Chapter 3

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Abstract

We report here a facile method of modulating the lengthscales of self-organized dewetting of polystyrene thin films by varying the extent of silane grafting on the substrate. The self-assembled monolayers (SAM) of octadecyltrichlorosilane (OTS) were grafted on glass substrates by exposing them to different doses of OTS vapors in a controlled, low-pressure environment. Measurement of water contact angles on the modified glass surfaces showed that the contact angles could be continuously increased from 40° to 70° by increasing the time of exposure to the OTS vapors from a few minutes to several hours. Polystyrene (PS) thin films were spin coated on the modified glass substrates and water-solvent mixture induced dewetting of the PS thin films was carried out, where the dewetting kinetics depended on the spreadability of water on the surface. We observed a reduction in the length scales of the dewetting, i.e. the wavelength of instability (λ) and droplet size (d), by increasing the extent of OTS exposure. The λ for a 50nm thick PS film decreased from 12 to 4 µm while the droplet diameter (d) also decreased, from 2.5 to 1.6 µm.

3.1 Introduction

Controlling the surface properties such as lubrication, adhesion and wetting has attracted immense interest in many everyday applications. In particular the wetting behaviour of the surface is extremely critical and can impart different functionalities in the materials. As they offer a way to vary the chemical properties of surfaces, therefore the number of applications is large. Increasingly, surfaces are modified using organosilane self-assembled monolayers

(SAM) to achieve desired surface characteristics like minimal friction, wearing resistance, low surface energy, chemical affinity or inertness. Depending on the application, complete wetting may be desirable as in case of paint coating on various smooth surfaces whereas in other cases wetting may be undesirable and needs to be prevented. Some examples where wetting is undesirable include anti-fouling coatings on ship hulls, non-stick coatings on frying pans or car windshields and rear-view mirrors, sensors, advanced lithography, lubrication, and anti-stiction coatings for MEMS. Surface properties of materials can be modulated additive or subtractive methods.[1] The subtractive methods use various techniques to selectively remove material by chemical etching, laser ablation, plasma or corona treatment etc. Although these methods are fairly simple and scalable and therefore are adopted by industries widely, they still lack in achieving precise control at molecular-level in the distribution of the functional groups and molecules. The additive methods include self- assembly and the controlled deposition of molecules (typically amphiphilic) as in Langmuir-Blodgett films (LB), polymer thin films, self-assembled monolayers (SAM), chemisorption on metal and oxide surfaces or nano coatings of various kinds. [2,3] These methods can be used to achieve superior properties with better precision. Surfaces are generally modified to increase selectivity, sensitivity of sensors, surface rigidity and detection performance. [4-7] Organic polymers are used to prepare monolayers that were either physically coated or chemically grafted onto substrates. [8,9] In particular, octadecyltrichlorosilane (OTS) SAM coatings on silica are utilized to fabricate dielectric barrier layers for field effect transistors, to manufacture functional coatings for micro fluid systems or to tune surface properties in micro electromechanical systems. In recent years, many studies have been done on the assembly of n-octadecyltrichlorosilane (OTS) on silicon oxide surfaces to form a SAM.[10,11] Self-assembly of molecules onto surfaces has various scientific and industrial applications.[12] One of the preferred method to prepare SAMs on glass surface is silanization, i.e. self-assembly of organosilane molecules ($RSiX_3$, where R is

an organic functional group and X is a leaving group after the reaction) on glass or metal oxide surface.[13] The organic functional group or side chain of the organosilane molecules can be modified to make the surface super-hydrophilic[14,15] or super-hydrophobic.[16,17]
One of the most commonly used organosilane is tri-alkoxy-silane in which silicon atom is positioned at the center of the tetrahedron and three similar hydrolysable alkoxy groups (such as methoxy or ethoxy) occupy three or the four corners of the tetrahedron and the fourth corner is occupied by a functional group that reacts to the substrate. A wide range of silanes are commercially available having carboxyl, thiol, amine or other functional groups. Amongst the tri-alkoxy-silanes, octadecyltrichlorosilane (OTS) is the most widely used to make SAMs on different substrates. Previous works have confirmed that the monolayers derived from longchain alkyltrichlorosilanes are highly ordered. [18]

OTS SAMs can be fabricated on various substrates such as glass, silica or oxidized silicon either by dip coating in diluted OTS solutions [19-21], casting pure OTS [22] or vapor depositions. [23-26] All these approaches begin with the hydroxylation of the silica surface using wet chemical or dry plasma methods. In dip coating, clean substrates are immersed in a solution of target silane reagent for a specific period of time. One may purposely introduce water traces to study its effect. Generally, water from the atmosphere accelerates hydrolysis. Increased amount of water may cause formation of cluster of silane molecules resulting into fractal structures and poor quality SAMs. Another, method that is commonly used is that the clean substrates are exposed to silane vapor in vacuum in the presence of heat or no heat. In a proper vacuum condition, the availability of water is limited and thus the resulting SAMs may not show full coverage.

In 1980, Sagiv investigated the formation of octadecyltrichlorosilane (OTS) self-assembled monolayers with glass substrates for the first time. Since then various researchers have studied the formation of OTS monolayers on a variety of substrates i.e., mica, silicon, silica and glass substrates by self-assembly of OTS molecules due to its numerous applications in different research areas.[27] Various researches have been done on different aspects of reaction, including the hydrolysis of OTS molecules, the adsorption of OTS on substrate surfaces, the effect of the reaction temperature, the role of the solvents, the effect of the alkyl chain length and the functional group and the substrates materials and their pretreatments. Because of the exhaustive work done on OTS, ($CH_3(CH_2)_{17}SiCl_3$), it is one of the most widely used silane for making SAMs on a variety of substrates.[28-30] The chemisorption of OTS on Si/SiO_2 substrates has been well studied and the thermodynamics and kinetics of the process is well-understood.[31,32] One major problem in liquid-phase silanization is the copolymerization of OTS in the presence of atmospheric moisture, which leads to the formation of thick and disordered layers on substrate.[33] It is a well-known fact that OTS hydrolyses in the presence of atmospheric moisture. On exposing OTS solution in the open air, the formation of silanol takes place due to hydrolysis of OTS molecules. This limits the use of organosilanes in liquid-phase methods because of low reproducibility and expansive process. Because of the formation of large and unremovable agglomerates, a liquid-phase method is unsatisfactory for the formation of silane coatings in many applications. To overcome these limitations, deposition of organosilanes from vapour-phase has been proposed because due to low density of silane molecules in vapor phase the self-polymerization is very less. Also, vapor-phase have better precision over liquid-phase method.

A small quantity of water is needed to enhance adherence of OTS through the hydrolysis of chloro group, however excessive water may cause co-polymerization of OTS molecules in the bulk solution.

3.1.1 The lotus effect

There are many different ways that water droplets can interact with a surface. How well water bonds to the surface in comparison to how well it bonds to itself determines the nature of the interaction. It varies from being super-hydrophilic, where water may completely and thoroughly wet a surface to produce a flat puddle due to a strong water-surface interaction through to super-hydrophobic, with a weak water-surface interaction where water is successfully repelled from the surface to form a droplet that is close to spherical.[34,35] The lotus effect, named after the lotus plant, *Nelumbo nucifera*, which explains the self-cleaning activity of particular leaf surfaces, is one example of super-hydrophobic surfaces that can be found in nature.

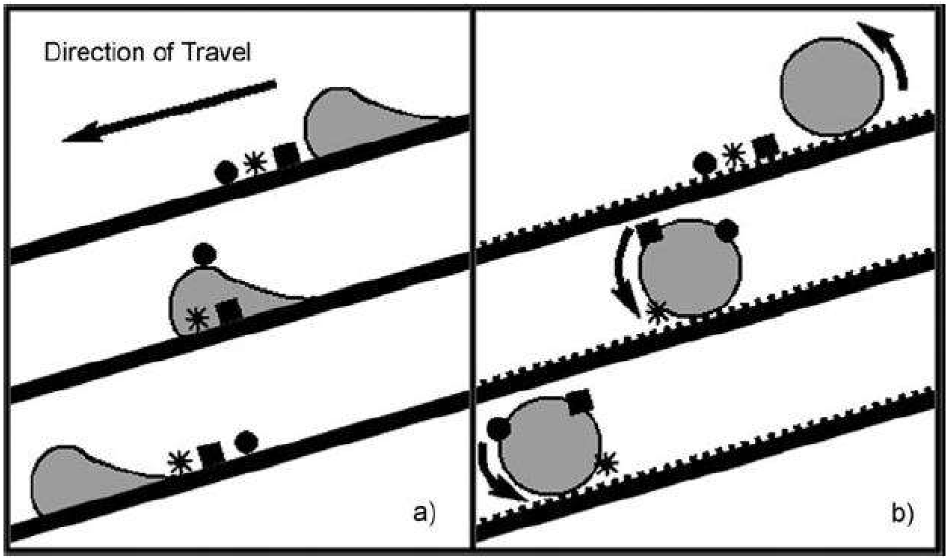

Figure 12: Diagram demonstrating the cleaning mechanism on smooth (a) and rough (b) super-hydrophobic surfaces.

Water will form nearly spherical droplets that roll across the surface instead of sliding if the leaf exhibits a high enough hydrophobicity. More foreign objects are picked up due to the rolling action. The surface of the lotus leaf adopts this self-cleaning process and makes it easier for water droplets to roll and pick up dirt as they go.[36] The leaves themselves are covered in a waxy substance that serves to repel water and has protrusions that make the waxy surface extremely rough. When both of these surface properties are present, water droplets roll rather than slide. The rough, hair-like nanostructures (figure 12 and 13) may also function to trap air beneath the water droplets, enhancing the rolling motion. The water contact angle for the etched PDMS surface is higher than 160° and sliding angle is lower than 5°. A PS-PDMS block polymer combined with PS homopolymer was electrospun by Ma et al. to create a superhydrophobic membrane in the form of a nonwoven fibre mat.

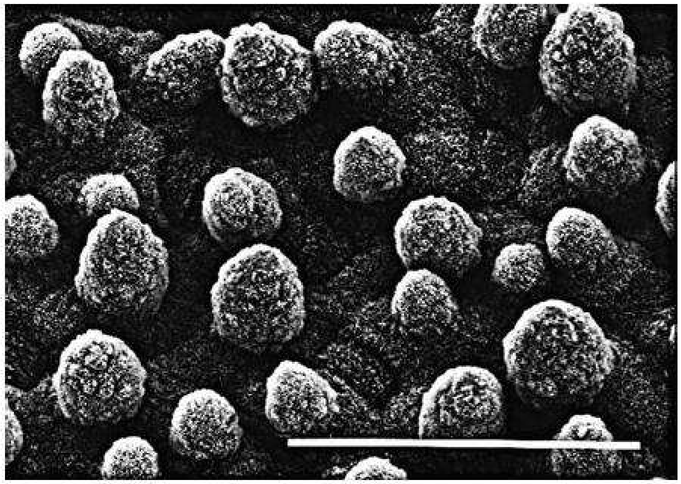

Figure 13: SEM images of Nelumbo nucifera (lotus) showing a highly rough surface microstructure (scale bar=50 mm). Reproduced from ref. [54].

Water strider legs (Figure 14) are another instance of severe hydrophobicity in nature. They have a well-defined microstructure that is covered with a layer of wax that is secreted.

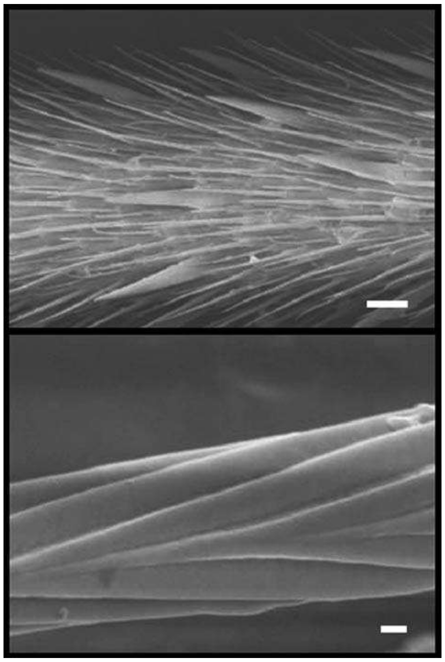

Figure 14: SEM images of a water strider leg. Reproduced from ref. [54].

Some insects' wings have hydrophobic properties as a result of surface microstructure and composition.[37] A network of microstructured scales on the surface of butterfly wings causes a directional rolling of water away from the butterfly's body, exhibiting super-hydrophobic qualities. These surface properties has inspired the design of artificial hydrophobic surfaces.

3.1.2 Surface Models and Characterization

3.1.2.1 Surface models

The way surface interacts with water can be predicted and explained using models. The Wenzel and Cassie-Baxter models are the two that are most frequently used. The water contact angle (θ), or the angle formed by the droplet and the surface (Figure 15), is used in both of these models as a direct indicator of surface hydrophobicity. A surface is considered hydrophobic if the contact angle it has with water is larger than 90^o, and hydrophilic if it is lower than 90^o. The more hydrophobic, or water-repellent, a surface is, the greater the contact angle.

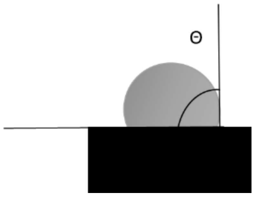

Figure 15: The water contact angle (Θ) shown as the angle between the plane of a surface and the tangent at which the liquid droplet makes contact with the surface.

3.1.2.2 Wetting behaviour

When a liquid comes into touch with a solid, it will expand along the solid surface, a phenomenon known as wetting. The degree of wetting is usually calculated by using contact angle. Equation 5 illustrates the state of a droplet at rest on an ideal, smooth surface according to Young's equation.

$$\gamma_{sv} = \gamma_{lv}\cos\Theta_y + \gamma_{sl} \qquad (5)$$

where γ_{sv}, γ_{lv} and γ_{sl} respectively are the surface tensions for solid–vapor, liquid–vapor, and solid–liquid interfaces and Θ_y is the CA of the liquid droplet as shown in the figure 16.

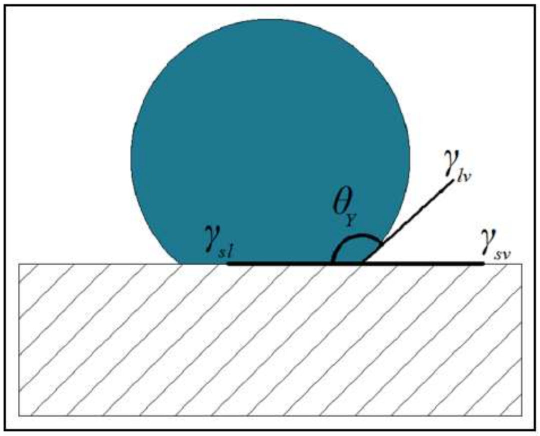

Figure 16: Figure explaining Young’s equation

Two theories—the Wenzel model and the Cassie-Baxter model describe the state of the droplet on a rough surface. Equation (2) and Figure 17(a) illustrate how the droplet is in uniform contact with the rough surface according to the Wenzel model.

$$\cos\Theta_W = R_f \cos\Theta_Y \qquad (6)$$

where R_f is the roughness factor and Θ_w is the Wenzel CA.

The heterogeneous wetting is described by the Cassie-Baxter model. According to equation (3) and Figure 17(b), only the rough surface of the peaks is in touch with the droplets, and the valleys between the droplets and the rough surface are filled with air

$$\cos \Theta_{CB} = f_1 (\cos\Theta_1 + 1) - 1 \quad (7)$$

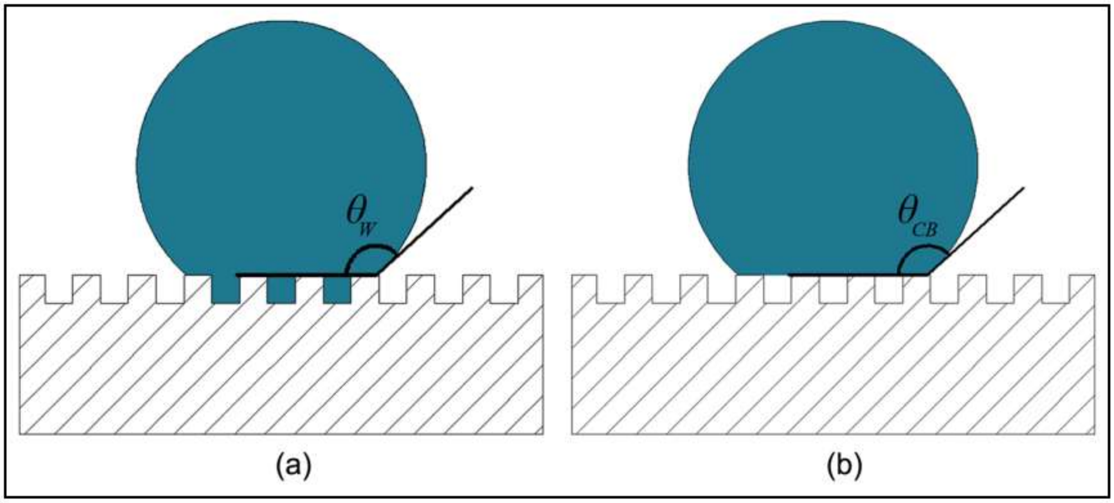

Figure 17: (a) Wenzel model and (b) Cassie–Baxter model.

Where f_1 is the area fraction of the solid surface in contact with the liquid droplet, Θ_{CB} is the CA of the liquid droplet, and Θ_1 is the CA of component 1. When the CA is larger than 150, the solid surface can be referred to as a superhydrophobicity surface.[38]

3.1.3 Conventional fabrication of hydrophobic surface

Now a days a wide variety of physical and chemical method have been developed to synthesize a hydrophobic gradient surface through one of the following methods

1) Creating a surface rough on hydrophobic material
2) Modifying a rough surface with hydrophobic coating

3.1.3.1 Creating a surface rough on hydrophobic material

In this method hydrophobic polymer are used as substrate to obtained superhydrophobicity. By making the surface of polymer material rough the hydrophobic behavior can be observed. A laser etching method was reported to make superhydrophobic polydimethylsiloxane (PDMS) surface, which contains micro-, submicro- and nano-composite structures.[39] A PS-PDMS block polymer combined with PS homopolymer was electrospun to create a superhydrophobic membrane in the form of a nonwoven fibre mat. The combined effect of surface enrichment in siloxane and surface roughness of the electrospun mat itself is attributed for the superhydrophobicity.[40] By casting the polymer solution in which nonsolvents were utilised in conjunction with p-xylene solvent as a polymer precipitator to increase the extent of polymer phase separation, superhydrophobic gel-like porous popypropylene coating were created.[41] Using a two-step solution method, ZnO rods were produced. Due to the surface roughness and low surface energy of the plane of the nanorods exposed on the film surface, the ZnO nanorods films showed superhydrophobicity.

3.1.3.2 Modifying a rough surface with hydrophobic coating

Even though creating superhydrophobic surfaces from intrinsically hydrophobic materials just requires a single step, Unfortunately, many materials lack the necessary low surface free energy to be intrinsically hydrophobic. These intrinsically hydrophilic materials typically require a two-step process to create superhydrophobic surfaces, first creating a rough surface and then modifying it with substances like fatty acids, organic silanes, and alkane thiols, which can provide a low surface free energy after linked to the surface. When the substrate is slightly tilted, water droplets roll off these surfaces very quickly. By employing a femtosecond laser to etch silicon wafers, a method for producing micro/nanoscale roughness on silicon wafers was reported.[42] Fluoroalkylsilane molecules were deposited on the resulting surfaces to produce contact angles greater than 160° and minimal hysteresis. A vapor-liquid-solid mechanism was used to create silicon nanowires on Si/SiO2 substrates. After being modified with the fluoropolymer C4F8, the resulting rough surfaces showed superhydrophobicity.[43]

3.1.4 Chemical modification with silane

3.1.4.1 Formation of silane monolayer

Silanes can react with metal oxide surfaces from either the liquid or gas phase in mild conditions. Figure 18 depicts the general reaction of various silane types to hydroxilated surfaces.

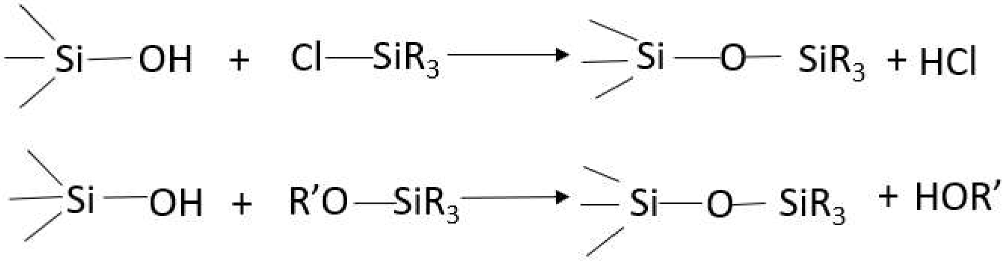

Figure 18: Reaction of silanes with hydroxilated surfaces

When trying to control the reaction, the high reactivity of silane can be a hindrance. The rate of the reaction and its extent depend on a number of variables, including temperature, the type of silane used, the solvent used, the amount of water present during the reaction, and the reaction time itself. It has been observed since the beginning that one of the main determinants in the formation of the silane layer is the concentration of water on the surface and in solution. It was suggested that silanes were hydrolized with water at the surface, and that this was followed by a condensation with the hydroxyl groups present at the solid-liquid interface.[44] The role of water was further explained in the reaction of chlororsilanes. Since there was no chance for lateral polymerization, they determined that the process would not continue to completion in the absence of water.[45]

3.1.4.2 Silane coupling agents

Silane coupling agents are generally illustrated

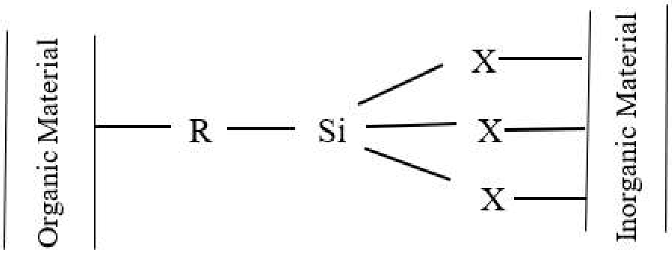

Figure 19: Silane coupling agent

Silicone (Si) is the center of the silane molecule which contains an organic functional group (R) [ex: vinyl, amino, chloro, epoxy, mercapto, etc.], with a second functional group (X) [ex: methoxy, ethoxy, etc.].(figure 19) The functional group (R) will attach to an organic resin, whereas the functional group (X) will attach to an inorganic substrate to provide a "coupling" action. Generally, silane coupling agents are utilised as mediators to bind organic molecules to inorganic materials. Silanes will thereby enhance the electrical and mechanical strength characteristics of materials in both wet and dry conditions. Silane coupling agents are primarily used in crosslinked polyethylene power cables and reinforced polymers. Resins, concrete, sealant primers, paint, adhesives, printing inks, and dyeing aids are other applications. When the silane molecule's inorganic group (X) hydrolyzes, silanol is formed, and it bonds to the inorganic substance through a siloxane bond as shown in figure 20. Heating results in a strong bond between the organic material and the inorganic material.

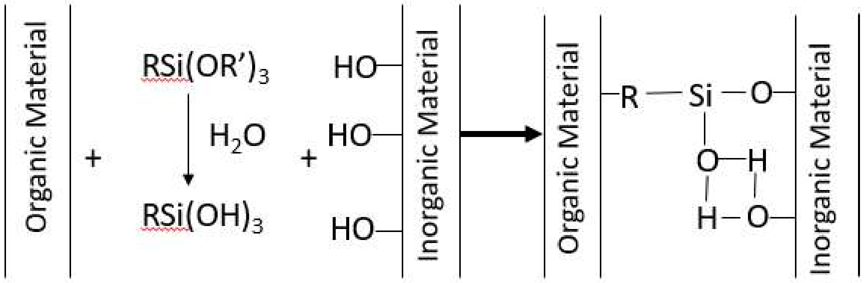

Figure 20: Reactions where silane is acting as a coupling agent.

3.2 Material and Methods

3.2.1 Materials and chemicals

Octadecyltrichlorosilane (OTS) was procured from Sigma-aldrich and used as received**.** HPLC grade chemicals used Methyl Ethyl Ketone, acetone, tetrachloroethylene (TCE), methanol, ammonium hydroxide, hydrogen peroxide, Concentrated sulphuric acid were purchased from Merk, Mumbai, India. The materials like micropipette and micropipette tube, glass slide holder, vials, dropper were purchased from M.S. Scientific, India.

3.2.2 Equipments

The equipments used in the present work were spin coater, vortex mixer, hot plate, sonicator, laminar flow chamber, dessicator, hair dryer, etc.

3.2.3 Glasswares

Beaker, measuring cylinders, pipette, volumetric flasks, petridishes etc. were used which were made of boro-silicate glass. Prior to use all the glass wares were sterilized with sulphuric acid and potassium dichromate and thereafter rinsed properly with distilled water.

3.2.4 Method

3.2.4.1 Cleaning of Silicon wafers

The silicon wafers were thoroughly cleaned before use in order to remove dust particles and organic contaminants from the substrate. The silicon wafers were cleaned by RCA1 protocol. In this firstly, the silicon wafers were soaked in 10% soap solution. Then the substrates were cleaned by brushing for 1min. for each substrate. Later it was rinsed without froth. Then it is boiled in Trichloroethylene (TCE) solution followed by boiling it into acetone and methanol. 511 solution is prepared by mixing 40 ml ammonium hydroxide, 40 ml of hydrogen peroxide and 200 ml of water in a beaker. The substrates are boiled in this solution at 100ºC for half an hour. Pirannah solution a highly oxidizing solution is prepared by mixing 3 parts of concn. sulphuric acid to 1 part of hydrogen peroxide. The substrates were slowly dipped in this solution and kept for 15 min. The substrates are finally stored in DI water.

3.2.4.2 Silanization

500 µl (0.5 ml) OTS was also placed adjacent to the glass slide in the vacuum desiccator. The pressure in the vacuum desiccator is reduced by connecting to a vacuum pump, which kept running during the experiment. The substrate was removed from the vacuum desiccator at different time intervals ranging from 1 minute to 12 hours. The glass slides were rinsed with hexane to remove any physiosorbed organosilane molecules and subsequently dried and cured in vacuum oven at 100ºC for 10 minutes. The contact angle was measured using contact angle goniometer by sessile drop technique. For water contact angle measurements, 10 µl droplets of DI water were placed on the SAM films at several locations, using a micro-pipette. The schematic diagram is shown in Figure 21.

3.2.4.3 Dewetting procedure

Silanized glass substrates were coated with PS (M_w=280 kg mol^{-1}, Sigma Aldrich) by spin coating (3000 rpm for 60 s.) using 1% w/v solution of PS in toluene. The spin-coated PS thin films were then annealed in vacuum oven at 70°C for 3 h to minimize the residual stresses and for the removal of reminiscent solvent. Dewetting of these PS films was carried out in a mixture of Water, MEK and acetone in the ratio of 15:7:3. After the dewetting is complete, dewetted structures were examined using an optical microscope.

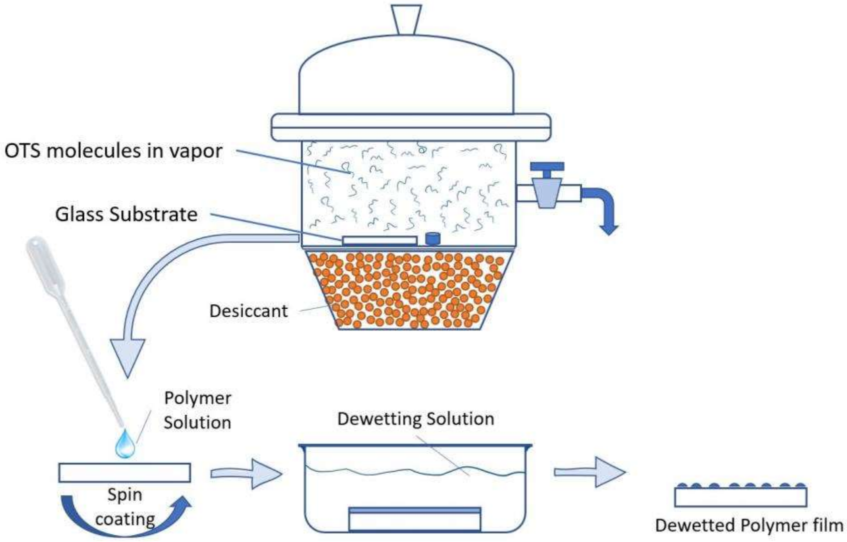

Figure 21: Schematic diagram of preparation of SAM on glass substrate in a desiccator by vapor phase silanization and subsequent coating of PS thin film and its dewetting under mixture of water and solvent.

3.3 Result and Discussion

Silylating agents like OTS are used to modify the nature of the glass substrate. The reaction of OTS molecules with glass slides to form self-assembled monolayers was reported previously. [46,47] Reaction with freely vibrating and with adjacent H-bonded surface hydroxyl groups both has been suggested. [47,48] Despite of the extensive range of applications, the nature of the interaction of OTS with hydroxylic substrates remain ambiguous.[21]

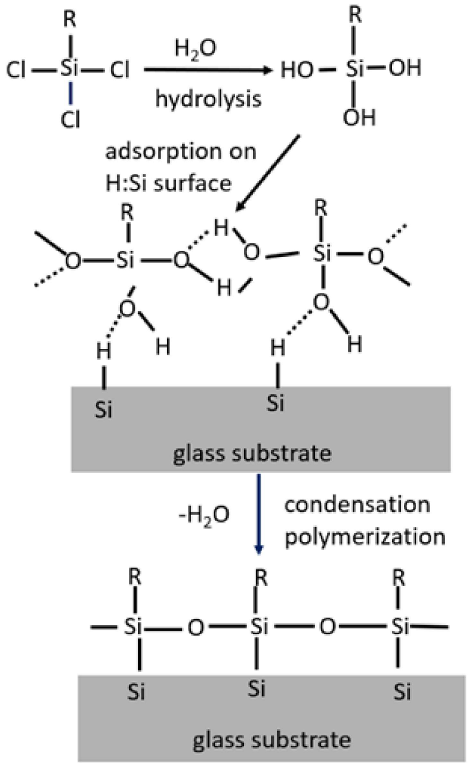

Figure 22: The mechanism of covalent linking of OTS molecules on glass surface**.**

However, there is a three-step mechanism, which is commonly accepted and shown in Figure 22, the first step is the hydrolysis of the chloro moieties of OTS at the hydroxylic substrate surface that forms a silanetriol, which then physically adsorbs onto the substrate via hydrogen bonding and ultimately forms $Si_{substrate}$-O-Si_{silane} and Si_{silane}-O-Si_{silane} cross-linking types of covalent bonds. Adsorption of amphiphilic molecule onto polar substrates forms hydrophobic densely packed monomolecular films. Alkyl- and fluoro- alkyl-substituted silanes of the general formula $RSiX_3$ where R is $CH_3(CH_2)_{17}$, $CF_3(CF_2)_5(CH_2)_2$ or $CF_3(CF_2)_7(CH_2)_2$ and X is Cl, OMe, or OEt, are the most commonly used reagents for this reaction. [22-26] The hydrophilic head, $SiCl_3$, Si $(OMe)_3$, or Si $(OEt)_3$ is polar and hydrolyses in aqueous solution to produce silanol groups which can condense with silanol groups on the surface of silica to form siloxane linkages while exposing the hydrophobic tail, CH_3 or CCl_3 to the atmosphere.

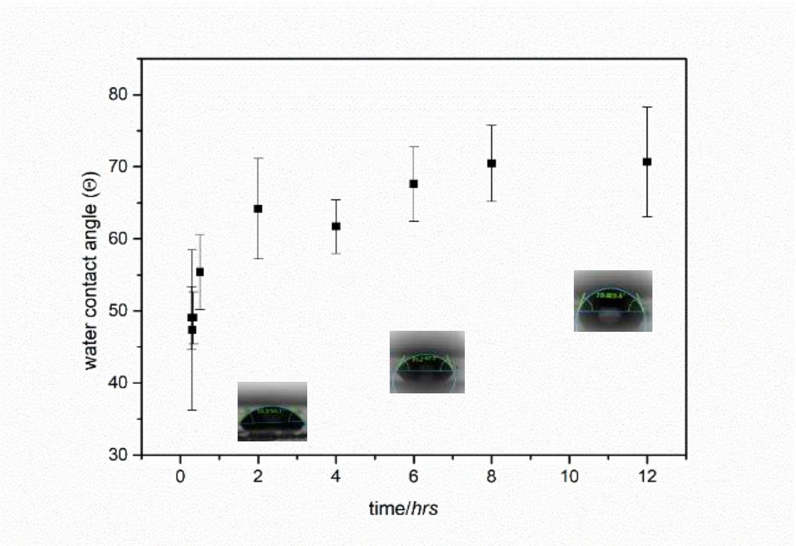

Figure 23: Effect of change in the surface density of grafted OTS molecules (which is a function of OTS vapor exposure time for glass) on water contact angle (θ) on glass substrate. The water contact angle was found to be less than 5° on RCA-1 cleaned glass slides. The glass surface was exposed to the vapor of OTS in a vacuum desiccator for varying extent of time.

The reaction occurs spontaneously, and no catalyst is needed.[27] The wettability study provides information about OTS coverage and degree of uniformity. Silanized samples were examined with sessile drop contact angle goniometer under ambient conditions. The average value of several 10 µl droplets of DI water placed at different locations on the substrate. The reported angles are the average values measured at more than 10 points and the standard deviation as error. The results indicate that the OTS had been grafted on the glass surface to the different extents depending on the time of exposure. To analyze the effect of time on the silane film growth and the resulting change in the wetting behaviour, a series of reaction times ranging from 1 min to 12 h were taken. Figure.23 shows the contact angle variation observed as a function of increasing exposure time for a fixed amount of OTS (500 µl) in the desiccator. It was observed that until 15 minutes there was no detectable change in the water contact angle possibly because of the patchy coverage of silane molecules on substrate. After 15 to 17 minutes when the OTS-SAM was formed on the glass substrate, the contact angle jumps to nearly 45^{o} indicating the larger surface coverage resulting significant change in hydrophobic property of the OTS modified glass substrate. The contact angle increased rapidly at the initial stage (up to 2 hours) and then plateaued out as complete coverage is approached. After 8 hours no significant change in the contact angle was observed and the maximum contact angle achieved was nearly 70°. The contact angle measurements also showed that due to the chemical grafting of OTS molecules on the substrate it was quite resistant to environmental changes and the contact angle remains same over the time of at least a week. Also, according to the kinetics of adsorption, in the initial time, there are many hydroxyl (-OH) groups on the surface that will act as driving force for the adsorption of -Si-OH in OTS molecules on glass surface. On increasing the reaction time, the density of -OH groups decreases and the already adsorbed OTS molecules on the surface tend to decreases the new adsorption of OTS molecules, therefore plateauing out the water contact angle.

To harness the property of varying extent of wettability of glass surface, we investigated the room temperature instability and dewetting of ultrathin(<100nm) polystyrene (PS) films induced by water-solvent solution mixture, on silanized glass substrates and examined its effect on the length scales of instability. It has been reported earlier that the dewetting of PS thin-films can be tremendously intensified by submerging it in a homogeneous liquid mixture of water and solvent as compared to dewetting in air by heating above the glass transition temperature.[51] Dewetting under water-solvent mixture reduces the lengthscale of dewetting (i.e. average distance between droplets and the droplet size) by more than an order of magnitude and produces droplets having significantly higher aspect ratio thereby enabling them to be used as the nano lenses in optical applications. The proposed mechanism of dewetting is the diffusion of solvent molecules in polymer film lowers down the glass transition temperature below room temperature thereby allowing the polymer film to self-organize in to droplets as it was coated on a nonwettable substrate. The dewetting starts with the homogenous nucleation of holes on the film which grow in size and then coalesce to form a ribbon network of polymer which eventually breaks into droplets.[51] The kinetics of dewetting is determined by the viscosity of polymer and the wettability of substrate. Higher proportion of solvent in the dewetting liquid as well as the low molar mass of polymer will decrease the polymer viscosity and increase the speed of dewetting process. [52,53] Whereas the wetting of the substrate with the dewetting liquid potentially can accelerate the receding contact line of droplet. It has also been reported that a polymer thin film does not dewet when coated on a hydrophobic substrate.[49] Here we show the effect of different extent of silanization on the dewetting lengthscale. The 50 nm thick PS films were coated on surface modified glass substrates and kept in a dewetting liquid mixture of water, methyl-ethyl ketone (MEK) and acetone in the ratio 15:7:3. The substrates were taken out from the dewetting mixture after 30 min and dried in hot air. The optical microscope images of the dewetted samples are shown in Figure 24. Figure 24a shows the dewtted PS film on cleaned bare glass surface whereas Figure 24 b-d show the dewetted structure on cleaned glass substrates that were exposed to the OTS vapours for 17 minutes, 4 hours and 12 hours respectively. It is evident that on the substrates having higher water contact angle dewetting liquid spreads slower therefore allowing more holes to nucleate during the dewetting process thereby increasing the number density of droplets in the

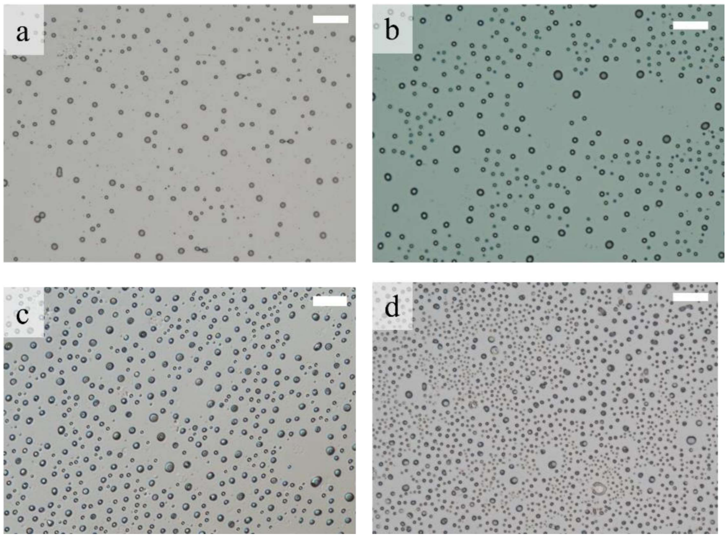

Figure 24: Optical micrographs for dewetted PS films on glass substrates with varying extent of OTS vapor exposure. Length scale variation of a 50 nm PS film on glass substrate for (a) bare glass and glass substrates exposed to OTS vapor for (b) 17 min, (c) 4 hrs and (d) 12 hrs. (scale bar: 50 µm)

final structure. The similar observations were made in an earlier work where slower dewetting kinetics resulted in reduced lengthscale of dewetting.[53]

The instability wavelength (*λ*) and droplet diameter (*d*) were measured for different substrates keeping the PS film thickness constant (50 nm). The instability wavelength (λ) for bare glass substrate was 11.9 ± 1.9 µm which got reduced; for 17 min OTS vapor exposed substrate to 9.9 ± 2.1 µm, for 4 hrs exposed substrate to 6.9 ± 3.5 µm and for 12 hrs exposed substrate to

4.2 ± 0.4 µm. Similarly, the droplet size also got reduced from 2.47 ± 0.40 µm for bare glass substrate to 1.66 ± 0.11 µm for 12 hours exposed substrate as shown in figure 25. Therefore, it can be concluded that the characteristic lengthscales i.e., instability wavelength (*λ*) and particle diameter (*d*) for OTS grafted substrates is significantly smaller than the bare glass substrate. The effect can be attributed to the fact that in case of OTS grafted substrates the kinetics of hole growth is much slower owing to its reduced affinity to water, because of which a greater number of holes can be nucleated resulting in a greater number of droplets. This decreases the characteristic length scales of dewetting in case of OTS grafted glass substrates. Also, due to silanization the surface energy of the substrate decreases which causes the destabilizing forces such as van der Walls to win over stabilizing force of surface tension. Consequently, the surface disturbances grow more easily and hit the surface to form hole. Therefore, the number of holes formed in silanized surface is more which results in lesser values of λ and d.

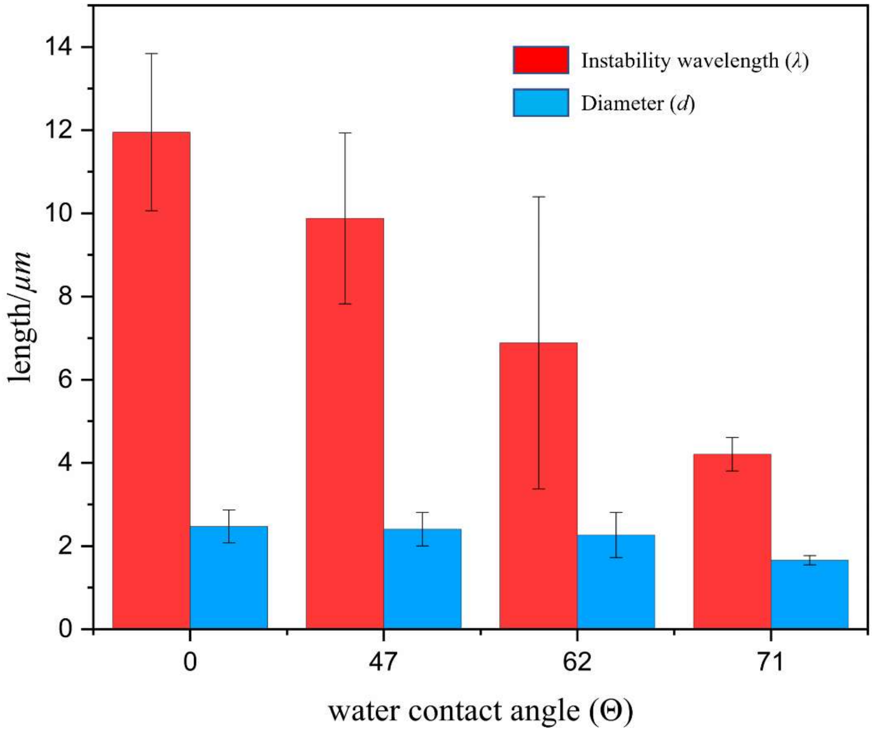

Figure 25: Variation in instability wavelength (λ) and diameter (d) with the level of silanization in terms of reaction time (h). The red color denotes instability wavelength and the blue color denotes the diameter.

It provides new mean to control the lengthscale of dewetting in addition to the film thickness [51], solvent composition [53] and physico-chemical heterogeneity on the substrate.[51] Using any of the above-mentioned methods or a combination thereof enables us to fine tune the desired shape and size of the polymer droplets and their distribution on a variety of surfaces which can be further be used as lenses and arrays in optical applications [51], selective placement of catalyst particles [54], multifunctional coatings and patterned surfaces etc.

3.4 Conclusions

It is demonstrated that a low-density uniform OTS SAMs can be formed on glass substrate using vapor phase silane grafting. Time evolution of water contact-angle on these substrates show quick formation of OTS SAMs (nearly 15 minutes) on glass which leads to increasing water contact angle on these substrates. The water contact angle increases with increase of exposure time of OTS at faster rate initially which then plateaued out to give a nearly constant value of 70°. Using these OTS grafted glass substrates for the self-organized dewetting of polystyrene thin films under an optimum mixture of good solvent and water, provides a new method to control the lengthscale of dewetting (λ and d). A three-fold reduction in wavelength and two-fold reduction in droplet diameter has been achieved by just varying the extent of OTS grafting on the substrate. This combined with the film thickness variation, and dewetting liquid composition variation provides greater flexibility in the process to fabricate high aspect ratio droplets for various applications.

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