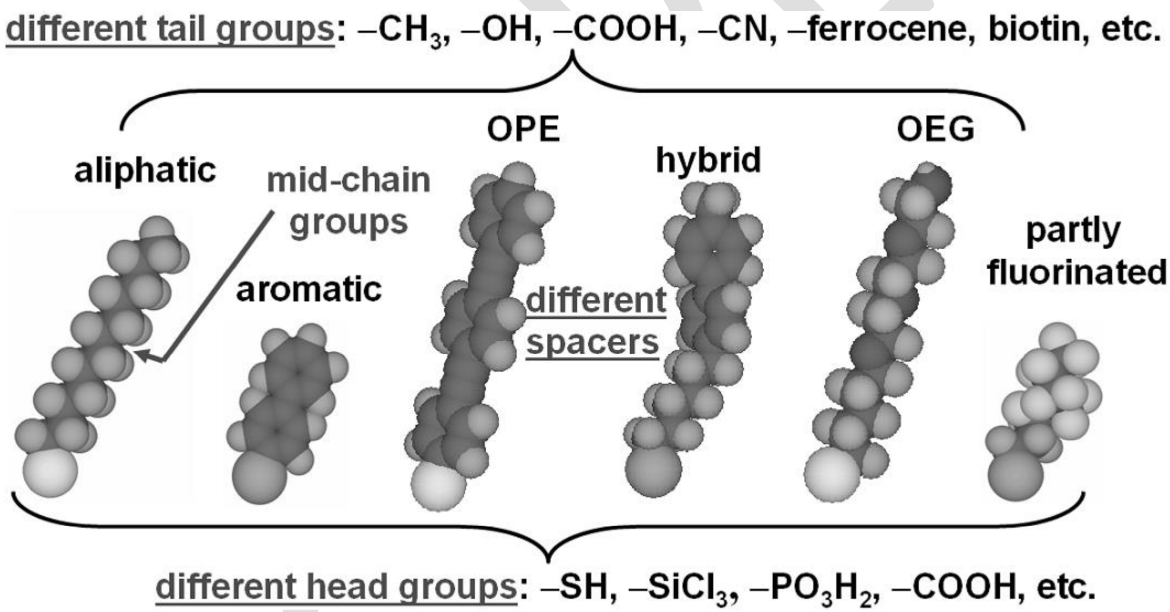

Fig. 25. Examples of precursors used for production of self-assembling molecules

[Source: http://nanotech.cuvalles.udg.mx/en/bottom-approach-interface-engineering-molecular-self-assembly-metal-surfaces]

Since nanoparticles do not scatter light hence if nanoparticles or small molecules are incorporated into the glass, the glass remains transparent. The fabrication of new structures with particular functions can be done by this self-assembly of particles in the laboratory by the researchers. Therefore, molecular self-assembly is recognition-directed fabrication process. To form ordered supermolecules the patterns are inserted which are specific for the product into the molecule in bottom–up approach— usage of supermolecular chemistry for nanostructures making (Ikkala & Ten Brinke, 2002).

'Lock and key' self-assembly of the matter is useful in understating this process. Researchers can organize a core to fit in a lock in another and vice versa. Once the assembly of two or more molecules takes place, the molecules bind together by lock and key mechanism in a particular geometry. No chemical bonds are formed by the self-assembly method in supermolecular chemistry: the molecules are bonded together by hydrogen bonding, van der Waals forces, donor-acceptor interaction and mediation effects e.g. solvents and metal-ion coordination.

A type of supermolecular structures is Transition metal-mediated structures. Metal ions in this structure act as the cement that binds the molecules (bricks) together. The fact that the properties of supermolecular structures are dramatically different to those of their components (variation in electric properties etc.). Self-assembly processes have been used to fabricate 2D and 3D structures. Currently, a two dimensional DNA structure that can be used as a template to arrange nanostructure with specificity and high precision which has an arbitrary shape, DNA origami method was established.

3.6. DNA Nanotechnology

In the bottom-up approach, another method uses the basic self-recognition and motifs properties of DNA to assemble already design nanostructures. This research work is called DNA nanotechnology. Through self-assembly process, the two other primary supermolecular that are fabricated are cyclodextrins and dendrites (Seeman, 1998).

To facilitate the DNA design origami structures, researchers at Aarhus University (Centre for DNA Nanotechnology) have developed a package of software; it was initially applied in the former logo of Aarhus University in the design of the dolphins.

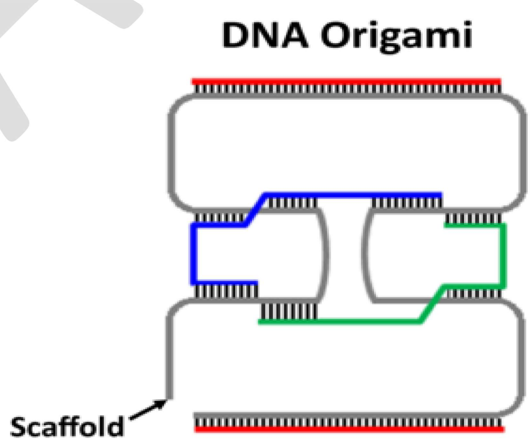

Fig. 26. Schematic of a nanotechnology based DNA origami method

[Source: https://www.nature.com/scitable/blog/bio2.0/beyond_genetics_dna_in_nanotechnology]

The program of the design was additionally applied to the design of 3D DNA box with 42 x 36 x 36 nm^3 dimensions which can be opened by external key signals. Various interesting applications are opened by the controlled access to the interior sections of the DNA contained in the DNA box, for example for the controlled discharge of nano-cargos and as a logic sensor for sequence signals (multiple) with their particular applications in the field of nanomedicine.

In nanotechnology, one of the recent development is represented by DNA nanotechnology. It has applications in the manufacturing of sensors (for imaging and diagnostics), drug release, nano-guides e.g. waveguides, electronics (transistors, wires), nano-motors and logic gates. For the computing of the future, it can lead to DNA computing and bottom-up electronics (Seeman, 2003).

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