Requirements for ALD Precursors

Table 5.2. Requirements for ALD Precursors

Requirement	Comments
Volatility	For efficient transportation, a rough limit of 0.1 Torr at the applicable maximum source temperature Preferably liquids or gases
No self-decomposition	Would destroy the self-limiting film growth mechanism
Aggressive and complete reactions	Ensure fast completion of the surface reactions and thereby short cycle times Lead to high film purity No problems of gas phase reactions
No etching of the film or substrate material	No competing reaction pathways Would prevent the film growth
No dissolution to the film	Would destroy the self-limiting film growth mechanism
Un-reactive byproduct	To avoid corrosion Byproduct re-adsorption may decrease the growth rate
Sufficient purity	To meet the requirements specific to each process
Inexpensive	
Easy to synthesize & handle	
Nontoxic and environmentally friendly	

Advantages of ALD (compared to other vapor phase deposition methods)

- (1) precise control of film thickness
  - 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.
- (2) conformal coverage.
  - due to the fact that the film deposition is immune to variations caused by nonuniform distribution of vapor or temperature in the reaction zone.

Applications and limitations of ALD

- ALD is an established technique for the production of large area electroluminescent displays, and is a likely future method for the production of very thin films needed in microelectronics.
- Limitations
  - Many other potential applications of ALD are discouraged by its low deposition rate, typically <0.2 nm (less than half a monolayer) per cycle.

Self Assembly

- Self-assembly
  - is a process in which a set of components or constituents spontaneously forms an ordered aggregate through their global energy minimization.
  - is a process that ordered arrangement of molecules and small components such as small particles occur spontaneously under the influence of certain forces such as chemical reactions, electrostatic attraction, and capillary forces.
  - Macromolecules (e.g. proteins, nucleic acid sequences, micelles, liposomes, and colloids)in nature adapt their final folding and conformation by self-assembly processes.
- Self-assembled monolayers or multiple layers of molecules
  - In general, chemical bonds are formed between the assembled molecules and the substrate surface, as well as between molecules in the adjacent layers.
  - The major driving force here is the reduction of overall chemical potential.
  - A SAM is defined as a 2-D film with the thickness of one molecule that is attached to a solid surface through a covalent bond.

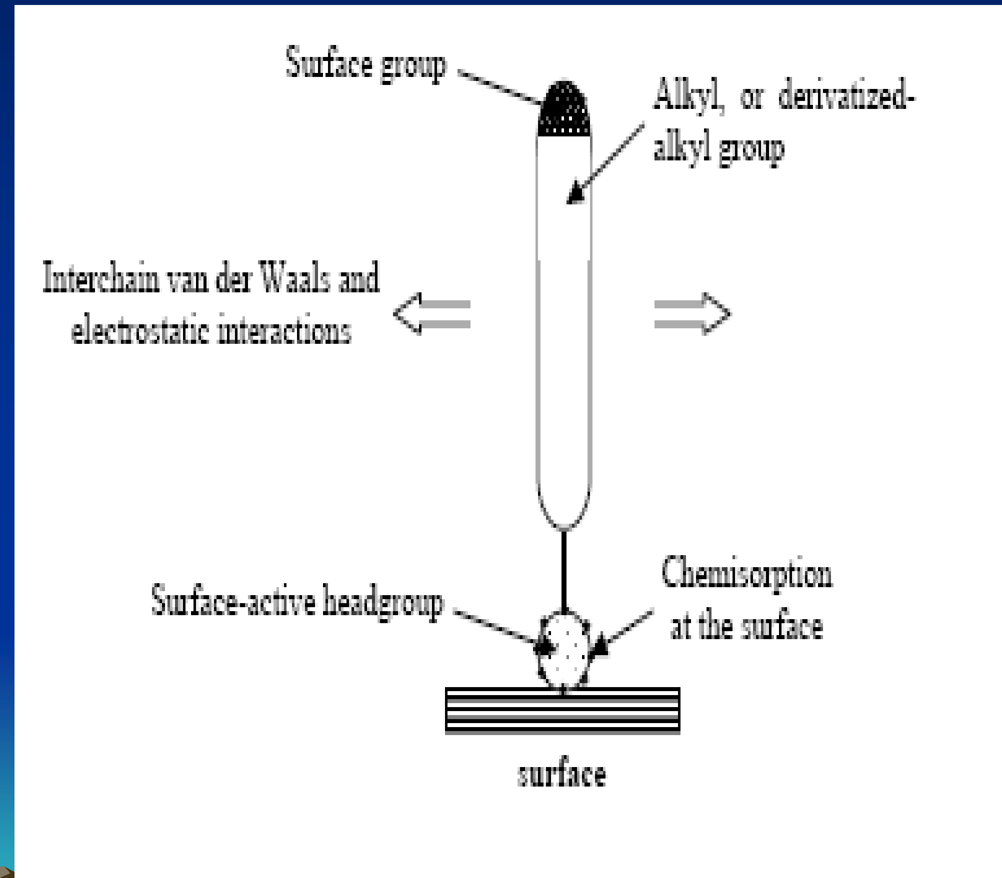
Self-assembled monolayers (SAMs)

- SAMs 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.

SAMs…

3 Parts of a self-assembling surfactant molecule :

- The head group that chemisorbs on the substrate surface.
  - very strong molecular-substrate interactions (e.g. covalent Si-O and S-Au bonds, ionic – CO_2^-- Ag^+ bond.
- The alkyl chain.
- The third molecular part is the terminal functionality
  - surface functional groups in SAMs are thermally disordered at room temperature.



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SAMs

- The driving force for the self-assembly includes
  - electrostatic force
  - hydrophobicity and hydrophilicity
  - capillary force
  - chemisorption.

- Types of self-assembly methods for the organic monolayers include
  - (1) organosilicon on hydroxylated surfaces, such as SiO_2 on Si, Al_2O_3 on Al, glass,
  - (2) alkanethiols on gold, silver, and copper,
  - (3) dialkyl sulfides on gold,
  - (4) dialkyl disulfides on gold,
  - (5) alcohols and amines on platinum, and
  - (6) carboxylic acids on aluminum oxide and silver.

- Self-assembly methods grouped based on the types of chemical bonds formed between the head groups and substrates.
  - (1) covalent Si-O bond between organosilicon on hydroxylated substrates that include metals and oxides,
  - (2) polar covalent S-Me bond between alkanethiols, sulfides and noble metals such as gold, silver, platinum, and copper, and
  - (3) ionic bond between carboxylic acids, amines, alcohols on metal or ionic compound substrates.

- Application of self-assembly:
  - the introduction of various desired functionalities and surface chemistry to the inorganic materials.

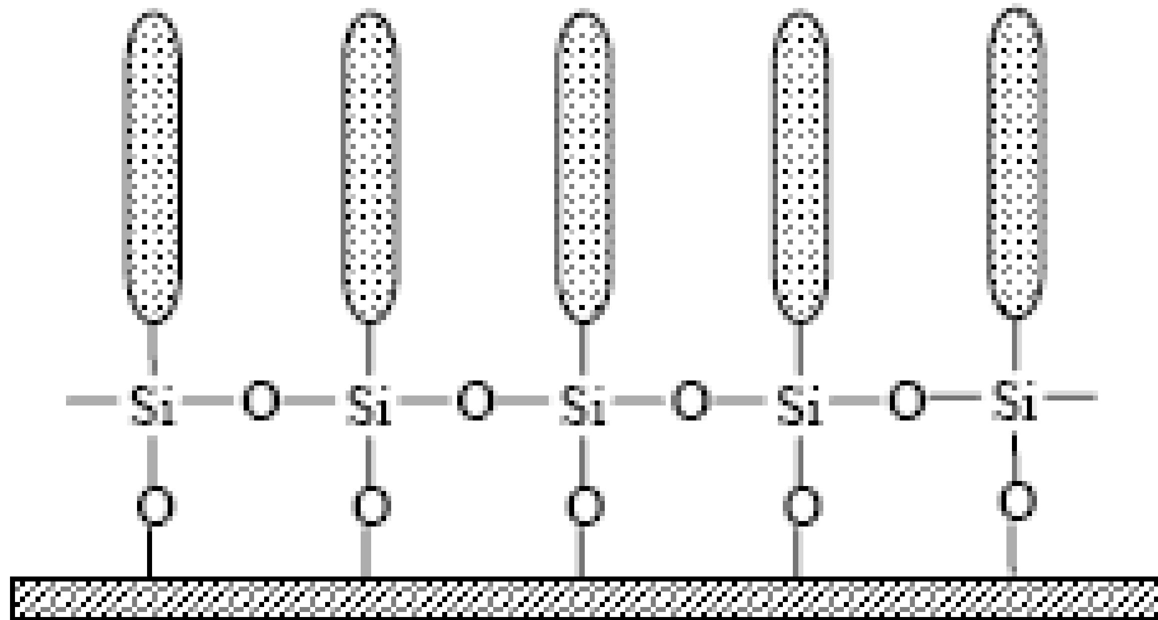
Monolayers of Organosilicon or Alkylsilane Derivatives

- Alkylsilanes: $RSiX_3$, R_2SiX_2, or R_3SiX, where X = chloride or alkoxy and R = a carbon chain that can bear different functionalities, such as amine or pyridinyl.
- The formation of monolayers is simply by reacting alkylsilane derivatives with hydroxylated surfaces such as SiO_2, TiO_2.

Monolayers of Organosilicon or Alkylsilane Derivatives

- Introduction of a hydroxylated surface into a solution of alkyltrichlorosilane in an organic solvent
- After immersion, the substrate is rinsed with methanol, DI water and then dried.
- Organic solvent is in general required for the self-assembly for the alkylsilane derivatives, since silane groups undergo hydrolysis and condensation reaction when in contact with water, resulting in aggregation.
- For alkylsilanes with more than one chloride or alkoxy groups, surface polymerization is commonly invoked deliberately by the addition of moisture, so as to form silicon-oxygen-silicon bonds between adjacent molecules.

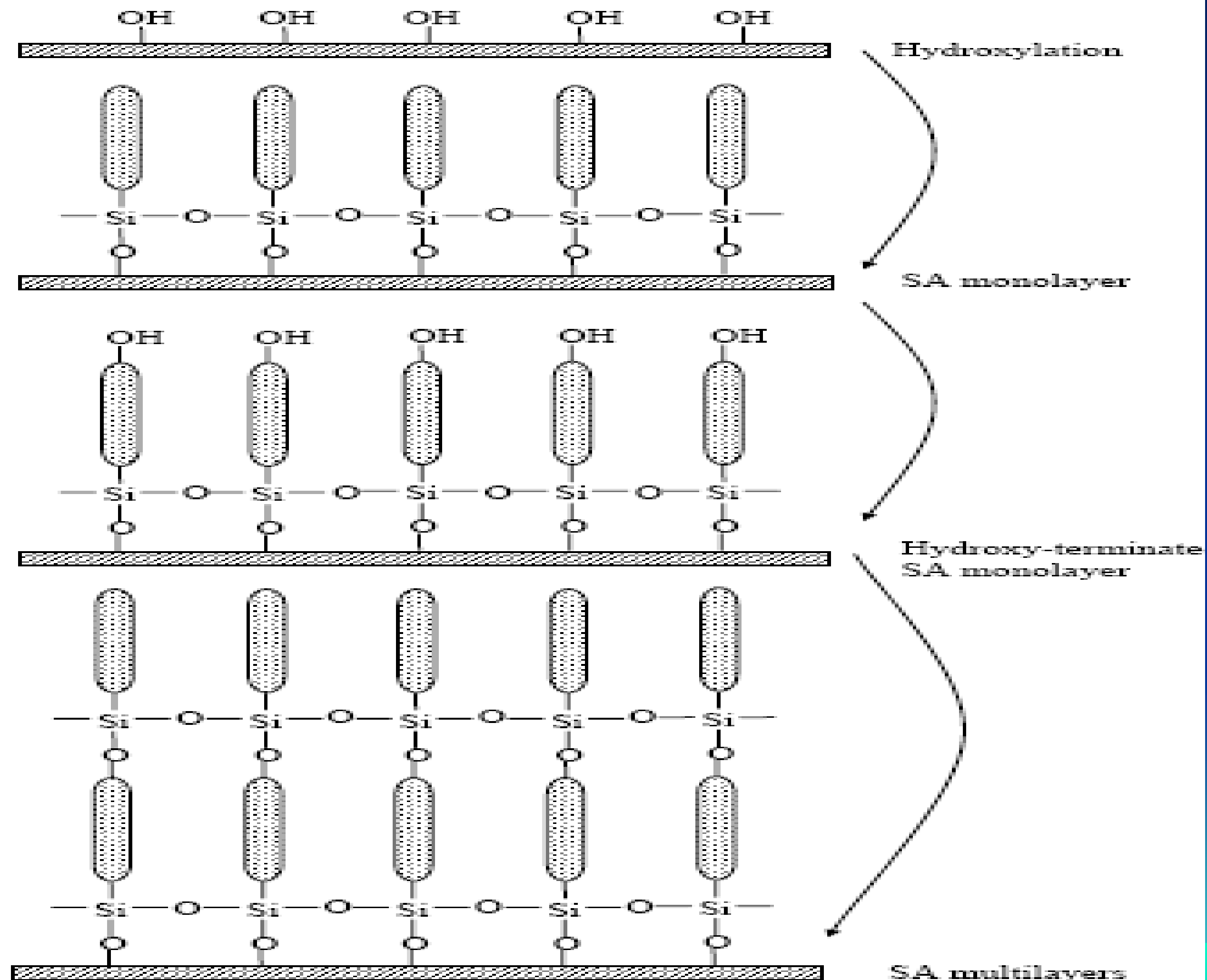
Monolayers of Organosilicon or Alkylsilane Derivatives



Multilayers of Organosilicon or Alkylsilane Derivatives

- The construction of an SA multilayer requires that the monolayer surface be modified to be a hydroxylated surface, so that another SA monolayer can be formed through surface condensation.
- Such hydroxylated surfaces can be prepared by a chemical reaction and the conversion of a nonpolar terminal group to a hydroxyl group.
  - e.g. a reduction of a surface ester group,
  - a hydrolysis of a protected surface hydroxyl group,
  - a hydroboration-oxidation of a terminal double bond.
  - oxygen plasma etching followed with immersion in DI-water
- A subsequent monolayer is added onto the activated or hydroxylated monolayer through the same self-assembly procedure and multilayers can be built just by repetition of this process.

Multilayers of Organosilicon or Alkylsilane Derivatives



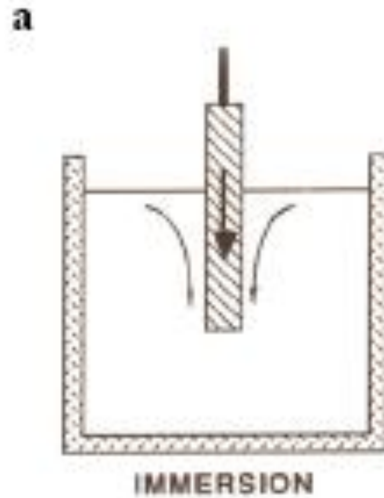
Sol-Gel Films

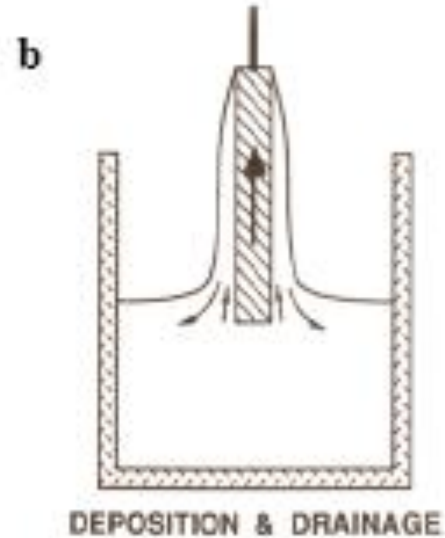
- Sol-gel processing
  - is widely used in the synthesis of inorganic and organic-inorganic hybrid materials
  - is capable of producing nanoparticles, nanorods, thin films, and monolith.
  - sol-gel films are made by coating sols onto substrates.
  - Commonly used methods for sol-gel film deposition
    - spin-coating
    - dip-coatings
    - spray
    - ultrasonically pulverized spray

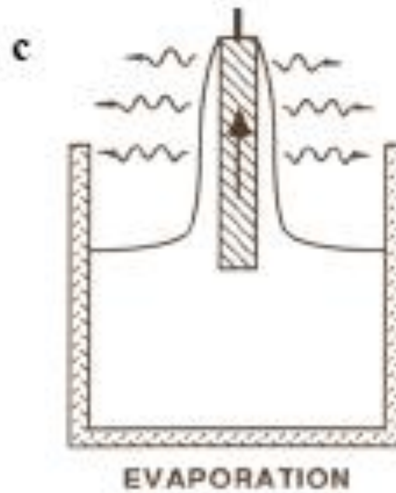
Dip-coating

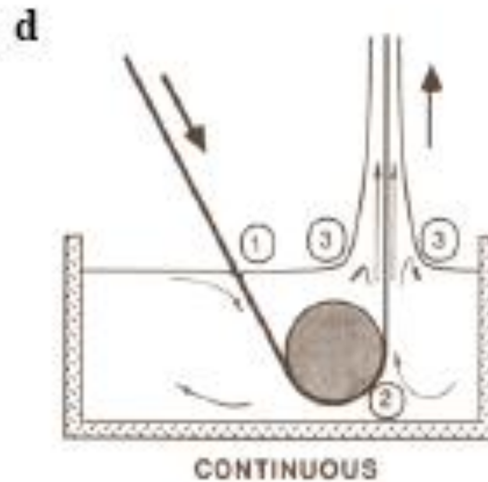
- a substrate is immersed in a solution and withdrawn at a constant speed. As the substrate is withdrawn upward, a layer of solution is entrained, and a combination of viscous drag and gravitational forces determines the film thickness.
- Stages of the dip-coating process (next slide)
  - Immersion
  - Deposition & drainage
  - Evaporation
  - Continuous
- The thickness of a dip-coated film is commonly in the range of 50-500 nm

Stages of the dip-coating process

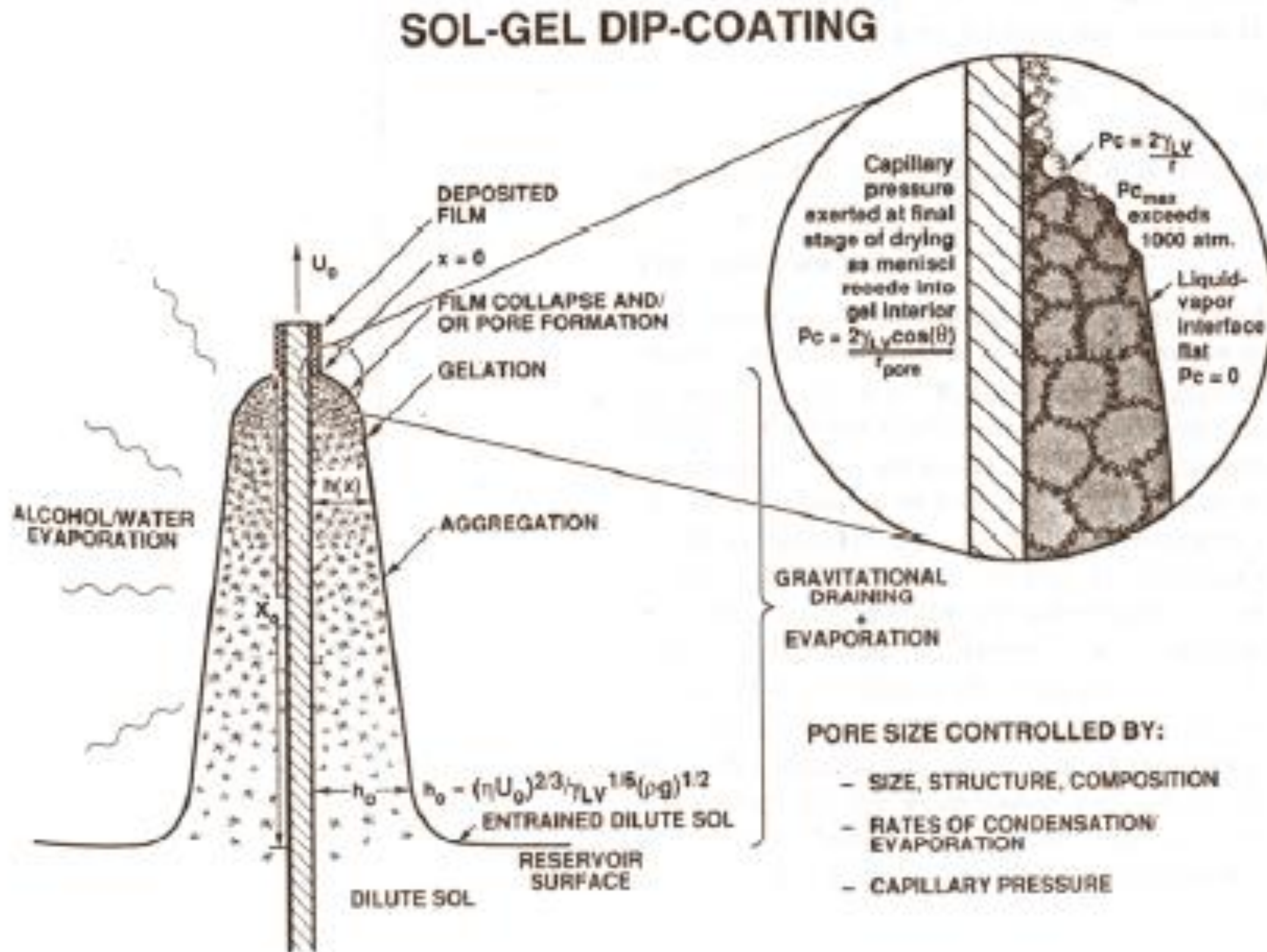








Sol-Gel Dip-Coating



Spin-coating

- is used routinely in microelectronics to deposit photoresists and specialty polymers.
- Four stages of spin coating:
  - delivery of solution or sol onto the substrate center
  - spin-up
  - spin-off
  - evaporation (overlaps with all stages)
- After delivering the liquid to the substrate, centrifugal forces drive the liquid across the substrate (spin-up). The excess liquid leaves the substrate during spin off. When flow in the thin coating is no longer possible, evaporation takes over to further reduce the film thickness.
- A uniform film can be obtained when the viscosity of the liquid is not dependent on shear rate (i.e., Newtonian) and the evaporation rate is independent of position.

- the film thickness can be controlled by adjusting the solution properties and the deposition conditions.
-
- In the process of creating a sol-gel coating, the removal of solvent or drying of the coating proceeds simultaneously with continues condensation and solidification of the gel network. The competing processes lead to capillary pressure and stresses induced by constrained shrinkage, which result in the collapse of the porous gel structure, and may also lead to the formation of cracks in the resultant films.
- The drying rate plays a very important role in the development of stress and formation of cracks particularly in the late stages and depends on the rate at which solvent or volatile components diffuse to the free surface of the coating and the rate at which the vapor is transported away in the gas.
- Stress develops during drying of a solidified coating due to constrained shrinkage. Solvent loss after solidification is a common source of stress in solvent-cast polymer coatings.Solvent content at solidification should be minimized to lower the stress in the coating.
- In the formation of sol-gel coating, it is very important to limit the condensation reaction rate during the removal of solvent upon drying, so that the volume fraction of solvent at solidification is kept small. To relieve stresses, the material can relax internally by molecular motion or it can deform. Internal relaxation slows as the material approaches an elastic solid and deformation is restricted by adherence to the substrate. Since the stress-free state shrinks during solidification and adherence to the substrate confines shrinkage in the coating to the thickness direction, in-plane tensile stresses result. Cracking is another form of stress relief. For sol-gel coatings, the formation of cracks limits the coating thickness commonly less than 1 micron.
- It should also been noted that sol-gel coatings are commonly porous and amorphous. For many applications, subsequent heat treatment is required to achieve full densification and convert amorphous to crystalline. Mismatch of thermal expansion coefficients of sol-gel coatings and substrates is another important source of stress, and a residual stress in sol-gel coatings can be as high as 350 MPa.
- Porosity is another important property of sol-gel film. Although for many applications, heat-treatment at elevated temperatures is employed to remove the porosity, the inherited porosity enables sol-gel film for many applications such as matrix of catalyst, host of sensing organic or biocomponents, electrode in solar cells. Porosity itself also renders other unique physical properties such as low dielectric constant, low thermal conductivity, etc.

Organic-inorganic hybrids

- a new type of materials, which are not present in nature,
- synthesized by the sol-gel method.
- The organic component can significantly modify the mechanical properties of the inorganic component.
- The organic and inorganic components can interpenetrate each other on a nanometer scale.
  - **Depending on the interaction between organic and inorganic components, hybrids are divided into two classes:**
    - **(1) hybrids consisting of organic molecules, oligomers or low molecular weight polymers embedded in an inorganic matrix to which they are held by weak hydrogen bond or van der Waals force and**
    - **(2) in those, the organic and inorganic components are bonded to each other by strong covalent or partially covalent chemical bonds.**
- The porosity can also be controlled as well as the hydrophilic and hydrophobic balance. Hybrids with new optical or electrical properties can be tailored. Some hybrids can display new electrochemical reactions as well as special chemical or biochemical reactivity.

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
- Amphiphile
  - A molecule that is insoluble in water, with one end that is hydrophilic (preferentially immersed in water) and the other that is hydrophobic (preferentially resides in air or in the nonpolar solvent)
  - E.g stearic acid $C_{17}H_{35}CO_2H$

Comparison of Typical Thin Film Deposition Technology

Process	Material	Uniformity	Impurity	Grain Size	Film Density	Deposition Rate	Substrate Temperature	Directional	Cost
Thermal Evaporation	Metal or low melting-point materials	Poor	High	10 ~ 100 nm	Poor	1 ~ 20 A/s	50 ~ 100 °C	Yes	Very low
E-beam Evaporation	Both metal and dielectrics	Poor	Low	10 ~ 100 nm	Poor	10 ~ 100 A/s	50 ~ 100 °C	Yes	High
Sputtering	Both metal and dielectrics	Very good	Low	~ 10 nm	Good	Metal: ~ 100 A/s Dielectric: ~ 1-10 A/s	~ 200 °C	Some degree	High
PECVD	Mainly Dielectrics	Good	Very low	10 ~ 100 nm	Good	10 - 100 A/s	200 ~ 300 °C	Some degree	Very High
LPCVD	Mainly Dielectrics	Very Good	Very low	1 ~ 10 nm	Excellent	10 - 100 A/s	600 ~ 1200 °C	Isotropic	Very High

Summary

- Films with thickness <100 nm can be deposited using a variety of techniques
- Methods offer varied degrees of control of thickness and surface smoothness
- MBE and ALD offer the most precise control of deposition at the single atomic level, and the best quality of the grown film.
- Disadvantages of MBE and ALD:
  - Complicated deposition instrumentation
  - Slow growth rate
- SA is another method offering a single atomic level control
- Limitation of SA
  - Limited to the fabrication of organic-inorganic hybrid films