Electrospinning

Electrospinning, also known as electrostatic fiber processing, technique has been originally developed for generating ultrathin polymer fibers. Electrospinning uses electrical forces to produce polymer fibers with nanometer-scale diameters. Electrospinning occurs when the electrical forces at the surface of a polymer solution or melt overcome the surface tension and cause an electrically charged jet to be ejected. When the jet dries or solidifies, an electrically charged fiber remains. This charged fiber can be directed or accelerated by electrical forces and then

collected in sheets or other useful geometrical forms. More than 30 polymer fibers with diameters ranging from 40 nm to 500 nm have been successfully produced by electrospinning.

The morphology of the fibers depends on the process parameters, including solution concentration, applied electric field strength, and the feeding rate of the precursor solution. Recently, electrospinning has also been explored for the synthesis of ultrathin organic-inorganic hybrids. For example, porous anatase titania nanofibers was made by ejecting an ethanol solution containing both poly(viny1 pyrrolidone) (PVP) and titanium tetraisopropoxide through a needle under a strong electric field, resulting in the formation of amorphous Ti02/PVP composite nanofibers .Upon pyrolysis of PVP at 500°C in air, porous Ti02 fibers with diameter ranging from 20 to 200nm, depending on the processing parameters are obtained.

Lithography

Lithography represents another route to the synthesis of nanowires. Various techniques have been explored in the fabrication of nanowires, such as electron beam lithography, ion beam lithography, STM lithography, X-ray lithography, proxial-probe lithography and near-field photolithography. Nanowires with diameters less than 10 nm and an aspect ratio of 100 can be readily prepared.

The fabrication of single crystal silicon nanowires reported by Yin et aL taken as an example to illustrate the general approach and the products obtained.

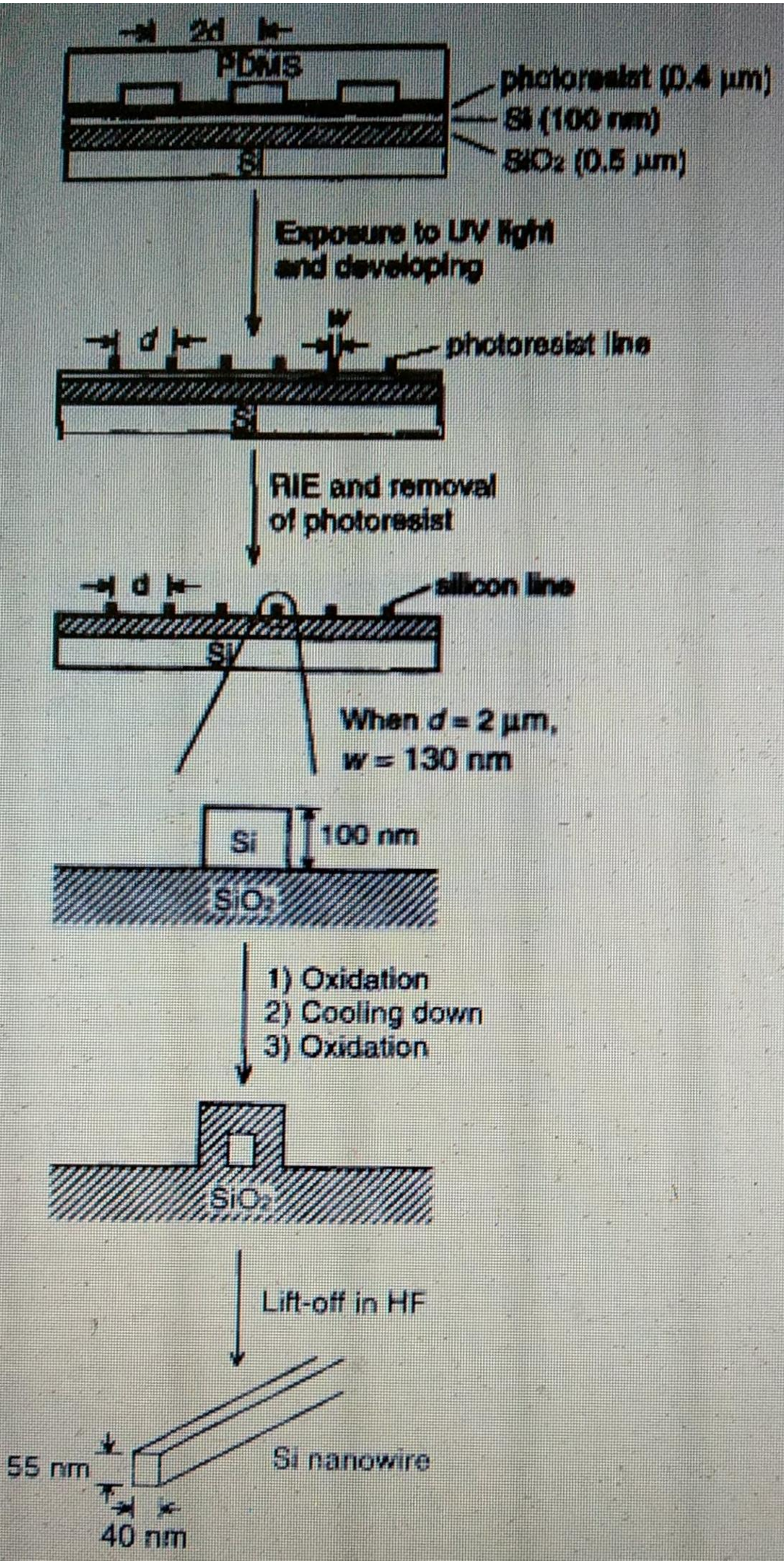

2d
PDMS
photoresist (0.4 μm)
Si (100 nm)
SiO₂ (0.5 μm)
Si
Exposure to UV light and developing
d
w
photoresist line
Si
RIE and removal of photoresist
d
silicon line
Si
When d = 2 μm, w = 130 nm
Si
100 nm
SiO₂
1) Oxidation
2) Cooling down
3) Oxidation
SiO₂
Lift-off in HF
55 nm
40 nm
Si nanowire

Figure outlines the schematic procedures used for the preparation of single crystal silicon nanowires. The nanoscale features were defined in a thin film of photoresist by exposing it to a UV light source through a phase shift mask made of a transparent elastomer, such as poly(dimethysi1oxane) (PDMS). The light passing through this phase mask was modulated in the near-field such that an array of nulls in the intensity were formed at the edges of the relief structures patterned on the PDMS mask. Therefore, nanoscale features were generated in a thin film of photoresist and the patterns were transferred into the underlying substrate using a reactive ion etching or wet etching process. Silicon nanostructures were separated from underlying substrate by slight over-etching.

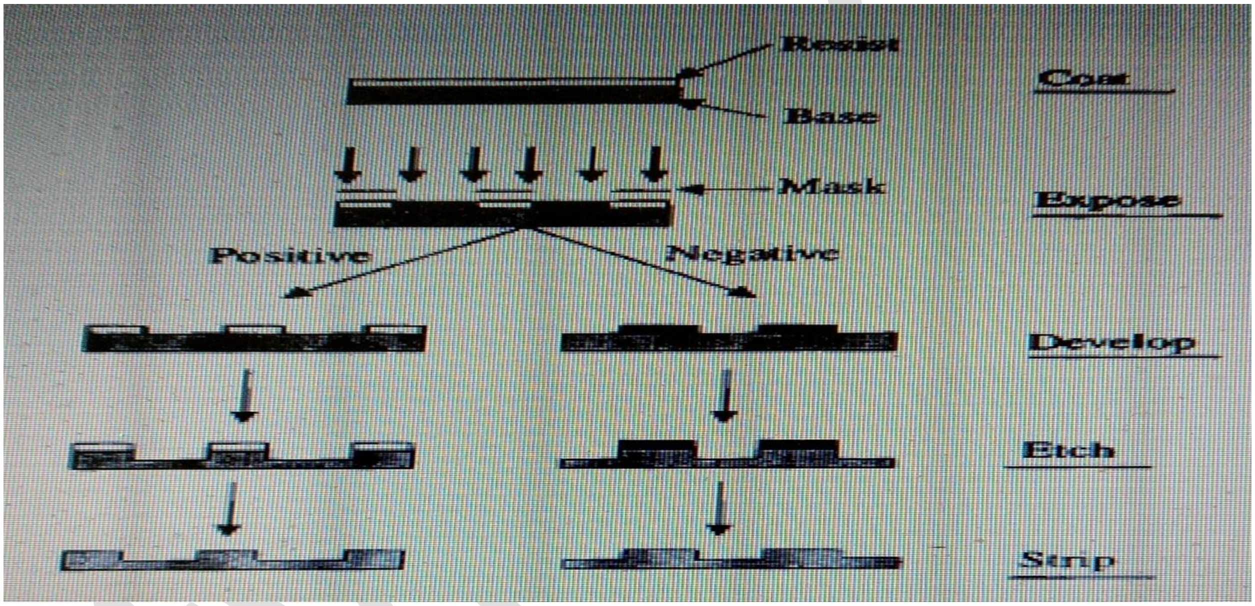
Lithography

Lithography is also often referred to as photoengraving, and is the process of transferring a pattern into a reactive polymer film, termed as resist, which will subsequently be used to replicate that pattern into an underlying thin film or substrate. Photolithography is the most widely used technique in microelectronic fabrication, particularly for mass production of integrated circuit.

Photolithography

Typical photolithographic process consists of producing a mask carrying the requisite pattern information and subsequently transferring that pattern, using some optical technique into a photoactive polymer or photoresist (or simply resist). There are two basic photolithographic approaches: (i) shadow printing and (ii) projection printing. The terms “printing” and “photolithography” are used interchangeably in the literature.

Figure outlines the basic steps of the photolithographic process, in which the resist material is applied as a thin coating over some base and subsequently exposed in an image-wise fashion through a mask, such that light strikes selected areas of the resist material. The exposed resist is then subjected to a development step. Depending on the chemical nature of the resist material, the exposed areas may be rendered more soluble in some developing solvent than the unexposed areas, thereby producing a positive tone image of the mask. Conversely, the exposed areas may be rendered less soluble, producing a negative tone image of the mask. The effect of this process is to produce a three-dimensional relief image in the resist material that is a replication of the opaque and transparent areas of the mask. The areas of resist that remain following the imaging and developing processes are used to mask the underlying substrate for subsequent etching or other image transfer steps. The resist material resists the etchant and prevents it from attacking the underlying substrate in those areas where it remains in place after development. Following the etching process, the resist is removed by stripping to produce a positive or negative tone relief image in the underlying substrate.

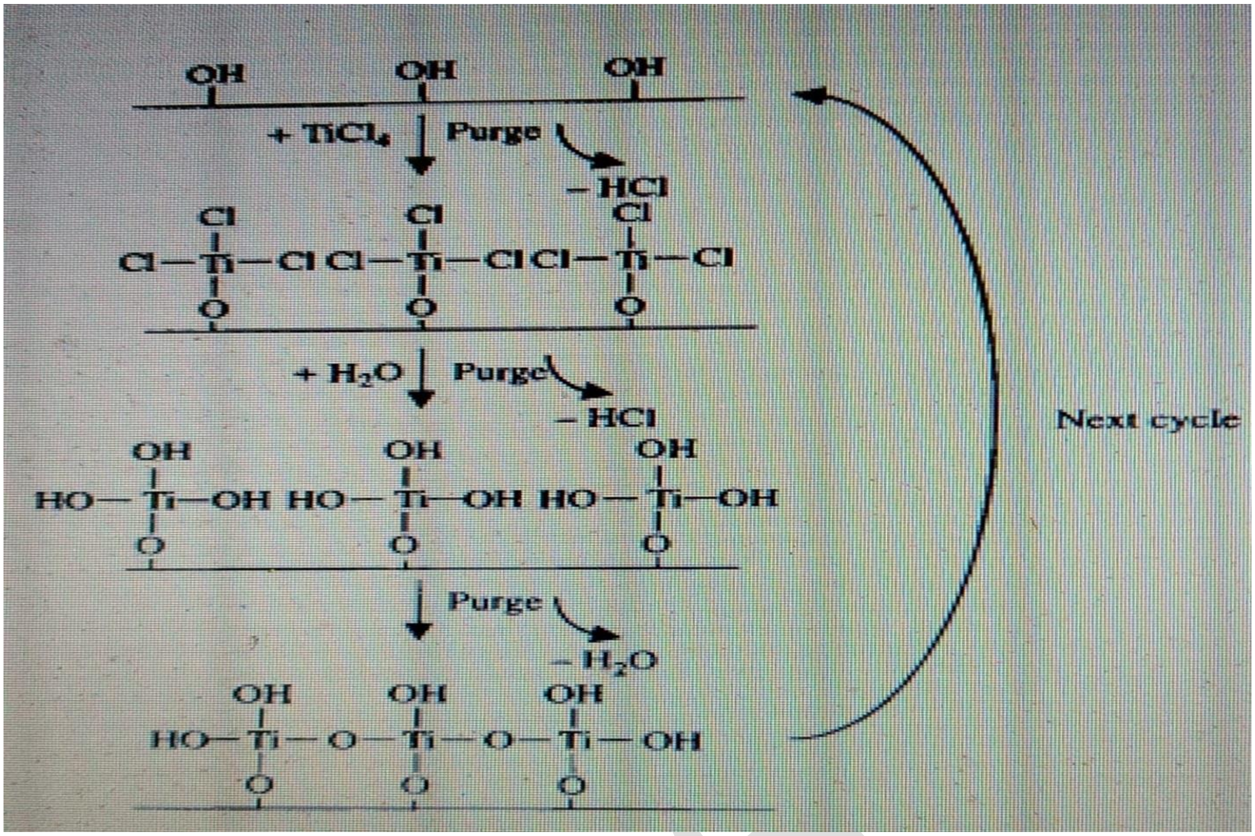


In contact-mode photolithography, the mask and wafer are in intimate contact, and thus this method can transfer a mask pattern into a photoresist with almost 100% accuracy and provides the highest resolution.

Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a unique thin film growth method and differs significantly from other thin film deposition methods. The most distinctive feature of ALD has a self-limiting growth nature, each time only one atomic or molecular layer can grow. Therefore, ALD offers the best possibility of controlling the film thickness and surface smoothness in truly nanometer or sub-nanometer range.

In the literature, ALD is also called atomic layer epitaxy (ALE), atomic layer growth (ALG), atomic layer CVD (ALCVD), and molecular layer epitaxy (MLE). In comparison with other thin film deposition techniques, ALD is a relatively new method and was first employed to grow ZnS film. ALD can be considered as a special modification of the chemical vapor deposition, or a combination of vapor-phase self-assembly and surface reaction. In a typical ALD process, the surface is first activated by chemical reaction. When precursor molecules are introduced into the deposition chamber, they react with the active surface species and form chemical bonds with the substrate. Since the precursor molecules do not react with each other, no more than one molecular layer could be deposited at this stage. Next, the monolayer of precursor molecules that chemically bonded to the substrate is activated again through surface reaction. Either the same or different precursor molecules are subsequently introduced to the deposition chamber and react with the activated monolayer previously deposited. As the steps repeat, more molecular or atomic layers are deposited one layer at a time. Figure schematically illustrates the process of titania film growth by ALD.



The substrate is hydroxylated first, prior to the introduction of precursor, titanium tetrachloride. Titanium tetrachloride will react with the surface hydroxyl groups through a surface condensation reaction:

TiCl4 + HOMe -+ C13Ti-O-Me + HCl where Me represents metal or metal oxide substrates. The reaction will stop when all the surface hydroxyl groups reacted with titanium tetrachloride. Then the gaseous by-product, HCl, and excess precursor molecules are purged, and water vapor is subsequently introduced to the system. Titanium trichloride chemically bonded onto the substrate surface undergo hydrolysis reaction:

Ti-0-Me + H20 + (HO),Ti-O-Me + HC1

Neighboring hydrolyzed Ti precursors subsequently condensate to form Ti-0-Ti linkage:

(HO),Ti-O-Me + (H0)3Ti-O-Me +Me-O-Ti(OH),-O-Ti (H0)2-O-Me + H20

The by-product HCl and excess H20 will be removed from the reaction chamber. One layer of TiOz has been grown by the completion of one cycle of chemical reactions. The surface hydroxyl groups are ready to react with titanium precursor molecules again in the next cycle. By repeating the above steps, second and many more TiO2 layers can be deposited in a very precisely controlled way. The growth of ZnS film is another often used classical example for the illustration of the principles of ALD process. ZnC1 and H2S are used as precursors. First, ZnCl, is chemisorbed on the substrate, and then H2S is introduced to react with ZnCl, to deposit a monolayer of ZnS on the substrate and HCl is released as a by-product. A wide spectrum of precursor materials and chemical reactions has been studied for the deposition of thin films by ALD. Thin films of various materials including various oxides, nitrides, florides, elements, II-VI, II-VI and III-V compounds, in epitaxial, polycrystalline or amorphous form deposited by ALD are summarized in Table .The choice of proper precursors is the key issue in a successful design of an ALD process. For example, elemental zinc and sulfur were used in the first ALD experiments for the growth of ZnS. Metal chlorides were studied soon after the first demonstrations of ALD. Metalloragnic compounds including both organometallic compounds and metal alkoxides are widely used. For non-metals, the simple hydrides have mostly been used: H20, H202, H2S, H2Se, H2Te, NH,, N2H4, PH3, ASH,, SbH3 and HF.

In comparison to other vapor phase deposition methods, ALD offer advantages particularly in the following aspects: (i) precise control of film thickness and (ii) conformal coverage. Precise control of film thickness is due to the nature of self-limiting process, and the thickness of a film can be set digitally by counting the number of reaction cycles. Conformal coverage is due to the fact that the film deposition is immune to variations caused by nonuniform distribution of vapor or temperature in the reaction zone.ALD has demonstrated its capability of depositing multilayer structures or nanolaminates .

Superlattices

Superlattices are specifically referred to as thin film structures composed of periodically alternating single crystal film layers; however, it should be noted that the term superlattice was originally used to describe homogeneous ordered alloys.

Composite film supperlattices are capable of displaying a broad spectrum of conventional properties as well as a number of interesting quantum effects. When both layers are relatively thick, properties of bulk materials are observed due to the frequently synergistic extensions of the laws of property mixtures that are operative. However, when the layers are very thin, quantum effects emerge, since the wavefunctions of charge carriers in adjacent thin layers penetrate the barriers and couple with one another. Such structures are mostly fabricated by MBE; however, CVD methods are also capable of making superlattices. ALD is another unique technique in the fabrication of superlattice structures.

Organic superlattices can be fabricated using LB technique or by self-assembly. Some of semiconductor superlattice systems are listed in Table. Semiconductor superlattices can be categorized into compositional superlattices and modulation doping, i.e.selective periodic doping, superlattice. The fabrication of semiconductor superlattices is basically the controlled synthesis of band gap structures, which is also known as band gap engineering. Esaki and Tsu were the pioneers in the synthesis of semiconductor thin film superlattices in 1 970.

Thin films can also be made through wet chemical processes. There are many methods developed and examples include electrochemical deposition, sol-gel processing and self-assembly.

In comparison with vacuum deposition methods, solution based film deposition methods offer a wide range of advantages including the mild processing conditions so that they are applicable and widely used for the fabrication of thin films of temperature sensitive materials. Mild processing conditions also lead to stress free films.

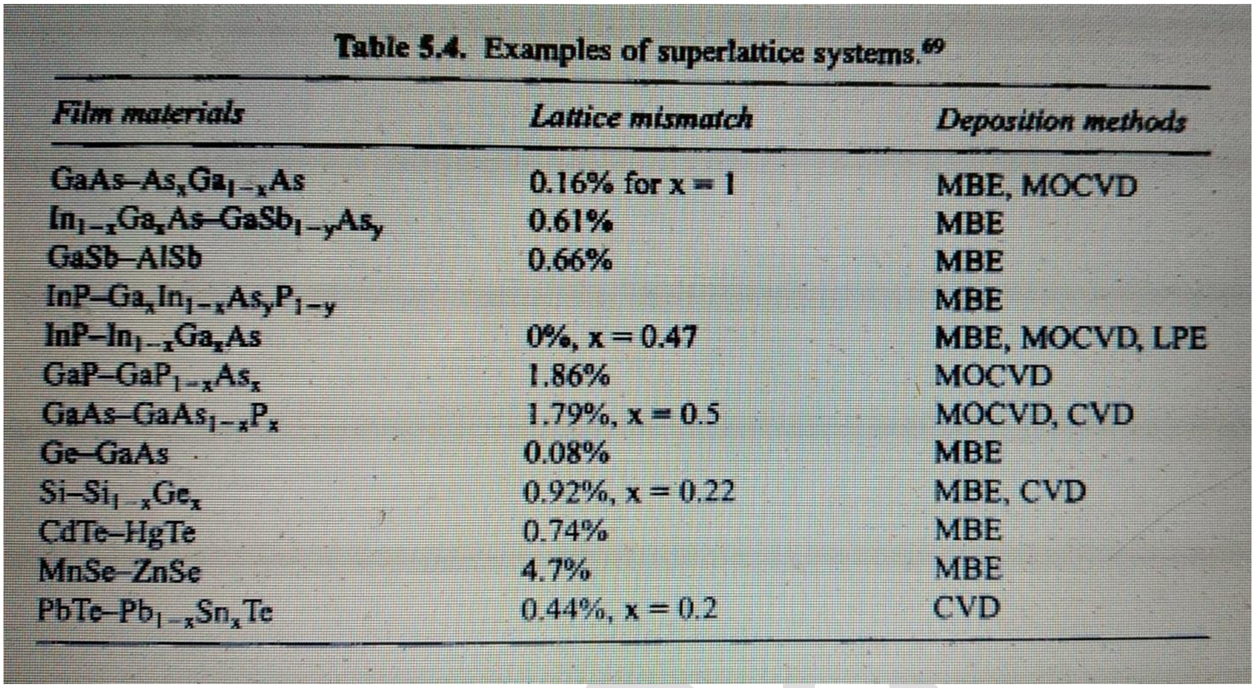


Table 5.4. Examples of superlattice systems.[69]

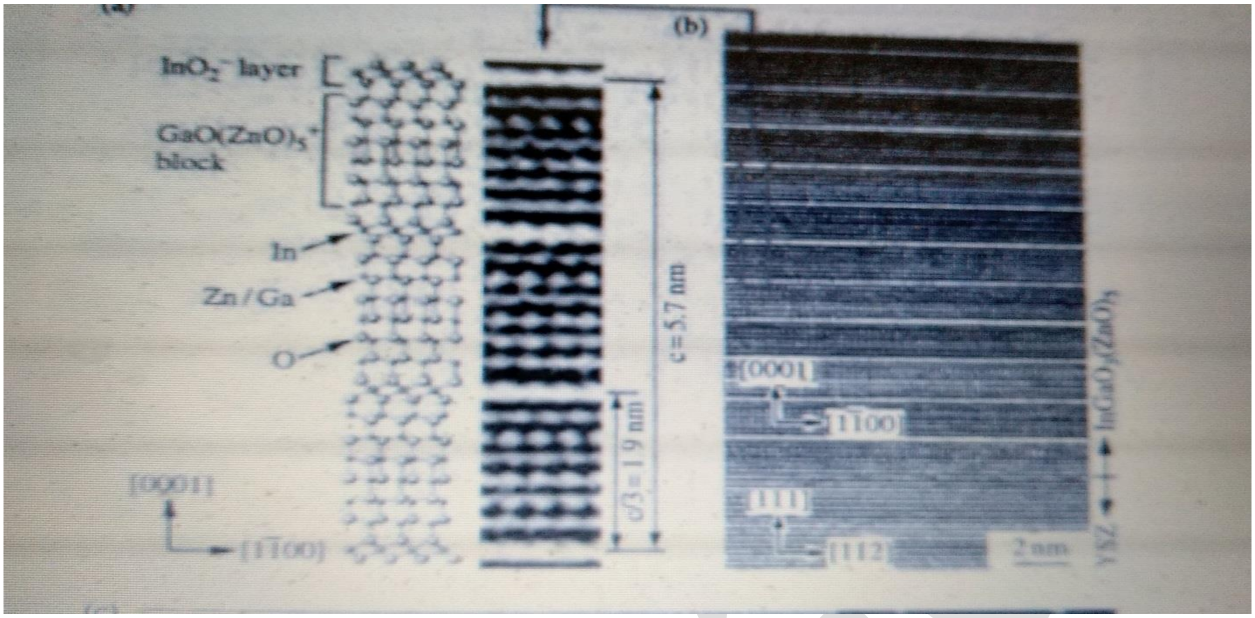
Film materials	*Lattice mismatch*	*Deposition methods*
GaAs–$As_xGa_{1-x}As$	0.16% for x = 1	MBE, MOCVD
$In_{1-x}Ga_xAs$–$GaSb_{1-y}As_y$	0.61%	MBE
GaSb–AlSb	0.66%	MBE
InP–$Ga_xIn_{1-x}As_yP_{1-y}$		MBE
InP–$In_{1-x}Ga_xAs$	0%, x = 0.47	MBE, MOCVD, LPE
GaP–$GaP_{1-x}As_x$	1.86%	MOCVD
GaAs–$GaAs_{1-x}P_x$	1.79%, x = 0.5	MOCVD, CVD
Ge–GaAs	0.08%	MBE
Si–$Si_{1-x}Ge_x$	0.92%, x = 0.22	MBE, CVD
CdTe–HgTe	0.74%	MBE
MnSe–ZnSe	4.7%	MBE
PbTe–$Pb_{1-x}Sn_xTe$	0.44%, x = 0.2	CVD

Self-Assembly

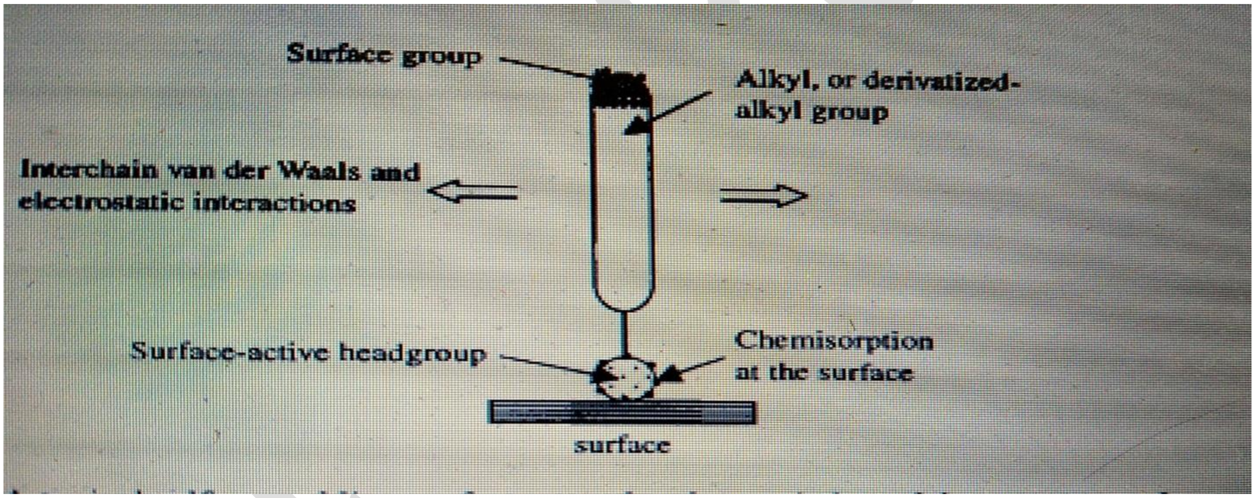
Self-assembly is a generic term used to describe a process that ordered arrangement of molecules and small components such as small particles occurred spontaneously under the influence of certain forces such as chemical reactions, electrostatic attraction and capillary forces. In this section, we will focus our discussion on the formation of monolayer or multiple layers of molecules through self-assembly.

In general, chemical bonds are formed between the assembled molecules and the substrate surface, as well as between molecules in the adjacent layers. Therefore, the major driving force here is the reduction of overall chemical potential. A variety of interactions or forces have been explored as driving forces

For the self-assembly of nanometer subjects as the fundamental building blocks. Self-assembled monolayers are molecular assemblies that are formed spontaneously by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent. A typical self-assembling surfactant molecule can be divided into three parts as sketched in Fig.(b)



(a) Fig; Structure of InGa03(ZnO)5 : Schematic of the crystal structure



The first part is the head group that provides the most exothermic process, i.e. chemisorption on the substrate surface. The very strong molecular-substrate interactions result in an apparent pinning of the head group to a specific site on the surface through a chemical bond, such as covalent Si-0 and S-Au bonds, and ionic -C02-Ag^+ bond.

The second part is the alkyl chain, and the exothermic energies associated with its interchain van der Waals interactions are an order of magnitude smaller than the chemisorption of head groups on substrates.

The third molecular part is the terminal functionality; these surface functional groups in SA monolayers are thermally disordered at room temperature. The most important process in self-assembly is the chemisorption, and the associated energy is at the order of tens of kcal/mol (e.g. -40-45 kcal/mol for thiolate on gold). As a result of the exothermic head group-substrate interactions, molecules try to occupy every available binding site on the surface and adsorbed molecules may diffuse along the surface. In general, SA monolayers are considered ordered and closely packed molecular assemblies that have a two-dimensional crystalline-like structure, though there exist a lot of defects.

The driving force for the self-assembly includes: electrostatic force, hydrophobicity and hydrophilicity, capillary force and chemisorption. In the following discussion, we will focus on the formation of SA monolayers Surface that chemisorb on the substrates.

There are several types of self-assembly methods for the organic monolayers and these include (i) organosilicon on hydroxylated surfaces, such as Si02 on Si, Al_2O_3 on Al glass, etc- (ii) alkanethiols on gold, silver and copper, (iii) dialkyl sulfides on (v) alcohols and amines on platinum and (vi) carboxylic acids on aluminum oxide and silver. Another way to group the self-assembly methods could be based on the types of chemical bonds formed between the head groups and substrates. There are (i) covalent Si-0 bond between organosilicon on hydroxylated substrates that include metals and oxides, (ii) polar covalent S-Me bond between alkanethiols, sulfides and noble metals such as gold, silver, platinum and copper, and (iii) ionic bond between carboxylic acids, amines, alcohols on metal or ionic compound substrates.

One of the important applications of self-assembly is the introduction of various desired functionalities and surface chemistry to the inorganic materials. In the synthesis and fabrication of nanomaterials and nanostructures, particularly the core-shell structures, self-assembled organic monolayers are widely used to link different materials together.

Langmuir-Blodgett Films

Langmuir-Blodgett films (LB films) are monolayers and multilayers of amphiphilic molecules transferred from the liquid-gas interface (commonly water-air interface) onto a solid substrate and the process is generally referred to as Langmuir-Blodgett technique (LB technique).Langmuir carried out the first systematic study on monolayers of amphiphilic molecules at the water-air interface and the first study on a deposition of multilayers of long-chain carboxylic acid onto a solid substrate was carried out.

The amphiphile is a molecule that is insoluble in water, with one end that is hydrophilic, and therefore is preferentially immersed in the water and the other that is hydrophobic and preferentially resides in the air or in the nonpolar solvent. A classical example of an amphiphile is stearic acid, $C_{17}H_{35}C0_{2}H$. In this molecule, the long hydrocarbon tail, $C_{17}H_{35}$ - is hydrophobic, and the carboxylic acid head group, $-C0_{2}H$ is hydrophilic. Since the amphiphiles have one end that is hydrophilic and the other that is hydrophobic, they like to locate in interfaces such as between air and water, or between oil and water. This is the reason they are also called surfactants. However, it should be noted that the solubility of an amphiphilic molecule in water depends on the balance between the alkyl chain length and the strength of its hydrophilic head. Certain strength of the hydrophilic head is required to form LB films. If the hydrophilicity is too weak, no LB film can be formed. However, if the strength of the hydrophilic head is too strong, the amphiphilic molecule is too soluble in water to allow the formation of a monolayer. The soluble amphiphile molecules may form micelles in water when their concentration exceeds their critical micellar concentration.

Table summmarizes the properties of different head groups.

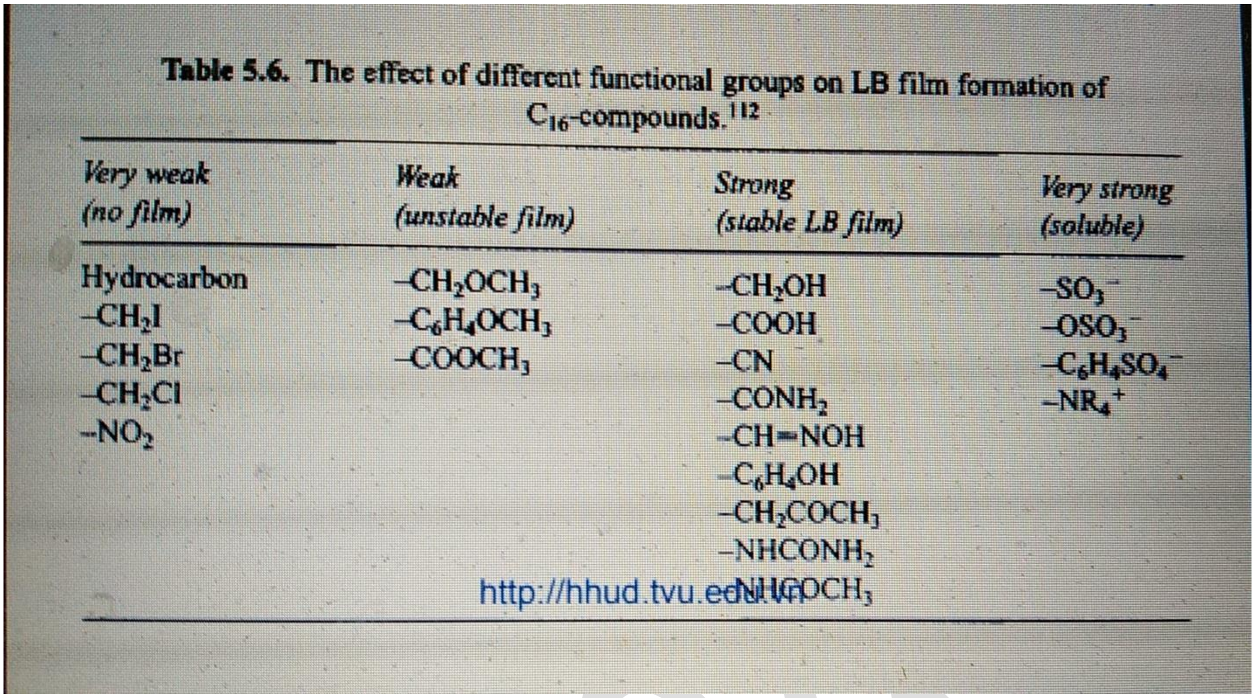
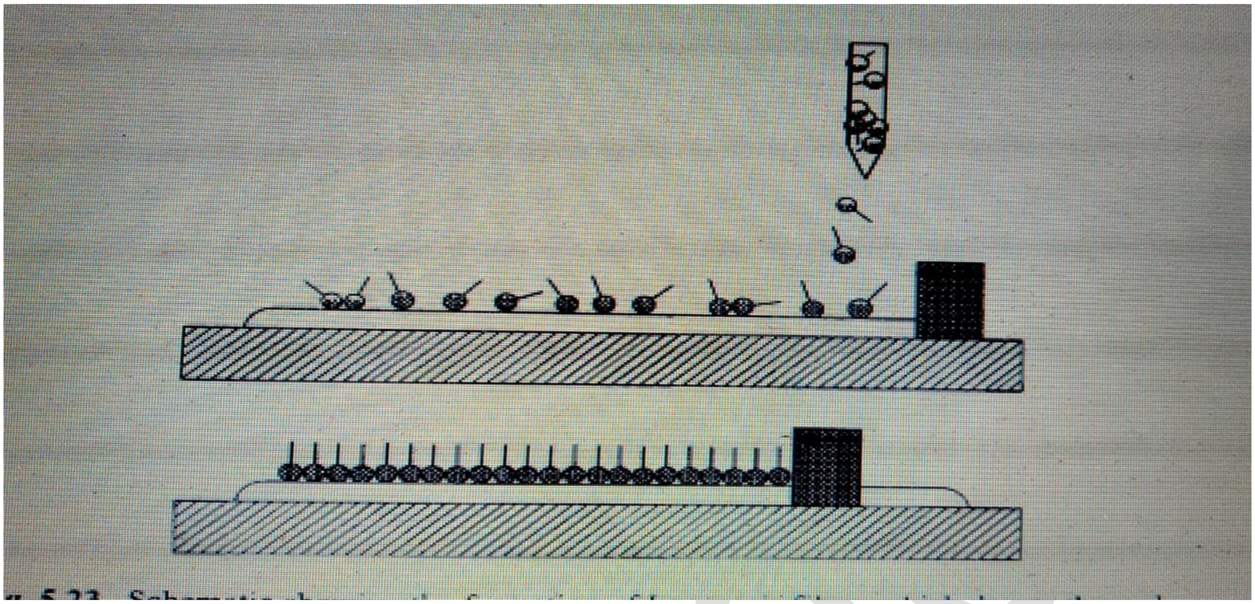


Table 5.6. The effect of different functional groups on LB film formation of C_{16}-compounds.[112]

Very weak (no film)	*Weak (unstable film)*	*Strong (stable LB film)*	*Very strong (soluble)*
Hydrocarbon	$-CH_2OCH_3$	$-CH_2OH$	$-SO_3^-$
$-CH_2I$	$-C_6H_4OCH_3$	$-COOH$	$-OSO_3^-$
$-CH_2Br$	$-COOCH_3$	$-CN$	$-C_6H_4SO_4^-$
$-CH_2Cl$		$-CONH_2$	$-NR_4^+$
$-NO_2$		$-CH{=}NOH$	
		$-C_6H_4OH$	
		$-CH_2COCH_3$	
		$-NHCONH_2$	
		$-NHCOCH_3$	

The LB technique is unique, since monolayers can be transferred to many different substrates. Most LB depositions have involved hydrophilic substrates where the monolayers are transferred in the retraction mode. Glass, quartz and other metal substrates with an oxidized surface are used as substrate, but silicon wafer with a surface of silicon dioxide is the most commonly used substrate. Gold is an oxide-free substrate and also commonly used to deposit LB films. However, gold has a high surface energy (-1000 mJ/m^2) and is easily contaminated, which results in an uneven quality of LB films.



The purity of the organic amphiphiles under study is of great importance, since any contamination in the amphiphile will be incorporated into the monolayer. Figure schematically shows the formation of Langmuir films, which denote the molecular films at the water-air interface, a drop of a dilute solution of an amphiphilic molecule in a volatile solvent, such as CHC13, is spread on the water-air interface of a trough. As the solvent evaporates, the amphiphilic molecules are dispersed on the interface. The barrier moves and compresses the molecules on the water-air interface; the intermolecular distance decreases and the surface pressure increases. A phase transition may occur, which is assigned to a transition from the “gas” to the “liquid” state. In the liquid state, the monolayer is coherent, except the molecules occupy a larger area than in the condensed phase. When the barrier compresses the film further, a second phase transition can be observed from the “liquid” to the “solid” state. In this condensed phase, the molecules are closely packed and uniformly oriented.

Two methods are commonly used to transfer monolayers from the water-air interface onto a solid substrate. The more conventional method is the vertical deposition . When a substrate is moved through the monolayer at the water-air interface, the monolayer can be transferred during emersion (retraction or upstroke) or immersion .

The more conventional vertical deposition method for the formation of LB films on substrates. (dipping or down stroke). A monolayer usually will be transferred during retraction when the substrate surface is hydrophilic, and the hydrophilic head groups interact with the surface. However, if the substrate surface is hydrophobic, the monolayer will be transferred in the immersion, and the hydrophobic alkyl chains interact with the surface. If the deposition process starts with a hydrophilic substrate, it becomes hydrophobic after the first monolayer transfer, and thus the second monolayer will be transferred in the immersion. Multiple layer films can be synthesized just by repeating the process.

Another method to build LB multilayer structure is the horizontal lifting, also referred to as Schaefer's method. Schaefer's method is useful for the deposition of very rigid films. In this method , a compressed monolayer is first formed at the water and air interface, a flat substrate is placed horizontally on the monolayer film. When the substrate is lifted and separated from the water surface, the monolayer is transferred onto the substrate.

Thermal stability and order-disorder transition are two important issues for any practical applications of LB films.

Self-assembly and LB technique offer the possibility of design and the construction of stable organic superlattices. For example, SA can be applied to assemble electron donor and electron acceptor groups, separated by well-defined distances - that can exchange electrons following optical excitation. This may allow the construction, for example, of an electronic shift register memory based on molecular electron transfer reactions.

Electrochemical Deposition

Electrochemical deposition or electrodeposition is a very well established thin film growth method. The key parameters in the electrodeposition of elemental films can be conveniently grouped into thermodynamic and kinetic considerations. The electrochemical potential of a metal electrode, E, is given by the Nernst equation:

$E = Eo + (R_gT/n_i F)$ In a_i where Eo is the standard electrode potential, or the potential difference between the electrode and the solution, when the activity, a_i of the ions is unity, F, the Faraday's constant, R,, the gas constant and T, temperature. The Nernst equation represents an equilibrium state. When the electrochemical potential is deviated from its equilibrium value by, for example, applying an external electric field, either reduction (leading to deposition of solid) or oxidation (dissolution of solid) reaction will take place on the surface or metal electrode till a new equilibrium state is reached. The difference in potential is referred to as the over-potential or over-voltage. A careful control of over-potential is very important to avoid electrolysis of solvent or deposition of impurity phase. In addition, the interactions of the solute ion M^{m+} with the solvent, or with complex-forming ligands should be considered. These interactions and other factors such as the ionic strength of the solution must be carefully controlled. Besides thermodynamics, there are many kinetic factors that influence the deposition of elemental films. The rate of the electron transfer reaction, i.e. the oxidation-reduction kinetics, influences the nature and morphology of the deposit. The nucleation rate of crystals is a function of the over potential, and also influences the nature of the deposit. In the case of a diffusion limited deposition, the rate of mass transport of solute species to the electrode surface has great effect on the rate of deposition that can be achieved. Electrolyte agitation can lessen the diffusion layer thickness and favor rapid deposition, but maximum stable growth is generally produced in solutions of relatively high solute activity, high diffusion coefficient (low solution viscosity), and low growth velocity. Dissociation kinetics of solvated or complex ions influences the metal ion activity at the electrode surface and may limit the deposition rate that can be achieved for desired deposition morphology.

For the growth of films by electrodeposition, a few practical concerns deserve a brief discussion here:

(1) Though aqueous solutions are often used, nonaqueous solvent or molten salts are also used. Electrolysis of water is one of the main reasons that nonaqueous solvent or molten salts are used.

(2) The electrical conductivity of the deposit must be high enough to permit the deposition of successive layers. The electrodeposition is therefore applied only for the growth of metal, semiconductors and conductive polymer films.

(3) Deposition can be accomplished at constant current or constant potential, or by other means, such as involving pulsed current or voltage.

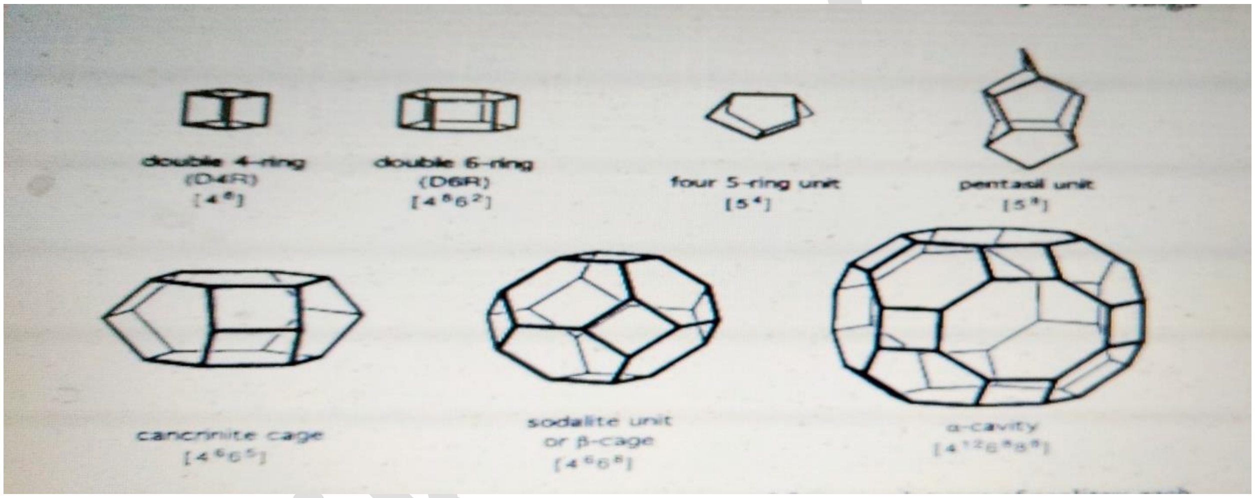
(4) Post treatment may be employed to improve the characteristics of the deposits.

Crystalline microporous materials: zeolites

Zeolites are crystalline aluminosilicates and were first discovered in 1756.There are 34 naturally occurring zeolites and nearly 100 synthetic type zeolites.

A zeolite has a three-dimensional framework structure with uniformly sized pores of molecular dimensions, typically ranging from ~0.3 to 1 nm in diameter, and pore volumes vary from about 0.1 to 0.35cc/g. Zeolites have a broad diverse spectrum of applications, and examples include catalysts, adsorbents and molecular sieves.

Zeolites are tectoaluminosilicates with a formal composition $M_{2/n}0.Al_2O_3.xSi0_2.yH_2O$ (n = valence state of the mobile cation, M^+ and x ≥2), in that they are composed of TO4 tetrahedra (T = tetrahedral atom, i.e. Si, Al), each oxygen atom is shared between adjacent tetrahedral, which leads to the framework ratio of O/T being equal to 2 for all zeolite. A dimensional framework is formed by 4-corner connecting TO_4 tetrahedra. When a zeolite is made of pure silica without any defects, each oxygen atom at the corner is shared by two $Si0_4$ tetrahedra and the charge is balanced. When silicon is replaced by aluminum, alkali metal ions, such as K^+, Na+, alkaline earth ions, such as Ba2+, Ca2+, and protons, H^+ are typically introduced to balance the charges. Such a framework formed is relatively open and characterized by the presence of channels and cavities. The size of the pores and the dimensionality of the channel system are determined by arrangement of TO_4 tetrahedra. More specifically, the pore sizes are determined by the size of the rings that are formed by connecting various numbers of TO_4 tetrahedra or T atoms. An 8-ring is designated to a ring comprised of 8 TO_4 tetrahedra and is considered to be a small pore opening (0.41 nm in diameter), a 10-ring medium one (0.55 nm), and a 12- ring large one (0.74 nm), when rings are free of distortion. Depending on the arrangement or the connection of various rings, different structures or pore openings, such as cages, channels, chains and sheets, can be formed. Figure shows some of these subunits, in which each cross point is designated to a TO_4 tetrahedron for clarity. In this figure, the designations in terms of the n-rings defining the faces of these subunits are also included. For example, a cancrinite cage subunit is defined by six 4-rings and five 6-rings, and is thus designated a $[4^6 6^5]$ cage.



Zeolites are normally prepared by hydrothermal synthesis technique. A typical synthesis procedure involves the use of water, a silica source, an alumina source, a mineralizing agent and a structure-directing agent. The sources of silica are numerous and include colloidal silica, fumed silica, precipitated silica and silicon alkoxides. Typical alumina sources include sodium aluminate, boehmite, aluminum hydroxide, aluminum nitrate and alumina. The typical mineralizing agent is hydroxyl ion, OH- and fluorine ion, F-. The structure-directing agent is a soluble organic species, such as quaternary ammonium ion, which assists in the formation of the silica framework and ultimately resides within the intracrystalline voids. Alkali metal ions can also play a structure-directing role in the crystallization process. Table 6.4 lists the reactants, synthesis temperatures, and the physical and chemical properties of zeolites Na-A and TPA-ZSM-5.

The syntheses can be sensitive to the reagent type, the order of addition, the degree of mixing, the crystallization temperature and time and the composition.

There are numerous complex chemical reactions and organic-inorganic interactions occurring during the synthesis process.

Zeolites are subsequently formed through nucleation and crystallization from these systems. At least three types of crystal building units have been suggested for the growth of zeolites: (i) tetrahedral monomeric species are considered as the primary building units, (ii) secondary building units are the crystal building units, and (iii) clathrates are the building units in the nucleation and crystallization of zeolites.

0rganic-Inorganic Hybrids

Organic-inorganic hybrids are materials in which organic and inorganic components interpenetrate each other in nanometer scale and both form percolated three-dimensional networks commonly by sol-gel processing. Such organic-inorganic hybrids have also been termed Ormosils (organically modified silicates) or Ormocers (organically modified ceramics) in literature.

Hybrids are generally divided into two classes:

(i) hybrids that consist of organic molecules, oligomers or low molecular weight polymers embedded in an inorganic matrix to which they are held by weak hydrogen bonds or van der Waals forces, and

(ii) hybrids in that the organic and inorganic components are linked to each other through covalent bonds.

Class I hybrids can be considered as molecular scale nanocomposites where organic components are physically trapped in an inorganic matrix; whereas class II hybrids can be considered as a huge molecule that links organic and inorganic components through true chemical bonds.

Class I hybrids

There are a few routes developed for the synthesis of class I hybrids, including hydrolysis and condensation of alkoxides inside soluble organic polymers, mixing alkoxides and organic compounds in a common solvent, and impregnating a porous oxide gel with organic compounds. All three techniques have been widely explored for the formation of various organic-inorganic hybrids. For example, hybrids comprising organic dyes embedded in inorganic matrix, such as silica, aluminosilicate and transition metal oxide, composed of polymers in inorganic matrix, such as poly(N-vinyl pyrrolidone)-silica'and poly (methylmethacrylate)-silica are made by hydrolysis-condensation of alkoxides together with soluble organic polymers. Simultaneous gelation of the organic and inorganic components by mixing alkoxides and organic components in a common solvent is a method to ensure the formation of interpenetrated three-dimensional networks of both organic and inorganic components. However, the challenge is to prevent phase segregation and precipitation of organic components during hydrolysis and condensation processing, some precursor modification is desired. Various silica-based hybrids with organics including polyparaphenylene and polyaniline were synthesized using this approach. Infiltration of organic components into highly porous inorganic gel networks is yet another method to make class I hybrids such as PMMA-si1ica. Ordered hybrids can also be made by intercalation of organic compounds in ordered inorganic hosts, which include clay silicates, metal phosphates, layered metal oxides, halides or chalcogenides. For example, alkyl amines can be intercalated in between vanadium oxide layers that was made by hydrolyzing and condensing $VO(OPr^n)_3$ in n-propanol.

Class II hybrids

Class II hybrids comprise organic and inorganic components chemically bonded with each other and truly differ from organic-inorganic nanocomposites. In general, such hybrids are synthesized by hydrolyzing and polymerizing organic and inorganic precursors simultaneously. Inorganic precursors are referred to inorganic salts, such as $Sicl_4$ & and $ErCl_3$, organic salts, such as $Cd(acac)_2$, and alkoxides, such as $Al(OR)_3$ and $Ti(OR)_4$ where R is alkyl group. All the coordination groups associated with the metal cations in inorganic precursors are hydrolysable, i.e. readily replaceable by hydroxyl andor 0x0 groups during hydrolysis and condensation process. Organic precursors consist of at least one unhydrolyzable coordination group and examples are $Si(OR)_3R'$ and $Si(OR)_2R_2^{'}$, which are also known as organoalkoxysilanes where R' is also an alkyl group linked to Si through Si-C bond. Such unhydrolyzable organic groups are referred to as pendant organic groups. For organoalkoxysilanes, no three-dimensional network would be formed if there are more than one pendant organic group attached to each silicon atom.

There are other forms of organic precursors in which unhydrolyzable organic groups bridge two silicon atoms. Such organic groups are referred to as bridge groups. Examples of such organoalkoxysilanes are given in Fig.

Since metal-carbon bonds are very stable during sol-gel processing and unhydrolyzable, the organic group R associated with the precursors will be incorporated into inorganic sol-gel network directly together with the metal cations. Typical hydrolysis and condensation reactions in the formation of such hybrids can be described as follows, taking silica-based hybrids as an example:

$Si(OR)4 + 4H20 \rightleftarrows Si(OH)4 + 4 HOR$ (1)

$Si(OR),R + 3H20 \rightleftarrows Si(OH)3R' + 3HOR$ (2)

$Si(OH)4 + Si(OH)3R' \rightleftarrows (HO)3Si\text{-}O\text{-}Si(OH)2R'$ (3)

$Si(OH)3R + Si(OH)3R' \rightleftarrows R'(H0)2Si - 0- Si(OH)2R$ (4)

It should be noted that although organoalkoxysilanes are the most useful and widely used family of organometallics for the synthesis of hybrid oxideorganic materials, other organometallics are also synthesized and used for the synthesis of organic-inorganic hybrids by co-condensation. For example, butenyl chains were linked to Sn atom directly with C-Sn bonds. The incorporation of organic components into inorganic matrix through either physical trapping or chemical bonding not only introduces and modifies various physical properties. The presence of organic components would 21also exert appreciable influences on the sol-gel processing and the resultant microstructures. Organic groups may have catalytic effects to promote hydrolysis and condensation reactions. Long-chained organic ligands may also introduce steric diffusion barrier or increase the viscosity of the sol, resulting in a diffusion-limited condensation or polymerization process. Depending on the nature and amount of organic components introduced into the systems, highly porouszo5 or relatively dense hybrid can be prepared without subjecting to heat-treatment at elevated temperatures. Some unique hierarchical microstructures can also be obtained by combining both highly porous and relatively dense structures with appropriately designed processing.

Organic-inorganic hybrids with ordered nanostructures can be easily achieved by evaporation-induced self-assemblyas demonstrated by Brinker .