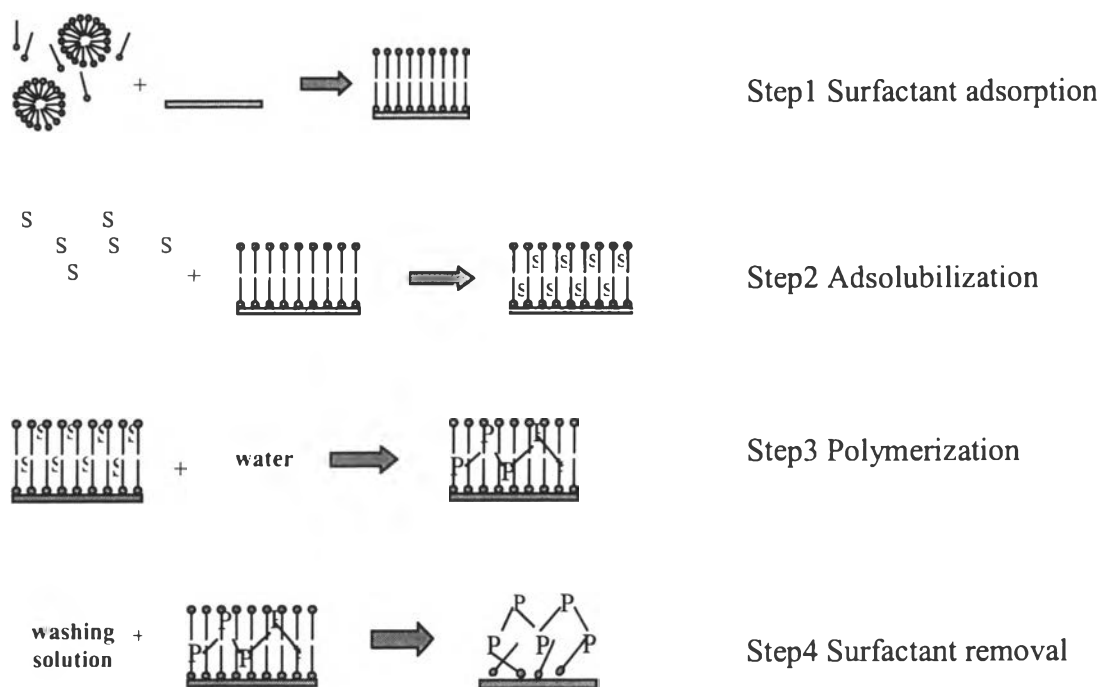


## CHAPTER II LITERATURE SURVEY

### 2.1 Admicellar Polymerization

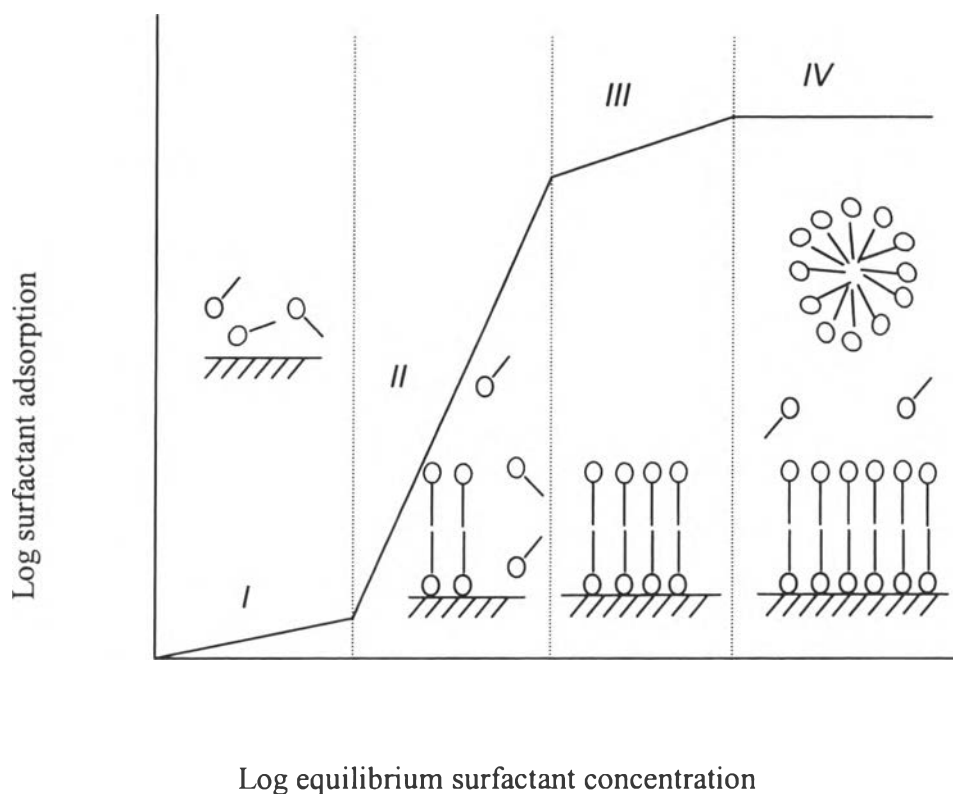
Admicellar polymerization is typically a four-step process as shown in Figure 2.1.



**Figure 2.1** Schematic of the steps in the admicellar polymerization process (O'Haver *et al.*, 1994).

#### 2.1.1 Surfactant Adsorption

When surfactant is present in water solution containing a solid surface, the surfactant can migrate to one of four environments: to the bulk solution, to the solid surface, to a micelle, or to the vapor-liquid interface as shown in Figure 2.2.



**Figure 2.2** Typical adsorption isotherm of surfactant on solid oxide (Rosen, 1989).

In region I the surfactants are adsorbed as monomers and do not interact with one another. The onset of region II is indicated by the sharp increase in the slope of the isotherm. This increase in slope is due to the formation of micelle-like aggregates (admicelles) of adsorbed surfactants. The region II to region III transition can be explained by the transition of the nonionic surfactant from a head down to a head up orientation. Region IV is called the plateau adsorption region and, for most systems, the region III to region IV transition occurs near the Critical Micelle Concentration (CMC) of the surfactant. The adsorption becomes nearly constant above CMC because all additional surfactant goes into the micellar pseudophase at almost the same chemical potential as the surfactant in the first micelles to form and so the chemical potential of the surfactant does not increase as dramatically with surfactant concentration.

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors:

-surfactant: charge, that is, its cationic, anionic, nonionic; length of the ethylene oxide chain; head group size; and concentration in the solution related to the CMC;

-substrate: hydrophilic (mica, silica) or hydrophobic (graphite, molybdenum disulfide), porosity and pore size distribution; surface charge and heterogeneity, and crystalline structure;

Together these factors determine the mechanism by which adsorption occurs as well as the efficiency and effectiveness of adsorption. The formation of admicelles begins in region II of the adsorption isotherm. In this region, the surfactants are adsorbed onto the substrate surface as micelle-like aggregates, that is, as non-continuous aggregates. The adsorption of surfactant molecules is governed mainly by electrostatic and hydrophobic interactions (physical adsorption), though in some cases covalent or chemical bonds are also formed (chemisorption). Compared to ionic surfactants, the driving force behind the adsorption of nonionic surfactants is more complex and often consists of a combination of substrate/surfactant, surfactant/solvent, and surfactant/surfactant interactions (Dong and Mao, 2000). Previously, much of the understanding of nonionic surfactants was based on the study of polyoxyethylene alcohols. Patrick *et al.* (1997) imaged the self-assembled structure of nonionic surfactants, poly(oxyethylene)<sub>n</sub> dodecyl ether (C<sub>12</sub>E<sub>n</sub>) on highly oriented pyrolytic graphite. Stripes with a characteristic periodicity of 55 Å were observed for the C<sub>12</sub>E<sub>5-10</sub> series which were attributed to hemicylindrical hemimicelles. In 1998, Grant *et al.* studied the adsorption of a series of alkylpoly(ethylene oxide)C<sub>n</sub>E<sub>m</sub> surfactants on different substrates. They found that on hydrophilic silica, the formation of globular structures similar to bulk micelles was found. On hydrophobic silica, adsorption results in a surface layer that is laterally homogeneous and is probably a monolayer with ethylene oxide groups in contact with the solution. On graphite, the adsorbed layer is either long, thin aggregates (consistent with a hemicylindrical structure) or a laterally homogeneous layer (consistent with a monolayer with the head groups facing the solution). Nonionic C<sub>12</sub> and C<sub>14</sub> surfactants formed hemicylinders on graphite, while the C<sub>10</sub> surfactants with the same headgroups form a laterally homogeneous layer.

Dong and Mao (2000) studied the aggregation structure of  $C_{12}E_5$  nonionic surfactant on mica as a function of temperature at concentrations twice that of CMC. Below  $21^\circ\text{C}$ ,  $C_{12}E_5$  adsorbed as fragments tens of nanometers in size while above  $21^\circ\text{C}$  a smooth and continuous lamellar structure formed. In 1984 Levitz *et al.* studied the adsorption kinetics of Triton X-100® as a function of increasing surface coverage. They found that the surface aggregates first increase in size, then in number density, and finally in size again, resulting in a transformation from a fragmented structure to a continuous bilayer structure. On mica no adsorption was observed in some cases due to the weak interaction of oxyethylene surfactants with the substrate. But where adsorption was detected, several structures have been observed: a flat configuration, submonolayers with the hydrophobic moiety toward the mica (Rutland *et al.*, 1990) and a layer of cylindrical or wormlike micelles extending from mica surface (Giasson *et al.*, 1998).

### 2.1.2 Monomer Adsolubilization

The second step of admicellar polymerization is the solubilization of solutes into the adsorbed aggregates. This step may be done subsequent to surfactant adsorption or simultaneously with it. The adsolubilization of monomer depends on electrostatic contributions, monomer molecular volumes, the hydrophobic effect, and dipole interactions. Another possibility important factor is the solubility of the monomer in water; however, monomer concentrations are typically so low that solution polymerization does not seem to occur even when non-water-soluble initiators are used. Rouse *et al.* (1995) has concluded that nonpolar solutes preferentially partition to the core of the admicelle while solutes that are more hydrophilic preferentially partition to the palisade region of the admicelle. Solutes with intermediate polarity will adsolubilize into both the palisade and core regions.

### 2.1.3 Polymerization

During this step the adsolubilized monomer is polymerized. Wu *et al.* (1987) and Sakhalkar *et al.* (1995) observed that monomer continuously diffused into the admicelle during the reaction process. Wu suggested that the reaction was initiated and terminated inside the admicelle and that the reaction time decreased with increasing initiator concentration.

In case of metal alkoxide monomers when the monomers were adsolubilized into the admicelle, the sol-gel reaction may occur. The sol-gel process basically means the synthesis of an inorganic network by a chemical reaction in solution at low temperature. The most obvious features of this reaction are the transition from a liquid (solution or colloid solution) into a solid. Moreover, precursors for this reaction are able to form reactive inorganic monomers or oligomers. Most of the work in this field has been done using alkoxides as precursors since they provide a convenient source for inorganic monomers that are soluble in common solvents. The typical process consists of two steps. First, the reaction can start with two basically different systems. This process describes the transition of a system from liquid, mostly colloidal, into a solid, gel phase. Secondly, gelation may proceed due to condensation of colloidal particles (by sol destabilization), cluster growth, and then cross-linking of polymeric molecules (Gesser and Goswami, 1989). To produce fairly homogeneous solids, network forming components such as titanium metals, usually in the form of alkoxides, must be used. These accommodate the formation of a three-dimensional network during the condensation reaction.

### 2.1.4 Surfactant Removal

The final step in admicellar polymerization is removal of excess surfactant from the modified surfaces. This is usually accomplished by repeating or continuously contacting of the modified solids with excess water. Removing all of the surfactant is usually difficult, especially on porous substrates. Mass balances on porous systems suggest that even after vigorous washing, fully half of the surfactant remains on the modified particle. (O'Haver *et al.*, 1994) Moreover, in 1999 Kovtyukhova *et al.* revealed the pH of washing solution can effected TiO<sub>2</sub> particle repulsion on the NH<sub>2</sub>-terminated Si surface.

## 2.2 Atomic Force Microscopy (AFM)

The AFM first appeared in 1986 as an evolution from scanning tunneling microscopy. It takes on many different forms and configurations and, indeed, the AFM is just one type of scanning probe microscope (SPM) that is used in the characterization of interfaces. AFM's mode of operation is applicable to both conductive and non-conductive surfaces and to fluid and non-fluid environments. This has established uses for the AFM in a wide range of scientific and engineering endeavors. In the last few years, AFM has undergone extensive development but imaging is still its main caveat of use. Its popularity as a tool for imaging surfaces is almost certainly related to the imaging environment and substrate preparation requirements. The AFM can be used on a vast range of surfaces with the sample that has the thickness approximately less than 0.5 cm. Even the latter restriction is being obviated in many new commercial AFM head designs.

The surface can be imaged in air, water, vacuum, or some other fluid environment that retains compatibility with the materials of construction of the instrument. Sample preparation is therefore sub-critical relative to techniques such as transmission and scanning electron microscopy. As with nearly all techniques, the AFM is not a panacea of all ills and it has a number of limitations to go with its many advantages. These will be explored, along with its many advantages. For example, a clear disadvantage of the AFM technique is that it is purely a surface or topological technique. A consequence of this is that imaging of soft or motile surfaces is inherently difficult. Imaging artifacts are also of concern (Scales, 1999).

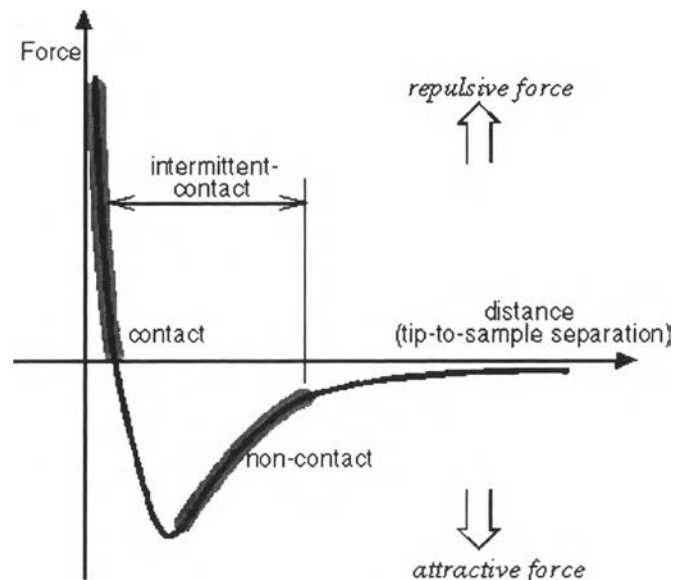
### 2.2.1 AFM Theory

Atomic Force Microscopy (AFM) can be used to investigate the structure and morphology of the surface. This is a powerful technique that allows the generation of topographic images of the surface with atomic resolution (figure of AFM instrument is shown in Fig. 2.3).



**Figure 2.3** AFM instrument

The principle behind AFM is similar to that of an old record player. A sharp tip (like needle) makes contact with the surface and moves up and down in response to the surface features. This tip is connected to a small cantilever. The tip is scanned over the sample and the features on the surface cause the cantilever to bend up and down. This deflection of the cantilever is monitored by shining a small laser beam on the back of the cantilever and measuring the change in the reflected position of the laser beam. Several forces typically contribute to the deflection of an AFM cantilever. The force most commonly associated with atomic force microscopy is an inter-atomic force called the van der Waals force. The dependence of the van der Waals force upon the distance between the tip and the sample is shown in Figure 2.4.



**Figure 2.4** Inter-atomic force vs. distance curve

A feed back loop is used to deepen the deflected laser beam signal constant by adjusting the sample height at each position. This change in height is recorded to give a topographic image of the surface. In order to collect an image, the cantilever is scanned back and forth over the sample and the signal from the z-piezometers are recorded as the tip is moved to keep the photodiode signal constant at the setpoint level. The size of the scan is set in the scan parameters anywhere from about 1 nm to 125 microns. The scan speed and direction are also controlled by software parameters.

There are three primary modes of AFM:

- contact mode AFM
- non-contact mode AFM
- tapping mode AFM

### 2.2.2 Contact Mode AFM

In contact mode AFM, also known as repulsive mode, and AFM tip makes soft physical contact with the sample. The tip is attached to the end of a cantilever with a low spring constant, lower than the effective spring constant holding the atoms of the sample together. The slope of the van der Waals curve is very steep in



the repulsive or contact regime. As a result, the repulsive van der Waals force balances almost any force that attempts to push the atom closer together. In AFM this means that when the cantilever pushes the tip against the sample, the cantilever bends rather than forcing the tip atoms closer to the sample atoms. In addition to the repulsive van der Waals force, capillary forces arise when water wicks its way around the tip, applying a strong attractive force that holds the tip in contact with the surface.

As long as the tip is in contact with the sample, the capillary force should be constant because the distance between the tip and the sample is virtually incompressible. The variable force in contact AFM is the force exerted by the cantilever. The total force that the tip exerts on the sample is the sum of the capillary plus cantilever forces, and must be balanced by the repulsive van der Waals force for contact mode AFM.

#### *2.2.2.1 Advantages of contact mode*

- High scan speed (throughput)
- Contact mode AFM is the only AFM technique which can obtain atomic resolution image
- Rough samples with extreme changes in vertical topography can sometimes be scanned more easily in contact mode.

#### *2.2.2.2 Disadvantages of contact mode*

- Lateral (shear) forces can distort features in the image.
- The forces normal to the tip-sample interaction can be high in air due to capillary force from the adsorbed fluid layer on the sample surface.
- The combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples due to scraping between the tip and sample

### 2.2.3 Non-contact Mode AFM

In the non-contact mode AFM, the distance between the tip and the sample surface is greater than 10 Å. Therefore, van der Waals, electrostatic, magnetic or capillary forces are used to produce topographic images. The cantilever is typically oscillated at a frequency which is slightly above the cantilever's resonance frequency with an amplitude of a few nanometers (<10nm), in order to obtain an AC signal from the cantilever. The cantilever's resonant frequency is decreased by van der Waals forces, which extend from 1 nm to 10 nm above the adsorbed fluid layer, and by other long range forces which extend above the surface. The decrease in resonant frequency causes the amplitude of oscillation to decrease.

#### 2.2.3.1 *Advantages of non-contact mode*

- No force is exerted on the sample surface.

#### 2.2.3.2 *Disadvantages of non-contact mode*

- Lower lateral resolution, limited by the tip-sample separation
- Slower scan speeds than contact mode and tapping mode to avoid contacting the adsorbed fluid layer which results in the tip getting stuck
- Non-contact usually only works on extremely hydrophobic samples, where the adsorbed fluid layer is at a minimum. If the fluid layer is too thick, the tip becomes trapped in the adsorbed fluid layer causing unstable feedback and scarping of the sample.

Due to these disadvantages, applications for non-contact mode AFM imaging have been limited.

### 2.2.4 Tapping Mode

Tapping mode imaging is a major advance in the atomic force microscopy imaging of soft, adhesive or fragile samples. This technique allows high resolution topographic imaging of sample surfaces that are easily damaged, loosely held to their substrate or otherwise difficult to image by other AFM techniques. Specifically tapping mode overcomes problems associated with friction, adhesion, and electrostatic forces. Tapping mode imaging overcomes the limitations of

conventional scanning modes by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilever's resonant frequency using a piezoelectric crystal. The piezo causes the cantilever to oscillate with a high amplitude (the free air amplitude is typically greater than 20 nm) when the tip is not in contact with the surface the oscillating tip is then moved toward the surface until it begins to lightly touch or "tap" the surface.

During tapping mode operation, the cantilever oscillation amplitude is maintained by a feedback loop. When the tip passes over a bump in the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. Conversely, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases. The oscillation amplitude of the tip is measured by the detector and input to the electronic controller. The digital feedback loop then adjusts the tip-sample separation to maintain constant amplitude and force on the sample.

#### *2.2.4.1 Advantages of tapping mode*

- Higher lateral resolution on most samples (1 nm to 5 nm)
- Lower forces and less damage to soft samples imaged in air
- Lateral forces are virtually eliminated, so there is no scraping

#### *2.2.4.2 Disadvantages of tapping mode*

- slightly slower scan speed than contact mode AFM

### **2.3 Energy Dispersive X-ray Spectrometer (EDS)**

Energy dispersive x-ray spectrometer (EDS) is one of the instruments which can be used to analyze composition of modified surface by using x-ray. X-rays are generated as a result of the ejection of an inner level electron (low energy) by an energetic electron from an electron column. The ejected electron is replaced by an

electron from a higher energy shell. The energy lost as it moves from a high energy shell to a low energy shell is released in the form of x-rays.

Each element has many energy levels and therefore many potential vacancy-filling mechanisms. As a consequence even pure elements emit x-rays at many energies. Because the atomic structure of each element is different, it follows that each element will emit a different pattern of x-rays.

These x-rays can be analyzed either by wavelength dispersive methods or energy dispersive methods. Energy dispersive systems use a semiconductor detector first developed in the 1960's. Basically it is a single 3 mm thick by 15 mm<sup>2</sup> crystal of silicon which has been treated with lithium (lithium drifted silicon).

An x-ray photon first creates a charge pulse in a semiconductor detector; the charge pulse is then converted into a voltage pulse whose amplitude reflects the energy level of the detected x-ray. This voltage pulse is converted into a digital signal which causes one count to be added to the corresponding voltage channel of a multichannel analyzer. Counting over some time, results in an x-ray spectrum.

## 2.4 Metal Alkoxide Modification

Transition metal alkoxides are known to hydrolyze rapidly, so much so that control of the hydrolysis reaction is one of the key issues for sol-gel processing (Sanchez and Ribot, 1994). Chemical modification of the transition metal alkoxides introduces functional groups which are relatively stable against hydrolysis, and is an effective way to achieve the controlled hydrolysis of transition metal alkoxides (Brinker and Scherer, 1990). Alkoxide reactivity can also be easily modified by changing the solvent. Metal alkoxides react with a variety of alcohols to set up the following type of equilibrium



It is also well known that hydrolysis of an alkoxide strongly depends on the length of the alkyl chain. Thus it should be possible to adjust the rate of gelation of an alkoxide by using different solvents. Transparent gels will be obtained upon acid

hydrolysis of  $\text{Si}(\text{OCH}_3)_4$ , the gelation time increases from 44 hours up to 152 hours when ethanol is used as a solvent instead of methanol. The other alkoxide modifier is acetylacetone, which has been reported in the sol-gel literature as a stabilizing agent for metal alkoxide precursors. Atsuo and co-workers (1998) used acetylacetone and isopropanol to stabilize titanium tetraisopropoxide (TIPP). Stabilization of TIPP insures that during hydrolysis only isopropoxy groups are removed which prevents the rapid growth of the  $\text{TiO}_2$  particles. Hideyasu and co-workers (2000) modified the reaction of titanium tert-butoxide with catechol ( $\text{C}_6\text{H}_4(\text{OH})_2$ ). Catechol is a well-known chelating agent to form catecholate complexes with various metals including titanium, since catecholate groups ( $\text{C}_6\text{H}_4\text{O}_2^{2-}$ ) possess strong affinity with metal ions possessing high oxidation states (Siedle *et al.*, 1987). The hydrolysis and condensation behavior of a resultant modified alkoxide was then studied. The hydrolysis of the modified alkoxide in the system with Ti:tetrahydrofuran (THF): $\text{H}_2\text{O}$  = 1:10:x ( $x = 0.5 - 10$ ) resulted in the partial hydrolysis, and all the hydrolyzed products after the drying under reduced pressure were soluble in THF and chloroform (Wu, *et al.*, 1987). There is uniform agreement that alkoxy units bonded to titanium can be replaced by acetate groups in solution. The level of modification of the TTIP by acetate groups is quite important because the alkoxy groups are known to be much more rapidly attacked by water in comparison to acetate groups (Brinker *et al.*, 1990).

## 2.5 $\text{TiO}_2$ Ultrathin Film Formation

In this study, the sol-gel process is employed for the synthesis of  $\text{TiO}_2$  ultrathin films. In 1999, Oswald *et al.* studied suitable precursor molecules for a two-dimensional sol-gel process. They succeeded in preparing titania-based thin films starting from Ti alkoxide amphiphiles (titanium-n-butoxide, titanium-di-n-butoxide, poly(di-n-butyltitanate) and titanium-n-nonoxide). The values of surface roughness investigated by tapping mode AFM were high, indicating that a homogeneous coating was not achieved. Three years later, Falaras and Xagas (2002) investigated the effect of the nature of the precursors (titanium butoxide and titanium isopropoxide) on the hydrolysis rate and the resulting particle size distribution,

roughness and surface complexity of the TiO<sub>2</sub> films. Applications of TiO<sub>2</sub> thin films are related to the shape and order of the nanoparticles that make up the films (Caruso *et al.*, 1998). Titanium isopropoxide presents higher hydrolysis rates leading to more rough and complex characteristics whereas titanium butoxide films show a relatively smoother surface and also gives a higher fractal dimension value.

In 1997, Stathatos *et al.* revealed a novel method for a mesoporous titania film formation. This method utilized nonionic surfactant in a nonaqueous system as a mold to form thin films. Moreover, this procedure is advantageous from many points of view such as film thickness can be easily controlled, since the existence of two phases in equilibrium in reverse micelles provides a friendly environment for non-destructive solubilization and finally this procedure can produce thin surfactant films of nonionic materials, like Triton X-100® which is impossible in the absence of alkoxide. In their study, they used titanium isopropoxide precursor because this transition alkoxide can react rapidly with water. Thus, using reverse micelles provided a means of controlling the hydrolysis rate. TiO<sub>2</sub> films, which have monodispersity and reproducibility, can be produced by this method.