CHAPTER 5

Study of Physico-Chemical Properties of TEOS Based Hydrophobic Silica Films using various Co-precursors
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5.1 Introduction

Wetting plays an important role in many natural and technological processes. A water repellent behavior of the solid surfaces is one of the most important characteristics in both theoretical research and industrial applications. The wettability of liquid to solid surface is governed by the chemical properties of solid surface and its surface morphology. To make the silica coating hydrophobic, an organic material is applied to the inorganic porcelain in such a manner that the surface behaves as a repellent towards water i.e. the water droplets tend to contract and forms nearly spherical pearl on the modified silica surface. Their potential and current applications are useful for windshields of cars, prevention of adhesion of snow to antennas, self-cleaning traffic indicators, the reduction of frictional drag on ship hulls, stain-resistant textiles, anti-oxidation, minimization of contamination in biotechnological applications and lowering the resistance to flow in microfluidic applications [1-2]. Due to this broad range of benefits, many attempts to understand and manufacture water repellent surfaces have been spent. Hence, many approaches, such as lithographic patterning [3], vertical alignment of nanotubes/nanofibers [4-6], sol–gel method [7], phase separation [8], layer-by-layer assembly technique [9-11], and glancing angle deposition [12] have been developed for the design and fabrication of superhydrophobic surfaces. Among these approaches, the sol-gel method has been found to be a simple and effective technique for depositing water repellent coatings onto substrates. Moreover, it gives rise to advantages such as large deposition areas, uniform deposits on the objects with desired shapes, and short processing times [13]. Several authors have reported that it is possible to combine excellent optical transparency with high water contact angles [14-18], but only a few studies also report a low sliding angle of water droplet [19-21]. These later
characteristics are required if a surface is to exhibit true self-cleaning properties. For most of the applications of these surfaces, the important issue is not the fact that the contact angle is high but how readily the liquid moves on the surface, which is a dynamic process.

The sol-gel method is a novel procedure among solution reactions which is based on the preparation of macromolecular network through the typical hydrolysis of metal alkoxide groups followed by the condensation of the silanols. There are many reports available on the synthesis of TEOS based hydrophobic silica films by co-precursor method [22-26]. Daoud et al [22] were successfully prepared transparent and durable superhydrophobic silica-coating films on cotton substrates at low temperatures via cohydrolysis and polycondensation of a hexadecyltrimethoxysilane (HDTMS), tetraethoxysilane (TEOS), and 3-glycidyloxypropyltrimethoxysilane (GPTMS) mixture. Yonghao Xiu et al [23] prepared superhydrophobic durable self-cleaning silica films by the incorporation of isobutyl-trimethoxysilane into tetramethoxysilane causing hydrophobic isobutyl groups to be present on the film surface, thus generating surface hydrophobicity. In the present work, the transparent water repellent silica films were synthesized by sol-gel co-precursor process. The hydrophobic silica films are prepared using the isobutyl-trimethoxysilane (iso-BTMS), hexadecyltrimethoxysilane (HDTMS) and trimethylethoxysilane (TMES) as a co-precursor to lower the surface free energy of the coated substrate.

5.2 Experimental

5.2.1 Preparation of silica films

To attain hydrophobic sol-gel coatings, usually, hydrophobic additives were added to a sol. The hydrophobic silica thin films are generally produced by two methods:

(i) Co-precursor method and
(ii) Surface derivatization method.
In the present research work, the former method was followed because it is simple and less time consuming compared to the latter method. In order to study the effect of isobutyltrimethoxysilane (iso-BTMS), hexadecyltrimethoxysilane (HDTMS) and trimethylethoxysilane (TMES) as a hydrophobic agent on the water repellent properties of the silica films, the silica films were synthesized by the sol-gel co-precursor method. The chemicals used were tetraethoxysilane, isobutyltrimethoxysilane, hexadecyltrimethoxysilane, trimethylethoxysilane (Sigma-Aldrich chemie, Germany), methanol (s.d.fine-chem limited, Mumbai), and ammonia (NH₃, Loba Chemie, India). All the reagents were used as received. Double distilled water was used for all the experiments. The glass substrates (from Blue Star®, India) of 1.5 cm x 5 cm were used as substrates in all experiments.

Silica alcosol was prepared by hydrolysis and polycondensation of methanol (MeOH) diluted tetraethoxysilane (TEOS) in the presence of ammonium hydroxide (NH₄OH) at room temperature (~ 27°C). In order to obtain adherent and transparent silica films, the molar ratio of TEOS:MeOH:H₂O was kept constant at 1:38.6:8.68 respectively, with 8 M NH₄OH throughout the experiments and the molar ratios of iso-BTMS/TEOS (A), HDTMS/TEOS (B), TMES/TEOS (C) were varied from 0 to 0.965, 0 to 22.9x10⁻² and 0 to 3.80, respectively. This mixture of silica alcosol and hydrophobic agents were stirred for at least 10 minutes before the dip-coating. The homogeneous alcosol thus obtained was transferred to airtight glass test tubes of 12 mm inner diameter and 85 mm height. The substrates were dipped vertically in alcosol and withdrawn with a speed of 3 mm/sec prior to gelation. No protective atmosphere was used for the deposition of silica films. After coating, the samples were dried at room temperature (~ 27°C) for at least 1 hour and annealed at 150°C for 2 h with a ramping rate of 1°C per minute to remove the residual solvent. The dried samples were taken out of the oven after cooling to the ambient temperature.
5.3 Results and discussion

5.3.1 Reaction Mechanism

In the sol-gel process, TEOS is hydrolyzed and condensed as per the following chemical reactions:

**Hydrolysis**

\[
\text{Si(OC}_2\text{H}_5)_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{C}_2\text{H}_5\text{OH} \quad (5.1)
\]

**Condensation**

**Water condensation**

\[
n \text{Si(OH)}_4 \rightarrow n \text{SiO}_2 + 2n \text{H}_2\text{O} \quad (5.2)
\]

**Alcohol condensation**

\[
\text{Si(OH)}_4 + \text{Si(OC}_2\text{H}_5)_4 \rightarrow 2\text{SiO}_2 + 4 \text{C}_2\text{H}_5\text{OH} \quad (5.3)
\]

However, using iso-BTMS as a co-precursor in the sol-gel processing stage, the Hs from the OH groups on the silica clusters are replaced by the hydrolytically stable \(\equiv\text{Si-C}_4\text{H}_9\) through \(-\text{O-SiC}_4\text{H}_9\) bonds as per the following chemical reaction,

\[
\begin{array}{c}
\text{Si-O-Si-OH + C}_4\text{H}_9\text{Si(OCH}_3)_3 \rightarrow \\
\text{Si-O-Si-OH + Si-O-Si-O-Si-C}_4\text{H}_9 + 3\text{CH}_3\text{OH}
\end{array}
\]

(5.4)

The hydrophobicity of the silica films is due to the attachment of hydrolytically stable \(\equiv\text{Si-C}_4\text{H}_9\) groups on the surfaces of SiO\(_2\) particles through the oxygen bonds. Hence as the A value increased, the hydrophobicity of the silica films also increased.

However, using HDTMS as a co-precursor in the sol-gel processing stage, the Hs from the OH groups on the silica clusters are replaced by the
hydrolytically stable $=\text{Si-C}_{16}\text{H}_{33}$ through $-\text{O-SiC}_{16}\text{H}_{33}$ bonds as per the following chemical reaction:

\[
\begin{align*}
\text{Si-O-Si} & \xrightarrow{\text{OH}} \text{Si-OH} + \text{C}_{16}\text{H}_{33}\text{Si(OCH}_{3}\text{)}_{3} \\
\text{Si-O-Si} & \xrightarrow{\text{O}} \text{Si-O-Si} + \text{C}_{16}\text{H}_{33}^{+} + 3\text{CH}_{3}\text{OH}
\end{align*}
\] (5.5)

The hydrophobicity of the silica films is due to the attachment of hydrolytically stable $=\text{Si-C}_{16}\text{H}_{33}$ groups on the surfaces of $\text{SiO}_{2}$ particles through the oxygen bonds. Hence as the $B$ value increased, the hydrophobicity of the silica films also increased.

During the sol-gel process, in the mixture of TEOS and TMES alkoxides, TEOS is preferentially hydrolyzed in the early stages of the reaction leading to the condensation reactions and formation of silica clusters as per the following chemical reaction,

\[
n\text{Si(OC}_{2}\text{H}_{5})_{4} + 2n\text{H}_{2}\text{O} \xrightarrow{\text{MeOH}} n\text{SiO}_{2} + 4n\text{CH}_{3}\text{OH}
\] (5.6)

At latter stages of the above reaction (5.6), the TMES monomers get hydrolyzed and condensed in the following manner:

**Hydrolysis:**

\[
(\text{CH}_{3})_{3}\text{Si(OC}_{2}\text{H}_{5}) + \text{H}_{2}\text{O} \xrightarrow{} (\text{CH}_{3})_{3}\text{Si-OH} + \text{C}_{2}\text{H}_{5}\text{OH}
\] (5.7)

**Alcohol condensation:**

\[
\text{Si-OH} + (\text{OC}_{2}\text{H}_{5})\text{Si(\text{CH}_{3})}_{3} \xrightarrow{} \text{Si-O-Si(\text{CH}_{3})}_{3} + \text{C}_{2}\text{H}_{5}\text{OH}
\] (5.8)

**Water condensation:**

\[
\text{Si-OH} + \text{HO-Si(\text{CH}_{3})}_{3} \xrightarrow{} \text{Si-O-Si(\text{CH}_{3})}_{3} + \text{H}_{2}\text{O}
\] (5.9)
Thus, the Si(CH$_3$)$_3$ groups are attached to the silica clusters through oxygen bonds leading to the formation of a hydrophobic silica film surface.

5.3.2 Gelation time

A simple laboratory method was applied for the determination of the gelation time of the sol. By tilting a test tube filled with a sol, the flowing behavior of the sol was observed. As soon as the sol loses fluidity the gelation point is reached [27]. The measurement was repeated three times and the error will be in the order of minutes.

Table 5.1 shows the effect of iso8BTMS/TEOS molar ratio (A) on the gelation time of silica alcosols. From table 5.1, it has been observed that with an increase in A value, the gelation time of the alcosol increases. This is due to the fact that, TEOS gets hydrolyzed in the early stages of the reaction to form silica clusters during which iso8BTMS acts as a co-precursor. As the iso8BTMS content increases in the sol, the hydrolysis and condensation reactions are slowed down due to less number of Si-OH groups and more non-hydrolysable butyl groups in the sol. At lower A values, only a few stable butyl groups get attached to the silica clusters and hence the gelation time was less. But, at higher A values, a large number of butyl groups get attached and hence, the gelation time was found to be more.

Table 5.2 shows the effect of HDTMS/TEOS molar ratio (B) on the gelation time of the silica alcosols. As the B value increased from 0 to 22.9×$10^{-2}$ the gelation time considerably reduced from 6 hours to 35 minutes. It has been reported that the gelation time increases with the increase in the quantity of the hydrophobic reagents [28, 29]. But, for hexadecyltrimethoxysilane, even though it has a longer chain length and belongs to the alkyl group, the gelation time was found to be reduced with the increase in the ratio of HDTMS/TEOS. This is possible because, under the basic conditions, the co-precursor, HDTMS, hydrolyses faster as compared to the TEOS precursor [30, 31]. Hence, with the increase in HDTMS the hydrolysis and the subsequent condensation reactions are accelerated leading to faster gelation.
Table 5.3 shows the effect of TMES/TEOS molar ratio (C) on the gelation time of silica alcosols. From table 5.3, it has been observed that with an increase in C value the gelation time of the alcosol increases. This is due to the fact that, TMOS gets hydrolyzed in the early stages of the reaction to form silica clusters during which TMES acts as a co-precursor. As the TMES content increases in the sol, the hydrolysis and condensation reactions are slowed down due to less number of Si-OH groups and more non-hydrolysable Si-(CH$_3$)$_3$ groups in the sol. At lower C values, only a few stable Si-(CH$_3$)$_3$ groups get attached to the silica clusters and hence the gelation time was less. But, at higher C values, a large number of Si-(CH$_3$)$_3$ groups get attached and hence, the gelation time was found to be more.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molar Ratio (iso-BTMS/TEOS) (A)</th>
<th>Gelation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>37 minutes</td>
</tr>
<tr>
<td>2.</td>
<td>0.192</td>
<td>1 hour 5 minutes</td>
</tr>
<tr>
<td>3.</td>
<td>0.386</td>
<td>1 hour 30 minutes</td>
</tr>
<tr>
<td>4.</td>
<td>0.579</td>
<td>3 hours 15 minutes</td>
</tr>
<tr>
<td>5.</td>
<td>0.772</td>
<td>4 hours 20 minutes</td>
</tr>
<tr>
<td>6.</td>
<td>0.965</td>
<td>7 hours</td>
</tr>
</tbody>
</table>

Table 5.1: Effect of iso-BTMS/TEOS molar ratio (A) on gelation time of sol.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molar Ratio (HDTMS/TEOS) (B)</th>
<th>Gelation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>6 hours</td>
</tr>
<tr>
<td>2.</td>
<td>5.7×10$^{-2}$</td>
<td>2 hours 40 minutes</td>
</tr>
<tr>
<td>3.</td>
<td>11.4×10$^{-2}$</td>
<td>1 hour 30 minutes</td>
</tr>
<tr>
<td>4.</td>
<td>17.2×10$^{-2}$</td>
<td>1 hour</td>
</tr>
<tr>
<td>5.</td>
<td>22.9×10$^{-2}$</td>
<td>35 minutes</td>
</tr>
</tbody>
</table>

Table 5.2: Effect of HDTMS/TEOS molar ratio (B) on gelation time of sol.
5.3.3 Surface Morphological Studies

The two-dimensional surface morphological study of the unmodified (A = 0) and iso-BTMS modified (A = 0.965) silica film has been carried out using the SEM micrograph. Figure 5.1 (a and b) shows the SEM images of unmodified and iso-BTMS modified silica films at 1000x magnification. In figure 5.1 (a), the unmodified silica film shows less dense, connected network like surface morphology. Whereas, in the case of iso-BTMS modified silica film (figure 5.1 b) highly dense, pores like surface morphology is observed.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molar Ratio (TMES/TEOS) (C)</th>
<th>Gelation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>25 minutes</td>
</tr>
<tr>
<td>2.</td>
<td>0.95</td>
<td>55 minutes</td>
</tr>
<tr>
<td>3.</td>
<td>1.90</td>
<td>1 hour 45 minutes</td>
</tr>
<tr>
<td>4.</td>
<td>2.85</td>
<td>16 hours</td>
</tr>
<tr>
<td>5.</td>
<td>3.80</td>
<td>32 hours 20 minutes</td>
</tr>
</tbody>
</table>

Table 5.3: Effect of TMES/TEOS molar ratio (C) on gelation time of sol.

Figure 5.1(a): SEM image of the unmodified (A = 0) silica film.
Figure 5.2a and 5.2b show the SEM images of the HDTMS modified (B = 22.9 \times 10^8) hydrophobic silica film at two different magnifications. The low magnification image (figure 5.2a) of the film confirms the small and dense pores. For detailed investigation of these pores, high magnified image (figure 5.2b) is recorded which gives the description of pore diameter. The high magnified SEM micrograph of the film shows macroporous surface morphology with each pore having pore diameter typically ranges from 60 to 70 nm, randomly distributed on the substrate.

Figure 5.1(b): SEM image of the iso-BTMS modified (A = 0.965) silica film.
Figure 5.2(a): SEM image of the HDTMS modified (B=22.9 x 10^{-2}) silica film with 5,000X magnification.

Figure 5.2(a): SEM image of the HDTMS modified (B=22.9 x 10^{-2}) silica film with 50,000X magnification.
Figure 5.3 shows 5000X magnified SEM image of TMES modified (C = 3.8) silica film. The microstructure of the silica film shows the clusters of particles having non-uniform sizes distributed on the glass substrate. The agglomeration of particles can be easily seen which puts limitations to calculate the actual grain size.

![SEM image of the TMES modified (C = 3.8) silica film.](image)

**Figure 5.3: SEM image of the TMES modified (C = 3.8) silica film.**

### 5.3.4 Atomic Force Microscopy (AFM)

The wettability of a surface is dependent on its chemical composition, but also on the topography. Figure 5.4 (a-d) shows the typical three dimensional atomic force microscopy (AFM) images of the as deposited (A = 0), the iso-BTMS modified (A = 0.965), the HDTMS modified (B = 22.9 x10⁻²) and the TMES modified (C = 3.8) silica films on the glass substrates, respectively. The image was recorded at 1×1 μm² planar in contact mode. The surface of the films has many dispersed islands that are distributed on the film surface. The root-mean-square (RMS) roughness value of the film was analyzed with AFM. The the as deposited (A = 0), the iso-BTMS modified (A
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= 0.965), the HDTMS modified (B = 22.9 x 10^2) and the TMES modified (C = 3.8) silica films showed a RMS roughness values of 8, 40, 32 and 35 nm, respectively.

Figure 5.4 (a): AFM image of the unmodified (A = 0) silica film.

Figure 5.4 (b): AFM image of the iso-BTMS modified (A = 0.965) silica film.
Figure 5.4 (c): AFM image of the HDTMS modified (B = 22.9x10^2) silica film.

Figure 5.4 (d): AFM image of the TMES modified (C=0.965) silica film.
5.3.5 Fourier Transform Infrared Studies

The chemical composition of the films deposited on glass substrate was investigated by the FT-IR spectroscopy using the KBr method in transmission mode. Several characteristic absorption peaks were observed in the range 450 to 4000 cm\(^{-1}\) indicating the presence of organic groups in the sample.

Figure 5.5 (a-c) shows the FT-IR spectra of the unmodified (A = 0) silica film and iso-BTMS modified silica films with molar ratio (A) 0.579 and 0.965, respectively. The strong absorption peak at 1074 cm\(^{-1}\) corresponded to the Si–O–Si asymmetric stretching vibration [32]. The presence of this peak confirms the formation of a network structure inside the film. The absorption bands observed at around 2950 cm\(^{-1}\) and 1400 cm\(^{-1}\) are due to stretching and bending of C–H bonds [33]. The peak at around 1600 cm\(^{-1}\) and the broad absorption band at around 3400 cm\(^{-1}\) are due to the –OH groups [34]. For unmodified (A = 0) film, less intense C–H absorption peak at 2950 cm\(^{-1}\) and 1400 cm\(^{-1}\) are observed, while at 1600 and 3400 cm\(^{-1}\) more broad O–H peaks are observed indicating hydrophilic nature of the silica film. However, with an increase molar ratio, the intensity of C–H absorption peaks at 1400 and 2950 cm\(^{-1}\) is increased confirming the hydrophobic nature of the silica films. In the case of the as deposited (A = 0) silica films, a strong peak at 3400 cm\(^{-1}\) indicates that a significant fraction of the silanol groups exist on the film surface, which are found to be disappearing with increase in A value. The number of C–H peaks is quite notable for the film prepared with A value of 0.965, which are found to be less for the film prepared with A values of 0 and 0.579. The intensity of O–H peaks decreased and that of C–H peaks increased with an increase in A value, clearly confirming an increase in the hydrophobicity of the silica films.
Figure 5.6 (a and b) shows the FTIR spectra of the HDTMS modified silica film with B values of $11.4 \times 10^{-2}$ and $22.9 \times 10^{-2}$. The OH peaks are found to be slightly decreasing for HDTMS modified silica film as compared to unmodified silica film ($A = 0$). It can be seen from the FT-IR spectra that with an increase in B values, the intensity of the C-H absorption peaks at 2980, 1400 cm$^{-1}$ and Si-C absorption peak at 840 cm$^{-1}$ increased, clearly indicating the replacement of surface H from the Si-OH groups by the non-hydrolyzable =Si–C$_{16}$H$_{33}$ groups and hence an increase in the hydrophobicity of the films. The numbers of C-H and Si-C peaks are quite notable for the HDTMS modified films, which are found to be less in the as deposited films, clearly indicating better surface modification in the former case.

Figure 5.5: FT-IR spectra of the iso-BTMS modified silica films prepared from $A$ values of (a) 0 (b) 0.579 and (c) 0.965.
Figure 5.7 (a and b) shows the FTIR spectra of the TMES modified silica film with C values of 1.90 and 3.80. The OH peaks are quite visible for silica films prepared with A = 0, which are found to be disappearing with an increase in C value. With an increase in C value, the intensity of the peak at 1600 cm$^{-1}$ and the broad OH absorption band at 3500 cm$^{-1}$ decreased, whereas the intensities of the C-H absorption peak at around 3000 cm$^{-1}$ and Si-C absorption peak at around 840 cm$^{-1}$ increased clearly indicating the replacement of the surface H from the Si-OH groups by the non-hydrolysable Si-(CH$_3$)$_3$ groups resulting in higher hydrophobicity. The Si-OH band seen in
all the FT-IR spectra indicates that surface hydroxyls still exist, even though the materials show the strong hydrophobic properties.

As expected, when organic moiety is removed by a thermal treatment in air, the hydrophobic character is irreversibly changed to hydrophilic. The influence of temperature on the water-repellency is systematically investigated in order to evaluate the thermal stability of the films. Thermal stability tests were conducted by putting the hydrophobic silica films in a furnace (Vulcan, 3-550, USA) at various temperatures. The hydrophobic silica films prepared with iso-BTMS ($A = 0.965$), HDTMS ($B = 22.9 \times 10^{-2}$) and TMES ($C = 3.80$) were thermally treated, the hydrophobic silica films retained their hydrophobicity up to a temperature of 235, 250 and 280°C, respectively and above this temperature the films became hydrophilic. This is due to the fact that, above
these temperatures the organic groups get converted into Si-OH groups leading to the adsorption of water.

5.3.6 Water contact angle measurements

The hydrophobicity is usually determined by measuring the contact angle of a water droplet contacting a surface. The results given in table 5.4 shows the change in static and dynamic water contact angle values and maximum frictional force required to slide a 10 mg water droplet on film surface, with increase in molar ratio of iso-BTMS/TEOS (A). The sliding angle of the water droplet was observed by first placing the water droplet on horizontal surface and then slowly tilting the film surface until the droplet starts moving. It is found that, the static water contact angle increased and water sliding angle decreased with increase in A values. The static water contact angle increased from 65º to 140º and water sliding angle decreased from 42º to 16º with an increase in A value from 0 to 0.965, respectively. No visual water residue was left on the film surface and water droplets rolled off at all locations over the film surface. The adhesion mainly comes from the van der Waals force produced by the liquid-solid interface between the water droplet and the coated substrate [35]. The unmodified silica film shows strong adhesion with the water droplet, and the water droplet can slide off the coated substrate by gravity at sliding angle of 42º and the maximum frictional force required to slide off the water droplet from the surface is 65.57 μN. However, for the iso-BTMS modified silica films (A = 0.965), the adhesion between water droplet and the film surface is weak. As a result, the water droplet can roll off the tilted substrate (SA = 16º) easily with the maximum frictional force of 27.01 μN. At low A value, the silica film surface covered with fewer alkyl groups, leading to hydrophilic character and hence has low contact angle and high sliding angle values. However, as the A value increased, more silicon alkyl groups get attached to the silica film surface and hence large contact angle and low sliding angle values. Particularly, for the sample coated from A = 0.965, the highest water contact angle reached 140º and lowest water sliding angle of 16º,
indicating that there is a significant effect of iso-BTMS modification on the hydrophobic property. This high static water contact angle and low sliding angle is due to the replacement of surface terminal polar –OH groups by non-polar butyl groups. As a conclusion, modification of silica films with iso-BTMS as a co-precursor could be one of the possible way for improving hydrophobicity of film surface. Figures 5.8 (a-c) shows images of water droplet on the silica film prepared from A values of 0, 0.579 and 0.965, respectively.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>iso-BTMS/TEOS Molar ratio (A)</th>
<th>Water contact angle (θ)</th>
<th>Water sliding angle</th>
<th>Maximum frictional force $f_{\text{max}}$ (µN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>65º</td>
<td>42º</td>
<td>65.57</td>
</tr>
<tr>
<td>2.</td>
<td>0.192</td>
<td>92º</td>
<td>37º</td>
<td>58.97</td>
</tr>
<tr>
<td>3.</td>
<td>0.386</td>
<td>108º</td>
<td>31º</td>
<td>50.47</td>
</tr>
<tr>
<td>4.</td>
<td>0.579</td>
<td>125º</td>
<td>26º</td>
<td>42.96</td>
</tr>
<tr>
<td>5.</td>
<td>0.772</td>
<td>132º</td>
<td>21º</td>
<td>35.12</td>
</tr>
<tr>
<td>6.</td>
<td>0.965</td>
<td>140º</td>
<td>16º</td>
<td>27.01</td>
</tr>
</tbody>
</table>

Table 5.4: Change in static and dynamic water contact angle values and maximum frictional force with increase in A values.
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Figure 5.8 (a) Shape of water droplet on the unmodified (A = 0) silica film.

Figure 5.8 (b) Shape of water droplet on the iso-BTMS modified silica film prepared from A = 0.579.
By increasing the initial molar ratio of the HDTMS/TEOS (B) from 0 to $22.9 \times 10^2$, the water contact angle values increased from 65° to 125°. The results given in table 5.5 shows the change in static and dynamic water contact angle values and maximum frictional force required to slide a 10 mg water droplet on film surface, with increase in B value. It is found that, the static water contact angle increased and water sliding angle decreased with increase in B values. The static water contact angle increased from 65° to 125° and water sliding angle decreased from 42° to 27° with an increase in B value from 0 to $22.9 \times 10^2$, respectively. The highest water contact angle of 125° was observed for B = $22.9 \times 10^2$. Figures 5.9 (a-b) shows a shape of water droplet on the silica film prepared with B = 11.4 x $10^2$ and 22.9 x $10^2$ respectively. The photographs clearly indicate that the water contact angle on the film surface increases with an increase in the B values. The water drop displayed a comparatively large water contact angle (125°) on the HDTMS modified silica film prepared from A = 0.965.
films than the contact angle (65°) on unmodified silica films, which testified that the hydrophobic surface has been created.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>HDTMS/TEOS Molar ratio (B)</th>
<th>Water contact angle (θ)</th>
<th>Water sliding angle</th>
<th>Maximum frictional force $f_{\text{max}}$ (μN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>65°</td>
<td>42°</td>
<td>65.57</td>
</tr>
<tr>
<td>2.</td>
<td>$5.7 \times 10^{-2}$</td>
<td>79°</td>
<td>39°</td>
<td>61.67</td>
</tr>
<tr>
<td>3.</td>
<td>$11.4 \times 10^{-2}$</td>
<td>98°</td>
<td>32°</td>
<td>51.93</td>
</tr>
<tr>
<td>4.</td>
<td>$17.2 \times 10^{-2}$</td>
<td>112°</td>
<td>30°</td>
<td>49</td>
</tr>
<tr>
<td>5.</td>
<td>$22.9 \times 10^{-2}$</td>
<td>125°</td>
<td>27°</td>
<td>44.49</td>
</tr>
</tbody>
</table>

Table 5.5: Change in static and dynamic water contact angle values and maximum frictional force with increase in B values.

Figure 5.9 (a) Shape of water droplet on the HDTMS modified silica film prepared from $B = 11.4 \times 10^{-2}$. 
The results of TMES modified silica films is given in table 5.5 which shows the change in static and dynamic water contact angle values and maximum frictional force required to slide a 10 mg water droplet on film surface, with increase in C value. It is found that, the static water contact angle increased and water sliding angle decreased with increase in C values. The static water contact angle increased from 65° to 130° and water sliding angle decreased from 42° to 24° with an increase in C value from 0 to 3.8, respectively. At lower TMES/TEOS molar ratios (C), the silica film surface is covered with fewer silicon alkyl groups, leading to hydrophilic character and hence resulting in lower water contact angle (θ). However, as the C value is increased, more Si(CH₃)₃ groups are attached to the silica film surface and hence larger θ values. Further it is clear from the figure 5.10 (a-b) that, as the C value increased, the contact angle also increased. The character of the silica film shifts from hydrophilic to hydrophobic due to the incorporation of CH₃ groups into the silica film with the help of TMES as the co-precursor.
Table 5.5: Change in static and dynamic water contact angle values and maximum frictional force with increase in C values.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>TMES/TEOS Molar ratio (C)</th>
<th>Water contact angle (θ)</th>
<th>Water sliding angle</th>
<th>Maximum frictional force $f_{max}$ (μN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>65º</td>
<td>42º</td>
<td>65.57</td>
</tr>
<tr>
<td>2.</td>
<td>0.95</td>
<td>69º</td>
<td>37º</td>
<td>58.97</td>
</tr>
<tr>
<td>3.</td>
<td>1.90</td>
<td>85º</td>
<td>30º</td>
<td>49</td>
</tr>
<tr>
<td>4.</td>
<td>2.85</td>
<td>123º</td>
<td>27º</td>
<td>44.49</td>
</tr>
<tr>
<td>5.</td>
<td>3.80</td>
<td>130º</td>
<td>24º</td>
<td>39.86</td>
</tr>
</tbody>
</table>

Figure 5.10 (a) Shape of water droplet on the TMES modified silica film prepared from B = 1.90.
5.3.7 Effect of humidity on the wetting properties of the silica films

For artificial superhydrophobic surfaces, the water repellent capability gradually degrades during long-term outdoor exposure and accumulation of contamination. Humidity is a measure of the amount of water vapor in the air. The hydrophilic silica films contain –OH groups on their surfaces, which react with the atmospheric moisture and the film structure gets deteriorated. The effect of humidity on the wetting properties of the hydrophobic silica films prepared with iso-BTMS (A = 0.965), HDTMS (B = 22.9 x 10^{-2}) and TMES (C = 3.80) silica films was carried out at relative humidity of 85% at 30°C temperature over 45 days. It was observed that there was no significant change in the contact angle for the all the silica films even up to 45 days. The effect of humidity on the water contact angle of the films with respect to number of days is shown in table 5.6. This reveals that the all hydrophobic silica films maintained high contact angle during the humidity test periods.
### 5.3.8 Optical transmission studies

The optical transmission of the modified hydrophobic silica films are shown in the visible wavelength range (350-750 nm). Figure 5.11 shows the optical transmission spectra of the iso-BTMS (A = 0.965), HDTMS (B = 22.9 x 10^{-3}) and TMES (C = 3.80) modified silica films. All the films are transparent because they do not absorb visible light. The iso-BTMS, HDTMS and TMES modified films showed 95, 92 and 76% of optical transmission, respectively.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Samples</th>
<th>CA (θ) before exposing to humid surrounding</th>
<th>CA (θ) after exposing to humid surrounding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>After 15 days</td>
</tr>
<tr>
<td>1.</td>
<td>iso-BTMS modified silica films</td>
<td>140°</td>
<td>140°</td>
</tr>
<tr>
<td>2.</td>
<td>HDTMS modified silica films</td>
<td>125°</td>
<td>123°</td>
</tr>
<tr>
<td>3.</td>
<td>TMES modified silica films</td>
<td>130°</td>
<td>129°</td>
</tr>
</tbody>
</table>

Table 5.6: Effect of humidity on a contact angle of the silica films
5.4 Conclusions

Optically transparent, water repellent silica films were synthesized at room temperature by sol-gel process using isobutyltrimethoxysilane (iso-BTMS), hexadecyltrimethoxysilane (HDTMS) and trimethyleneoxysilane (TMES) as a hydrophobic agent. The silica films prepared from iso-BTMS (A = 0.965), HDTMS (B = 22.9 x 10^{-2}) and TMES (C = 3.80) showed a static water contact angle of 140°, 125° and 130°, respectively and water sliding angle of 16°, 27° and 24°, respectively. All the modified silica films are strongly water repellent, optically transparent, adherent, thermally stable, and durable against humidity. As a conclusion, modified silica films revealed to be

Figure 5.11: Optical transmission of the (A) iso-BTMS (A = 0.965),
(B) HDTMS (B = 22.9 x 10^{-2}) and (C) TMES (C = 3.80) silica films.
effective for improving and maintaining film properties. By modification of silica sols with hydrophobic agents, sol-gel coatings could be prepared on glass substrate at room temperature owing to excellent water repellent properties without any addition of fluorine containing compounds.
References

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