5.6. Atomic Layer Deposition

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 is 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. Excellent reviews on ALD have been published by Ritala and Leskelä\textsuperscript{1,2}. 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 growth ZnS film\textsuperscript{3}. More publications appeared in open literature in early 1980's\textsuperscript{4,5,6}. 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, 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 in the way one layer at a time.

Figure 5.15 schematically illustrates the process of titania film growth by ALD. The substrate is hydroxylated first, prior to the introduction of titanium precursor, titanium tetrachloride. Titanium tetrachloride will react with the surface hydroxyl groups through a surface condensation reaction:

\[
\text{TiCl}_4 + \text{HO-Me} \rightarrow \text{Cl}_3\text{Ti-O-Me} + \text{HCl} \quad (5.35)
\]

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. Trichloride titanium clusters chemically bonded onto the substrate surface undergo hydrolysis reaction:

\[
\text{Cl}_3\text{Ti-O-Me} + \text{H}_2\text{O} \rightarrow (\text{HO})_3\text{Ti-O-Me} + \text{HCl} \quad (5.36)
\]

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

\[
(\text{HO})_3\text{Ti-O-Me} + (\text{HO})_3\text{Ti-O-Me} \rightarrow \text{Me-O-Ti(OH)}_2\text{-O-Ti (HO)}_2\text{-O-Me} + \text{H}_2\text{O} \quad (5.37)
\]

The by-product HCl and excess H\textsubscript{2}O will be removed from the reaction chamber. One layer of TiO\textsubscript{2} 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 TiO\textsubscript{2} 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. ZnCl\(_2\) and H\(_2\)S are used as precursors. First, ZnCl\(_2\) is chemisorbed on substrate, and then H\(_2\)S is introduced to react with ZnCl\(_2\) to deposit a monolayer of ZnS on 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, fluorides, elements, II-VI, II-VI, and III-V compounds, in epitaxial, polycrystalline or amorphous form deposited by ALD are summarized in Table 5.1\(^1\,\,2\).

**Table 5.1. Thin Film Materials Deposited by ALD\(^1\,\,2\)**

<table>
<thead>
<tr>
<th>II-VI compounds</th>
<th>ZnS, ZnSe, ZnTe, ZnS(_{1-x})Se(<em>x), CaS, SrS, BaS, SrS(</em>{1-x})Se(<em>x) CdS, CdTe, MnTe, HgTe, Hg(</em>{1-x})Cd(<em>x)Te, Cd(</em>{1-x})Mn(_x)Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-VI based phosphors</td>
<td>ZnS:M (M = Mn, Tb, Tm), CaS:M (M = Eu, Ce, Tb, Pb), SrS:M (M = Ce, Tb, Pb, Mn, Cu)</td>
</tr>
<tr>
<td>III-V compounds</td>
<td>GaAs, AlAs, AlP, InP, GaP, InAs, Al(<em>x)Ga(</em>{1-x})As, Ga(<em>x)In(</em>{1-x})As, Ga(<em>x)In(</em>{1-x})P</td>
</tr>
<tr>
<td>Nitrides</td>
<td>AlN, GaN, InN, SiN(<em>x), TiN, TaN, Ta(</em>{2})N(_5), NbN, MoN, W(_2)N, Ti-Si-N</td>
</tr>
<tr>
<td>Oxides</td>
<td>Al(_2)O(_3), TiO(_2), ZrO(_2), HfO(_2), Ta(_2)O(_5), Nb(_2)O(_5), Y(_2)O(_3), MgO, CeO(_2), SiO(_2), La(_2)O(_3), SrTiO(_3), BaTiO(_3), Bi(_2)Ti(_3)O(_9), In(_2)O(_3), In(_2)O(_3):Sn, In(_2)O(_3):F, In(_2)O(_3):Zr, SnO(_2), SnO(_2):Sb, ZnO, ZnO:Al, Ga(_2)O(_3), NiO, CoO(_x), YBa(_2)Cu(_3)O(_7-x), LaCoO(_3), LaNiO(_3)</td>
</tr>
<tr>
<td>Fluorides</td>
<td>CaF(_2), SrF(_2), ZnF(_2)</td>
</tr>
<tr>
<td>Elements</td>
<td>Si, Ge, Cu, Mo, Ta, W</td>
</tr>
<tr>
<td>Others</td>
<td>La(_2)S(_3), PbS, In(_2)S(_3), CuGaS(_2), SiC</td>
</tr>
</tbody>
</table>

The choice of proper precursors is the key issue in a successful design of an ALD process. Table 5.2 summarizes the requirements for ALD precursors\(^1\,\,2\). A variety of precursors have been used in ALD. 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\(^7\). Metallorganic compounds including both organometallic compounds and metal alkoxides are widely used. For nonmetals, the simple hydrides have mostly been used: H\(_2\)O, H\(_2\)O\(_2\), H\(_2\)S, H\(_2\)Se, H\(_2\)Te, NH\(_3\), N\(_2\)H\(_4\), PH\(_3\), AsH\(_3\), SbH\(_3\), and HF.

In comparison to other vapor phase deposition methods, ALD offer advantages particularly in the following aspects: (1) precise control of film thickness and (2) 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. Figure 5.16 are the X-ray diffraction spectra and the cross-sectional SEM image of 160 nm Ta(Al)N(C) film on patterned silicon wafer\(^8\). The film is polycrystalline and shows perfect conformality. The deposition temperature was 350 °C and
precursors used were TaCl$_5$, trimethylaluminum (TMA), and NH$_3$. However, it should be noted that excellent conformal coverage can only be achieved when the precursor doses and pulse time are sufficient for reaching the saturated state at all surface at each steps at all surfaces and no extensive precursor decomposition takes place. ALD has demonstrated its capability of depositing multilayer structures or nanolaminates and Figure 5.17, as an example, shows such a schematic representation of nanolaminates prepared onto glass substrates by ALD$^9$.

Table 5.2. Requirements for ALD Precursors

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

ALD is an established technique for the production of large area electroluminescent displays$^{10}$, and is a likely future method for the production of very thin films needed in microelectronics$^{11}$. However, many other potential applications of ALD are discouraged by its low deposition rate, typically <0.2 nm (less than half a monolayer) per cycle. For silica deposition, completing a cycle of reactions typically requires more than 1 minute$^{12,13}$. Some recent efforts have been directed towards the development of rapid ALD deposition method. For example, highly conformal layers of amorphous silicon dioxide and aluminum oxide nanolaminates were deposited at rates of 12 nm or > 32 monolayers per cycle, and the method has been referred to as “alternating layer deposition”$^{14}$. The exact mechanism for such a multilayer deposition in each cycle is unknown, but obviously different from the self-limiting growth discussed above. The precursor employed in this experiment, tris(tert-butoxy)silanol, can react with each other, and thus the growth is not self-limiting.

5.8. 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. Further discussion on self-assembly of nanoparticles and nanowires will be presented in Chapter 7. 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 Figure 5.19. 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-O and S-Au bonds, and ionic \(-\text{CO}_2\text{H}^+\) bond. The second part is the alkyl chain, and the exothermic energies associated with its interchain van der Waals interactions is 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., \(\sim 40-45\) 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 that chemisorb on the substrates. There are several types of self-assembly methods for the organic monolayers and these include (1) organosilicon on hydroxylated surfaces, such as SiO\(_2\) on Si, Al\(_2\)O\(_3\) on Al, glass, etc, (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. 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 (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.

One of the important applications of self-assembly that has been extensively studied is the introduction of various desired functionalities and surface chemistry to the inorganic materials. In the synthesis and fabrication of nanomaterials and nanostructures, particular the core-shell structures, self-assembled organic monolayers are widely used to link different materials together.
### 5.8.1. Monolayers of Organosilicon or Alkylsilane Derivatives

Typical formulas of alkylsilanes are $\text{RSiX}_3$, $\text{R}_2\text{SiX}_2$, or $\text{R}_3\text{SiX}$, where $X$ is chloride or alkoxy and $R$ is a carbon chain that can bear different functionalities, such as amine or pyridyl. The chemistry of organosilicon derivatives has been discussed in a great detail by Plueddemann.\(^\text{30}\)

The formation of monolayers is simply by reacting alkylsilane derivatives with hydroxylated surfaces such as $\text{SiO}_2$, $\text{TiO}_2$. In a typical procedure, a hydroxylated surface is introduced into a solution (e.g., $\sim 5 \times 10^{-3}$ M) of alkyltrichlorosilane in an organic solvent (e.g., a mixture of 80/20 Isopar-G/CCl\(_4\)) for a few minutes (e.g., 2-3 minutes). A longer immersion time is required for surfactants with long alkyl chains. A reduction in surfactant concentration in solution takes longer time to form a complete monolayer as illustrated in Figure 5.20, which presents the results of stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) monolayers on glass slides.\(^\text{31}\)

The ability of forming a complete monolayer is obviously dependent on the substrate, or the interactions between the monolayer molecules and the substrate surface. 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. In general, monolayers of alkylsilanes may be inherently more disordered than those of alkanethiols, where molecules have more freedom to establish a long-range order. For alkylsilanes with more than one chlorine 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 as sketched in Figure 5.21.

Monolayers of organosilicon were studied for applications in enzyme immobilization as early as in the late 60’s.\(^\text{32}\) Surface silanization for the preparation of hydrophobic surfaces for LB films.\(^\text{33}\) This has also been studied for the preparation of inorganic aerogels under ambient pressure and in the fabrication of low dielectric constant porous inorganic materials.\(^\text{35}\) As well be discussed in the next chapter, the fabrication of oxide-metal core-shell nanostructures is heavily relied on the formation of an organic monolayer linking core and shell materials. For example, in a typical approach to the fabrication of silica-gold core-shell nanostructures, organosilicon with amine as a functional group is used to form a monolayer on the surface of silica nanoparticles by self-assembly. The surface amine groups then attract gold nanoclusters in the solution, which result in the formation of a gold shell.

One of the ultimate goals of using SA films is the construction of multilayer films that contain functional groups that possess useful physical properties in a layer-by-layer fashion. Examples of those functional groups include electron donor or electron acceptor groups, nonlinear optical chromophores, moieties with unpaired spins. 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 hydroxy group. Examples include a reduction of a surface ester group, a hydrolysis of a protected surface hydroxy group, and a hydroboration-oxidation of a terminal double bond.\(^\text{36,37}\) Oxygen plasma etching followed with immersion in DI-water also effectively makes the surface hydroxylated.\(^\text{38}\) 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. **Figure 5.22** shows such a SA multilayer structure. However, it should be noted that in the construction of multilayers, the quality of monolayers formed by self-assembly may rapidly degrade as the thickness of the film increases\(^{20,39}\).

### 5.11. Sol-Gel Films

Sol-gel processing is widely used in the synthesis of inorganic and organic-inorganic hybrid materials and capable of producing nanoparticles, nanorods, thin films, and monolith. In the previous chapters, we discussed the fabrication of nanoparticles and nanorods using sol-gel processing. A general introduction to sol-gel processing was presented in Chapter 3. For more detailed information, the readers are recommended to excellent books by Brinker and Scherer\(^ {40}\), Pierre\(^ {41}\), and Wright and Sommerdijk\(^ {42}\). Sol-gel methods for oxide coatings were reviewed by Francis\(^ {43}\). Here we will focus our discussion only on the fundamentals and methods of the formation of sol-gel thin films. Prior to sol-gel transition or gelation, sol is a highly diluted suspension of nanoclusters in a solvent, and typically sol-gel films are made by coating sols onto substrates. Although some two-dozen methods are available for applying liquid coatings to substrates, the best choice depends on several factors including solution viscosity, desired coating thickness and coating speed\(^ {44}\). Most commonly used methods for sol-gel film deposition are spin- and dip-coatings\(^ {45,46}\), though spray and ultrasonically pulverized spray were also used\(^ {47,48}\).

In 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, \(H\)\(^ {49}\):

\[
H = c_1(\eta U_o/\rho g)^{1/2}
\]

\(5.40\)

Where \(\eta\) is the viscosity, \(U_o\) the withdrawal speed, \(\rho\) the density of the coating sol, and \(c_1\) is a constant. **Figure 5.27** illustrates various stages of the dip-coating process\(^ {50}\). It should be noted that the equation does not account the evaporation of solvent and continuous condensation between nanoclusters dispersed in the sol as illustrated in **Figure 5.28**\(^ {51}\). However, the relationship between the thickness and the coating variables is the same and supported by the experimental results\(^ {52}\), but the proportionality constant is different. The thickness of a dip-coated film is commonly in the range of 50-500 nm\(^ {53}\), though a thinner film of \(\sim 8\) nm per coating was also reported\(^ {54}\).

Spin-coating is used routinely in microelectronics to deposit photoresists and specialty polymers and has been well studied\(^ {55,56}\). A typical spin coating consists of four stages: delivery of solution or sol onto the substrate center, spin-up, spin-off, and 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 thickness of a spin-coated film, \(h\), is given by\(^ {57}\):
\[ H = (1 - \rho_A^\circ/\rho_A)(3\eta \epsilon/2\rho_A^\circ \omega^2) \]  \hspace{1cm} (5.34)

Where \( \rho_A \) is the mass of volatile solvent per unit volume, \( \rho_A^\circ \) its initial volume, \( \omega \) the angular velocity, \( \eta \) the liquid viscosity, and \( \epsilon \) the evaporation rate, which is related to the mass transfer coefficient. It is clear from the equation that 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 and Croll defines such as a stress as:

\[ \sigma = \frac{E(\sigma)(\phi_s - \phi_r)}{(1-\nu)3(1-\phi_t)} \]  \hspace{1cm} (5.35)

where \( E(\sigma) \) is a nonlinear elastic modulus and \( \nu \) the Poisson’s ratio of the coating, \( \phi_s \) and \( \phi_r \) are the volume fractions of solvent at solidification and residual after drying, respectively. The relationship shows that 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. A critical coating thickness, \( T_c \), has been defined:

\[ T_c = \frac{E G_c}{A \sigma^2} \]  \hspace{1cm} (5.36)

Where \( E \) is the Young’s modulus of the film, \( A \) is a dimensionless proportionality constant, and \( G_c \) the energy required to form two new crack surfaces. The concept of critical thickness is supported by experimental reports. For example, a critical thickness of 600 nm was reported in Ceria sol-gel films, and cracks formed above this thickness.

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\textsuperscript{63}.

Organic-inorganic hybrids are a new type of materials, which are not present in nature, and sol-gel is the obliged route to synthesize them\textsuperscript{64,41}. 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 organic component can significantly modify the mechanical properties of the inorganic component\textsuperscript{65}. The porosity can also be controlled as well as the hydrophilic and hydrophobic balance\textsuperscript{66}. Hybrids with new optical\textsuperscript{67,68} or electrical\textsuperscript{69} properties can be tailored. Some hybrids can display new electrochemical reactions as well as special chemical or biochemical reactivity\textsuperscript{70,71}.

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 molecules such as surfactants and diblock polymers have been used to form templates in the synthesis of ordered mesoporous materials, which will be another subject of discussion in the next chapter.

There are many other chemical solution deposition (CSD) methods. Fundamentals discussed above are generally applicable to other CSD methods. For example, the competing processes during drying, the development of stresses, and the formation of cracks are similar to that in sol-gel films.

Figures:
Figure 5.15
Figure 5.16

Figure 5.17
Figure 5.18

Surface group

Alkyl, or derivatized-alkyl group

Interchain van der Waals and electrostatic interactions

Surface-active headgroup

Chemisorption at the surface

Figure 5.19
Figure 5.20

Figure 5.21
Hydroxy-terminated SA monolayer

Hydroxylation

SA monolayer

Hydroxy-terminated SA monolayer

SA multilayers

Figure 5.22
Figure 5.27

Figure 5.28

\[ P_c = \frac{2\gamma L V}{2\gamma L V} \]

Gravitational draining and evaporation

Pore size controlled by:
- Size, structure, composition
- Rates of condensation/evaporation
- Capillary pressure

Alcohol/water evaporation

Gravitational draining and evaporation

Entrained dilute sol

Dilute sol

Reservoir surface

Gelation

Film collapse and/or pore formation

Deposited film

\[ h = \frac{\pi U_0^2}{V_L} \left( 1 - \frac{1}{\rho g} \right)^{1/2} \]

Aggregation

Capillary pressure exerted at final stage of drying as meniscus recedes into gel interior

Pc = 2\gamma L V

Pc,max exceeds 1000 atm.

Liquid-vapor interface flat

Pc = 0
5.13. References: