CHAPTER VII

TMOS based highly transparent and hydrophobic silica coatings by dip coat technique
CHAPTER 7

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7.1 Introduction:

The wettability of a solid surface by a liquid mainly depends on the chemical and microstructural properties of the surface. The hydrophobic coatings for anticorrosive applications on metallic, steel, polymer and other solid surfaces is an indeed need of the present industrial scenario. The transparent and hydrophobic coatings are very essential for the protection of sculptures and statues in order to prevent their deterioration with time since they contain natural minerals such as silica and aluminum that react with moisture present in the atmosphere. Furthermore, the hydrophobic coatings is not only a favorite ground for the researchers in the field of coating technology but also of immense interest to the technologists because of its wide range of applications such as self-cleaning surfaces, waterproof roofing, antirust automobiles and optoelectronic devices [1-4]. Surface interacts chemically with the environment in the variety of ways. The minimization of the surface energy (liquid-air) reflects in the wetting behavior of the surface by a liquid phase following the Young's relationship [5]:

\[ \gamma_{sv} = \gamma_{sf} + \gamma_{lv} \cos \theta \]  
(7.1)

This relation holds for smooth surfaces (ideal case). However, for rough surfaces (practical case), Wenzel incorporated contact angle relationship [6]:

\[ \cos \theta_w = \frac{\gamma_{lv}}{\gamma_{si}} \cos \theta_f \]  
(7.2)

Where, \( r \) is the roughness parameter of surface and is given by \( r = \frac{\text{rough area}}{\text{smooth area}} \). The Wenzel's relation indicates that if the intrinsic contact angle for a liquid on a solid surface is less than 90° then more roughening the surface will reduce the contact angle and vice versa.

Therefore, sol-gel processing can be conveniently used for the hydrophobic coatings on the almost all types of surfaces. This technology has been investigated for corrosion protection purposes for over fifteen years now. The report from Aegerter on stainless steel have shown the tarnishing of stainless steel at higher temperatures can be reduced by pure inorganic
coatings [7]. Investigations of Navarro and co-workers also enlighten that the improvement of corrosion protection can be achieved by inorganic glass-like coatings [8]. By employing various coating techniques such as dip coating method [9], spray pyrolysis method [10] and spin coat method [11], it is very easy to prevent the materials from an abrupt weathering and erosion. Amongst all types of coating methodologies, dip coat technique is the simplest, novel and cost effective technique, since it does not requires any sophisticated instrumentation and provides the reliability and multiple production process enhancement.

Therefore, by considering the importance of optically transparent and hydrophobic silica coatings, systematic experimental investigations have been carried out to coat the glass substrates using tetramethoxysilane (TMOS) as a precursor and trimethylchlorosilane (TMCS) as a surface modifying agent by dip-coat technique.

7.2 Experimental procedure:

7.2.1 Synthesis of silica films:

The synthesis of silica films involves three major steps: (1) the preparation of the alcosol, (2) dipping and drawing the substrates in the alcosol, and (3) annealing of the as deposited films. Initially, the glass surface was pre-treated by rinsing with labolene followed by an ultrasonic bath cleaning with double distilled water. Finally, substrates were dried and cleaned with acetone. Single step, base catalyzed sol-gel process was followed to prepare the alcosol. The chemicals used were tetramethoxysilane (TMOS, purum grade from Fluka Company, Switzerland) trimethylchlorosilane (TMCS, purum grade from Sigma Aldrich Company, Germany), methanol and ammonium hydroxide (ExcelaR and SQ grades, respectively from Qualigens Company, India).

TMOS was diluted at different concentrations in methanol (MeOH) solvent along with the TMCS. The basic water (NH₄OH) was added to the sol, drop by drop while stirring. The as prepared alcosol was poured into Borosil glass test tubes. The glass substrates of 73 X 13 X 1 mm. were dipped in the glass test tubes containing the coating sol. At different interval of time, the substrates were drawn out from the sol at a speed of 5 mm/sec.
In order to form good bonding between the substrate surface and the sol (adherency), the films were dried at room temperature (~27°C) for 30 minutes. Finally, the films were annealed at 50°C, 150°C and 200°C for 1 hour, 30 minutes and 15 minutes respectively. The molar ratios of MeOH/TMOS was varied from 10 to 18 whereas the desired low energy surface required for the hydrophobicity, was achieved by varying the TMCS/TMOS molar ratio from 0.6 to 1.4. The effect of basic catalyst concentration was studied by varying the NH₄OH concentration from 1 to 6M and H₂O/TMOS molar ratio from 1.6 to 4.1.

7.2.2 Methods of characterization:

The as prepared films were characterized for wettability by putting a water droplet of 2.4 mm diameter on the film surface and measured the contact angle using contact angle meter (Rame-hart Model 500-F1, USA). Organic chemical modifications were studied using Fourier Transform Infrared (FTIR) spectroscopy by FTIR spectrophotometer (Perkin Elmer Model 783). Optical transmission of the films was revealed by a systronic spectrophotometer-119 with bare glass substrate as a reference material in the visible range of wavelength. The microstructural investigations of the film have been carried out using Scanning Electron Microscope (SEM).

7.3 Results and discussion:

The sol-gel process involving hydrolysis and polycondensation reactions, called the alkoxide method due to the nature of the starting chemicals. Indeed, alkoxides are undoubtedly the most common and well established precursors used in the sol gel process. Tetramethoxysilane is one of the most widely used alkoxide precursor for the sol gel synthesized materials. TMOS silicon alkoxide contains all four hydrolysable methoxy groups which undergo hydrolysis and lead to the formation of monomeric units of –Si(OH)₄ which are responsible for the formation of network branching. The silanols groups condense to form siloxane bonds are shown sequentially in the following chemical reactions.
Hydrolysis:
\[ \text{Si(OCH}_3\text{)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{CH}_3\text{OH} \]..............(7.3)

Condensation:

Water condensation:
\[ n \text{Si(OH)}_4 \rightarrow n \text{SiO}_2 + 2n \text{H}_2\text{O} \]..................(7.4)

Or alcohol condensation:
\[ n \text{Si(OH)}_4 + n \text{Si(OCH}_3\text{)}_4 \rightarrow n\text{SiO}_2 + n \text{CH}_3\text{OH} \]..................(7.5)

7.3.1 Effect of MeOH / TMOS molar ratio (M):

Traditionally, the solvents are added in the reaction mixture, to prevent liquid - liquid phase separation during the initial stages of the hydrolysis reaction and to control the concentration of silicate and water that influence the gelation kinetics. The M value was found to affect the gelation time, hydrophobicity and optical transmission of the films, which was quantified in terms of the contact angle measurements, and optical absorption studies of the films, respectively. The respective results were tabulated in table 7.1. This is due to the fact that the dilution of TMOS with methanol causes the separation of TMOS molecules. Therefore, as the MeOH/TMOS molar ratio increases, the hydroxyl (-OH) groups disperses more in the less surface area. Therefore, due to the lower concentration of -OH groups on the surface, very few -OH groups will get replaced by hydrolytically stable Si(CH_3)_3 groups from the surface silylating agent, TMCS, during the silylation process. This led to the more hydrophilic surface and an ultimately lower contact angle.

However, the optical transmission of the as deposited films was found to increase with an increase in the MeOH/TMOS molar ratio. This is due to the fact that at lower value of MeOH/TMOS molar ratio, the viscosity of the sol is more. Therefore, the thickness of the film becomes higher than that of the thickness obtained for higher molar ratio.

According to an equation: \[ I = I_0 \exp t \]..................(7.6)

where, \( t \) is the thickness of the film, it is clear that lesser the thickness of the film, higher the transmission. Therefore, at lower molar ratios of MeOH/TMOS, the film thickness obtained is less and hence the higher optical transmission (Figure 7.1). The MeOH/TMOS molar ratio was kept constant at
14.8 for the further experiments, where the films are good hydrophobic (120°) and better optically transparent (85%).

Table 7.1: Variation in the hydrophobicity and optical transmission of the films with respect to molar ratio of MeOH/TMOS.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molar ratio TMOS:MeOH:TMCS:H₂O</th>
<th>Gelation time (minutes)</th>
<th>Contact angle (degrees)</th>
<th>Optical transmission (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:10:0.4:3.3</td>
<td>5</td>
<td>120</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>1:12:0.4:3.3</td>
<td>20</td>
<td>114</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>1:14:0.4:3.3</td>
<td>30</td>
<td>105</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>1:16:0.4:3.3</td>
<td>50</td>
<td>98</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>1:18:0.4:3.3</td>
<td>65</td>
<td>83</td>
<td>92</td>
</tr>
</tbody>
</table>

Figure 7.1: Photograph of the deposited film on the glass substrate (Glass slide A) and only the bare glass substrate (Glass slide B), respectively.
7.3.2 Effect of TMCS/TMOS molar ratio (S):

The as produced silica films contain a large number of hydroxyl groups which are responsible for the hydrophilicity of the films [12]. However, using TMCS as a surface modifying agent, the Hs from the -OH groups on the silica clusters, are replaced by hydrolytically stable =Si-(CH₃)₃ through -O-Si-(CH₃)₃ bonds as per the following chemical reactions:

\[
\begin{align*}
\text{Alcogel} & \xrightarrow{TMCS} \text{Silylated Silica Surface} \\
\text{Si-OH} & \xrightarrow{(H₃C)₃Si-Cl} \text{Si-O}-(H₃C)₃ + 2 \text{HCl} \quad \text{(7.7)}
\end{align*}
\]

The hydrophobicity of the films is due to the attachment of hydrolytically stable =Si-(CH₃)₃ groups on the surfaces of SiO₂ particles through the oxygen bonds. Hence as the S value increased, the hydrophobicity of the films also increased.

Figure 7.2 gives the θ values measured using the contact angle meter, for various molar ratios of S. It was observed that θ increased with an increase in the S value. The contact angle was maximum (120°) for S= 1.4. Figure 7.3 (a & b) shows the photograph of a water droplet on the as deposited films prepared with S = 0.4 and 1.4, respectively. These photographs very clearly indicate that the water droplet assumes better spherical shape with an increase in the S value.
Figure 7.2: Change in contact angle with the variation of TMCS/TMOS molar ratio.
Figure 7.3: Photograph of a water droplet on the films prepared with (A) $S = 0.4$ and (B) $S = 1.4$
| 8. | "Physical properties of methyltriethoxysilane (MTES) based superhydrophobic silica aerogels"  
     Poster presentation at **Aerogel Conference**, 4-5 Dec, 2007, **Boston, USA**. |
| 9. | "Absorption and desorption in superhydrophobic silica aerogel"  
     Poster presentation at **52nd DAE Solid State Physics Symposium**,  
     27-31 Dec 2007, **University of Mysore, Mysore, India**. |
   19th **MRSI -AGM**, 14-16 Feb, 2008 held at Shree Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram, India. |
| 11. | "Rheological pertinent due to sol gel transformations in the methyltriethoxysilane based flexible superhydrophobic silica aerogels"  
     Poster presentation at **National Conference on Advanced Materials and Characterization**, 23-25 July 2008, **Vellore Institute of Technology, Vellore, Tamilnadu, India**. |
| 12. | "MTES based superhydrophobic flexible silica Aerogels  
     Poster Presentation at the **International Conference on Nanomaterials and Applications (ICANAMA)**, 9-11 Dec, 2008 held at Shivaji University, Kolhapur, Maharashtra, India. |
| 13. | "Hydrophobic and physicochemical properties of TEOS based silica aerogels using phenyltriethoxysilane as a synthesis component"  
     Poster Presentation at the **International Conference on Nanomaterials and Applications (ICNAMA)**, 9-11 Dec, 2008 held at Shivaji University, Kolhapur, Maharashtra, India. |
| 14. | "TMOS based transparent hydrophobic silica thin films by co-precursor method using TMES as a hydrophobic agent"  
     Poster presentation at **53rd DAE Solid State Physics Symposium**,  
     16-20 Dec., 2008, **BARC, Mumbai, India**. |
7.3.3 Effect of Catalyst concentration (B):

To study the effect of the base catalyst (NH₄OH) concentration (B) on the hydrophobic properties of the film, the alcosol was prepared by keeping the molar ratio of TMOS: MeOH: TMCS: H₂O constant at 1: 14.8:1.4:3.3 and B value was varied from 1 to 6 M. It was found that contact angle increased to a maximum of 119° for B equal to 4 M and decreases for higher and lower B values as shown in figure 7.4. It is due to the fact that as B value was increased, the rate of condensation increased with lowering the gelation time. Therefore, there is an increase in the particle size and their connectivity leading to the increase in the contact angle. However, further increase in the concentration of the base catalyst leads to more basicity of the sol where silica begins to dissolve as a silicate. The silica particles are negatively charged and repel each other. Therefore, they do not collide, so the particle growth continues without the aggregation of the particles, which in turn results in a less hydrophobic surface.

Figure 7.5 shows the Scanning Electron Micrograph (SEM) of the film prepared at the base concentration equal to 4M which shows the good particle growth and well distributed network structure.
Figure 7.4: Effect of base concentration on the hydrophobicity of the samples.

Figure 7.5: Scanning Electron Micrograph (SEM) of the film prepared at B=4M.
7.3.4 Effect of H$_2$O/ TMOS molar ratio (H):

In order to study the effect of water quantity in the sol on the hydrophobic coatings, the H$_2$O/TMOS molar ratio (H), was varied from 1.6 to 4.1 as shown in figure 7.6. It has been observed that the contact angle of the film increased with an increase in H value up to 3.3. Further increase in H value led to decrease in contact angle. Since, the water directly participates in the hydrolysis reaction, lower amount of water results in a lower number of hydrolyzed monomers (Si-OH groups) with very limited cross-linking. Whereas, for higher value of H, the contact angle decreases due to the trapped H$_2$O molecules and more number of uncondensed Si-OH groups [13]. The presence of optimum amount of water, (H= 3.3) hydrolyses most of the alkoxide groups leading to the formation of highly branched uniform polymeric network.

![Contact Angle vs H Value](image)

Figure 7.6: Effect of H$_2$O/TMOS molar ratio on the hydrophobicity of the samples.
7.3.5 Effect of deposition time:

The substrates were dipped in the sol prepared at $M=14.8$ for various interval of time from 5 to 25 minutes. The maximum deposition time is observed upto 25 minutes, which is just prior to the gelation time. It was found that the coating was uniform and the hydrophobicity increased with deposition time. This is due to fact that when the sol is about to gel, the particle formation is about to complete and an uniform network, formed on the glass slides. If the substrates were taken out much prior to gelation, due to incomplete hydrolysis and condensation reactions, non-uniform film deposition was observed. However, at higher deposition time, the optical transmission of the films was observed lower because of an increase in the thickness of the film.

7.3.6 Fourier Transform Infrared (FTIR) spectroscopy and thermal studies:

The hydrophobicity of the films was confirmed from the Fourier Transform Infrared (FTIR) studies. Figure 7.7 shows the FTIR spectra of the as deposited film prepared with $M = 14.8$ and $S = 1.4$. Strong peaks are observed at 3000 and 1400 cm$^{-1}$ corresponding to the stretching and bending of C-H bonds [14]. The peaks at around 1100 and 770 cm$^{-1}$ are due to the asymmetric and symmetric the bending modes of SiO$_2$, respectively [15]. The peak at 845 cm$^{-1}$ is due to Si-C bonds [16]. The figure shows the peaks around 3200 and 1650 cm$^{-1}$ corresponding to O-H bonds clearly indicating the surface chemical modification of the hydrophilic films.

Temperature is the most important physical parameter in the materials science for testing the durability and properties of the material. In case of superhydrophobic silica films, the organic moiety can be reduced due to the temperature which causes an irreversible change in the hydrophobic property and the surface becomes hydrophilic. The thermal stability of the as deposited silica films were tested by putting the films in the furnace (Vulcan 3-550, Norway) at various temperatures and measured their contact angles. It was observed that the films are thermally stable up to the temperature of $220^\circ$C beyond which they turn into hydrophilic surfaces. The contact angle of the water droplet on such surface was about $8^\circ$. This is due to the fact that
above this temperature, the non-polar Si-(CH₃)₃ groups on the surface of the film get oxidizes to Si-OH groups which have a strong affinity to water. Therefore, surface shows hydrophilic behavior.

![FTIR spectra of the hydrophobic silica film prepared with M = 14.8 and S = 1.4.](image)

**Figure 7.7: FTIR spectra of the hydrophobic silica film prepared with M = 14.8 and S = 1.4.**

**7.4 Conclusions:**

Transparent and hydrophobic coatings of silica on the glass substrates were obtained by a single step sol-gel process by the dip coating method using TMOS as the precursor. Uniform, well adherent and highly transparent coating was observed at deposition temperature of 50°C for the molar ratio of TMOS:MeOH:TMCS:H₂O at 1:14.8:1.4:3.3 with NH₄OH (4M) as the base catalyst. The contact angle of water with the coated surface was found to be 120°. Further, the as deposited films are thermally stable up to the temperature of 220°C above which they becomes hydrophilic.
References: