III

MATERIALS & METHODS

3.1 Introduction

The materials and methods used to fabricate Superhydrophobic/ Hydrophobic films are discussed in this chapter. The materials were chosen depending upon their properties. Certain properties play a vital role in developing Superhydrophobic/Hydrophobic surfaces. These properties include adhesion, surface energy, vander waals interaction between the molecules. Of all the properties, surface energy has its own impact over the surface. A surface can be hydrophilic, hydrophobic and superhydrophobic depends upon the surface energy values. **[P.G. De Gennes et al.,]**. Surfaces can be classified as high energy surface, ranges between 500 – 5000 mN/m and low surface energy with the range between 10 – 50 mN/m. With low surface energy, less adhesion can be achieved between the liquid and solid interface, resulting in high surface roughness. Low surface energy materials such as alkoxides (i.e) alkylsilanes were chosen and combined with polymer to obtain uniform, less adhesive coatings. The silanes such as TEOS (Tetraethoxysilane), MTMS (Methyltrimethoxysilane) and PDMS (Polydimethoxysilane) were chosen. Materials used and the methods used to fabricate superhydrophobic/hydrophobic coatings are discussed.

3.2 Materials Used

In order to achieve the desired coatings, proper materials should be used. To develop Hydrophobic/ Superhydrophobic surfaces, less surface energy materials are chosen. Silanes are mixed with the polymers to obtain non-wettable uniform surfaces. Polymers were chosen because they adhere to the surface and alkoxide or alkylsilanes shows good repellency against water. This combination has made the coatings uniform and repellent to water. The materials used in preparing the solution and in fabrication of the films are tabulated in Table. 3.1 with their chemical formula and purity.

Table – 3.1 List of materials used in the Research work.

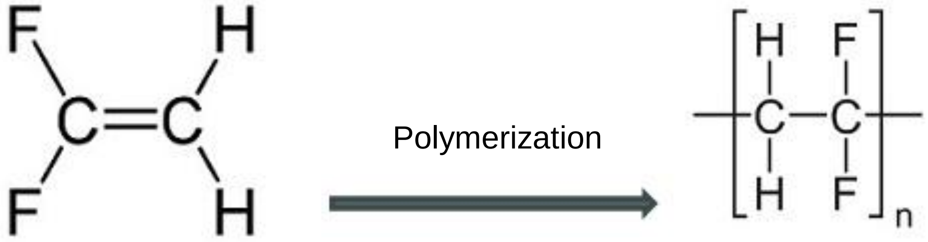
S.No.	**Materials Used**	**Chemical Formula**	**Brand**	**Purity (%)**
1.	Tetraethoxy silane	$[C_2H_5O]_4Si$	Alfa Aesar	≥ 99%
2.	Methyltrimethoxysilane	$[C_4H_{12}O_3]Si$	Sigma-Aldrich	≥ 98%
3.	Polydimethoxy silane	$[C_2H_5OSi]_n$	Alfa Aesar	≥ 99%
4.	Polyvinyledenefluoride	$-[C_2H_2F_2]_n-$	Sigma-Aldrich	≥ 99%
5.	Polymethylmethacrylate	$[C_5O_2H_8]_n$	Himedia	≥ 98%
6.	Polystyrene	$[C_8H_8]_n$	Himedia	≥ 98 %
7.	Ethanol	C_2H_5OH	Merck	≥ 99%
8.	HCl (Hydrocholric acid)	HCl	Merck	≥ 99%
9.	DMF (Dimethylformamide)	$[CH_3]_2NCH$	Merck	≥ 99%
10.	Toluene	C_7H_8	Merck	≥ 99%

3.3 Polymers

Polymers are large molecule consisting of repeated chemical units (‘mers’) joined together. They usually contain more than five monomers and some may contain hundreds or thousands of monomers in each chain. All plastics are polymers, but not all polymers are plastics. Commercial polymers are formed through chemical reactions in large vessels under heat and pressure Homopolymer results in polymerizing only one kind of monomer. Copolymer results from polymerizing different monomers. Most polymers consists of long and flexible chains with a string of C atoms as their backbone. Double bonds are possible in both chain and side bonds . Thermoplastics are two-dimensional molecules that maybe softened by heating and hardened by cooling. They are either linear polymers or slightly branched and has long molecules with side chains or molecular groups not attached. However thermosets are materials that are three-dimensional networks that cannot be reshaped by heating **[Jaspreet Singh et al.,].**Rather than melting thermosets degrade. Thermoset polymers are crosslinked and cannot be softened by heating. The properties, structure and applications of the used polymers have been listed below.

3.3.1 PVDF

Polyvinylidene fluoride or Polyvinylidene difluoride (PVDF) produced by the polymerization of vinylidene difluoride (CH_2=CF_2 monomer) and highly non-reactive thermoplastic fluoropolymer. The polymerization takes place in the suspension or emulsion from 10-150°C and pressure of 10-300 atm. It is a semi-crystalline polymer commercially available as powder, pellets and can be mold it into semi-transparent films. Its highly desirable insolubility and electrical properties result from the polarity of alternating CH_2 and CF_2 groups on the polymer chain.



1,1-difluoroethylene - PVDF Monomer

Structure of PVDF

When produced as the homopolymer (i.e. from 100% CH_2=CF_2 monomer), the majority of the PVDF chains have a regular structure of alternating CH_2 and CF_2 groups.

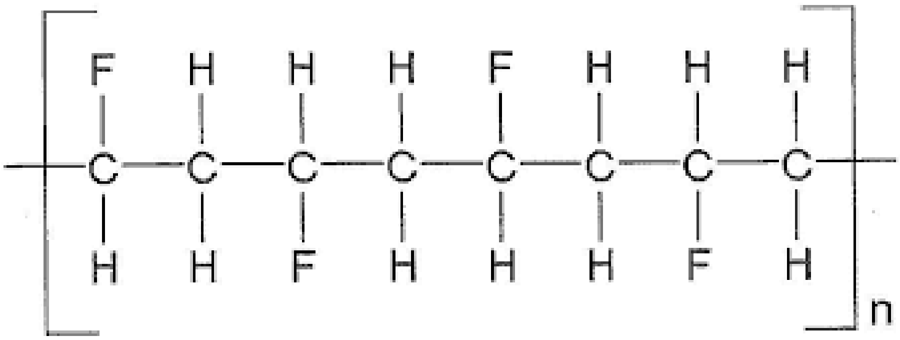


Fig 3.1 Structure of PVDF

The polymerization, however, is not completely regiospecific, so that the polymer contains occasional reversed monomer units (head-to-head and tail-to-tail) in the otherwise completely head-to-tail sequence (by definition the CF_2 groups are referred to as the 'head' and the CH_2 groups as the 'tail') [**Tim Dargaville et al., 2005**].

Properties

Chemical Formula	-	$-(C_2H_2F_2)_n-$
Appearance	-	Whitish or transculent solid
Molecular Weight	-	64.035 g/ml
Density	-	0.617 g/cc

- ***Crystal Structure***

It is typically a semi-crystalline polymer that is approximately 50% amorphous and has high regular structure with most VDF units (head-to-tail) with less percentage of monomer units (head-to-head) .

This fluoroplastic exist in **four possible conformations** named as α, β, γ, and δ phase.

- The C–F bonds are polar and the highest dipole moment is obtained with the alignment of all dipoles of the polymer in the same direction, corresponding to the β-phase of the PVDF. β-phase is the desirable phase to its piezoelectric characteristics of the polymer.

- The dipole moments of α crystallites are oriented in opposite directions, resulting in a zero net polarization. The α phase is the lowest energy conformation and is formed when the polymer is crystallized from the melt and is the non-polar form.

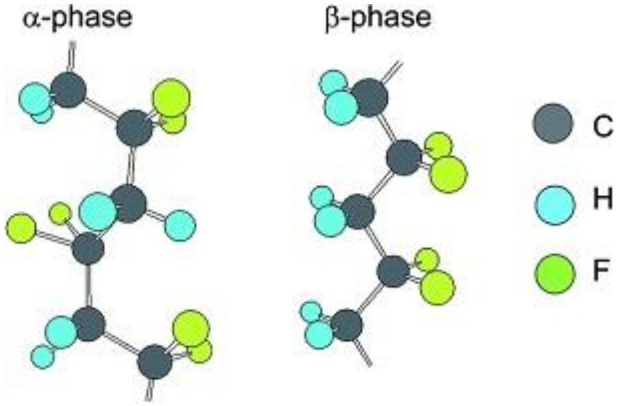
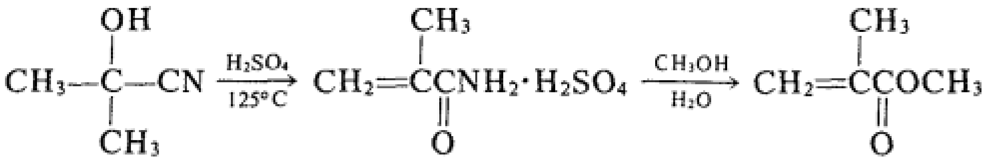


Fig 3.2 Alpha- and Beta-phase Structure of PVDF

(**Source:** Royal Society of Chemistry)

3.3.2 PMMA

Poly (methyl methacrylate) known as acrylic glass or plexiglass is a clear, colourless transparent plastic with higher softening point, better impact strength and weatherability. The strength of the material is higher than the molding grades owing to its extremely high molecular mass. Methyl methacrylate is made by heating acetone cyanohydrin (from the addition of'hydrocyanic acid to acetone) with sulfuric acid to form methacrylamide sulfate.



$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CN \xrightarrow[125^\circ C]{H_2SO_4} CH_2=\overset{CH_3}{C}\underset{\overset{\|}{O}}{C}NH_2\cdot H_2SO_4 \xrightarrow[H_2O]{CH_3OH} CH_2=\overset{CH_3}{C}\underset{\overset{\|}{O}}{C}OCH_3$$

PMMA is made by bulk or suspension polymerization. The production of cast sheets, rods and tubes are carried out by bulk polymerization, starting with a syrup of partially polymerized methyl methacrylate with a convenient viscosity for handling. . The polymerization is carried out at 60-70°C in an air oven or water bath, with a finishing treatment at 100°C [**Fred W Billmeyer., 2007].**

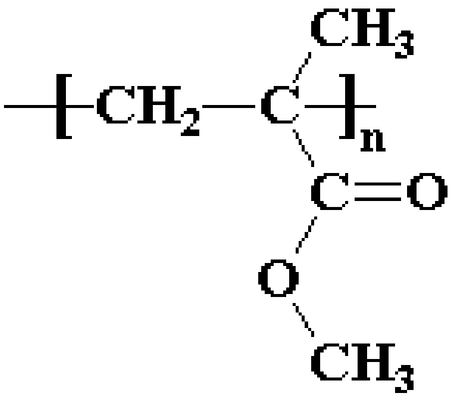


Fig. 3.3 Poly (methyl methacrylate)

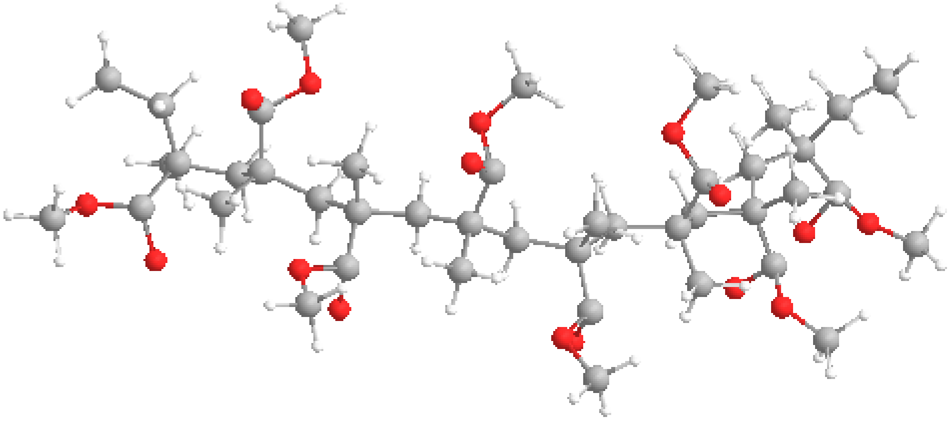


Fig. 3.4 3D structure of PMMA

Properties

➢ Chemical Formula	-	$[C_5O_2H_8]_n$
➢ Appearance	-	Whitish solid
➢ Molecular Weight	-	100.117 g/mol

- Density - 1.18 g/cm^3
- PMMA is a transparent and rigid thermoplastic material widely used a shatterproof replacement for glass. Because of its lack of complete stereoregularity and bulky side groups, it is amorphous.
- Excellent light transmission with high resistance to UV light and weathering.
- It is resistant to many aqueous inorganic agents including dilute alkalis and acids. It undergoes Pyrolysis almost completely to monomer by chain reaction.
- The outstanding property of PMMA is its optical clarity , lack of colour and 100% recyclable.
- The polymer has good mechanical and thermal properties with the tensile strength range as high as 10,000 psi. Heat-deflection temperatures are above 90°C **[S V Gohil et al.,]** .

3.3.3 PS

Polystyrene is a versatile plastic made by stringing together, or by polymerizing styrene. Styrene is obtained by reacting ethylene with benzene in the presence of aluminium chloride to yield ethylbenzene. Styrene is polymerized by using free-radical initiators primarily in bulk and suspension in bulk and suspension processes, although solution and emulsion methods are employed. It can be made into a foam material, called expanded polystyrene (EPS) or extruded polystyrene (XPS), valued for its insulating and cushioning properties **[Charles E Carraher]**. The vinyl polymer has a long hydrocarbon chain, with a phenyl group attached to every other carbon atom.

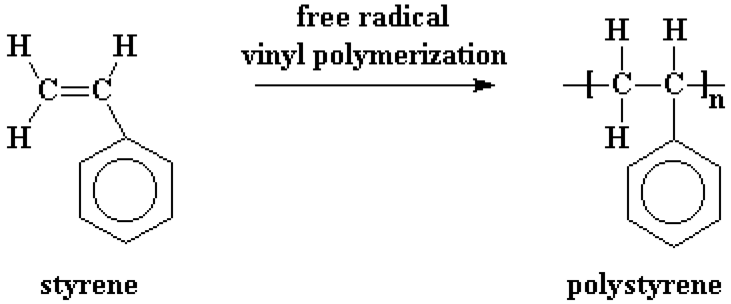


Fig. 3.5 Polymerization of Styrene

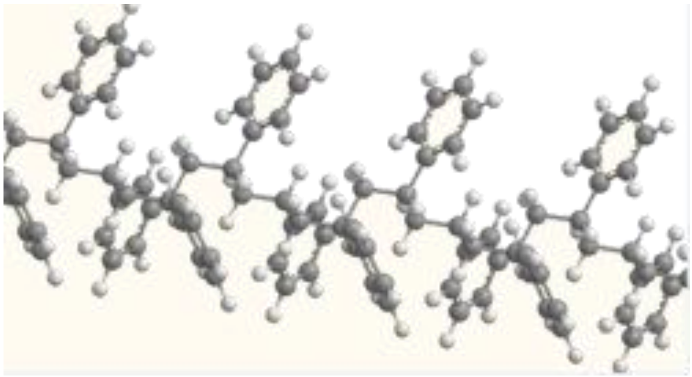


Fig. 3.6 3D structure of Polystyrene

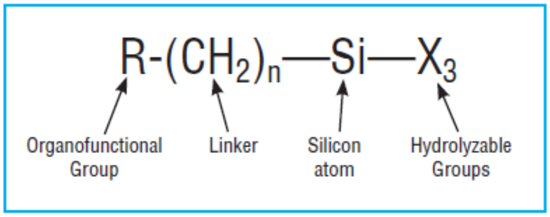
Properties

- Chemical Formula - $(C_8H_8)_n$
- Appearance - Pellets
- Molecular Weight - 500,000 g/mol
- Density - 1.04 g/cm^3
- PS is a synthetic aromatic polymer, a thermoplastic polymer which softens when heated and can be converted into semi-finished products such as films and sheets.
- It has high tensile strength, can withstand high impact and stands at the test of time and hence ideal for home-wares
- It can be easily moulded into different shapes due to its thermoplastic malleability and easily recyclable [**V Kumar et al.,].**
- Naturally transparent but can be coloured with colourants. It is clear, hard and brittle.

3.4 Silane

Silanes are an inorganic compound with chemical formula, SiH_4. They are colourless, has repulsive smell, somewhat similar to that of acetic acid. Silanes are of practical interest as a precursor to elemental silicon. Silanes are used as coupling agents to adhere fibers such as glass fibers and carbon fibers to certain polymer matrices, stabilizing the composite material. The silane coupling agent has the ability to form durable bond between organic and inorganic materials **[Kerstin Weissenbach et al.,]**. The silanes are very well known for their property to modify the surface and to incorporate the bulk properties of different phases into a uniform composite structure.

The general formula for a silane coupling agent is shown below,



Where, X is a hydrolysable group which can be alkoxy, acyloxy, halogen or amine. The process starts with hydrolysis (i.e) a reactive silanol group is formed, that can condense with other silanol groups and forms siloxane linkages.

Most widely used organosilanes have one organic substituent and three hydrolysable substituents. Initially, hydrolysis of three labile groups occurs followed by condensation. Finally, with drying or curing, a covalent linkage will be formed with the substrate with concomitant loss of water. At the interface, there is only one bond from each silicon of the organosilane to the substrate surface. The remaining two silanol groups are present either in condensed or free form. The R group remains available for covalent reaction or physical interaction with other phases **[B Arkles et al.,]** The properties of the alkylsilanes used in the current study have been explained below.

3.4.1 TEOS

Tetraethoxysilane (TEOS) or Tetraethylorthosilicate is a colourless liquid which degrades in water. It is prepared by the alcoholysis of silicon tetrachloride. Less denser than water and the vapours are heavier than air. It is the most prevalent alkoxide of silicon.

$$SiCl_4 + 4\ EtOH \rightarrow Si(OEt)_4 + 4\ HCl$$

In the batch production of tetraethoxysilane from silicon tetrachloride, the initial reaction product contains atleast 90 wt% tetraethoxysilane with 28 wt% SiO_2 content. Distillation removes alcohol and hence pure ethyl silicate of 98% can be obtained.

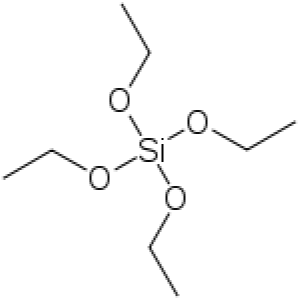


Fig. 3.7 Structure of TEOS

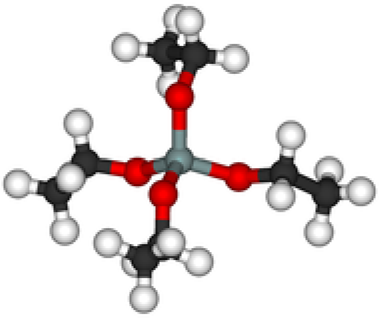


Fig. 3.8 3D structure of TEOS

Properties

Chemical Formula	-	$(C_2H_5O)_4Si$
Appearance	-	Colourless liquid
Molecular Weight	-	208.329 g/mol
Density	-	940 kg/m^3

- Soluble in ether and benzene. With water it is insoluble but reacts.

- Tetrahedral molecular structure which has alcoholic odour.
- Stable, Flammable, Incompatible with strong oxidizing agents, water, alkalis, mineral acids.
- Tetraethyl orthosilicate reacts exothermically with acids strong oxidizing acids may cause a reaction that is sufficiently exothermic to ignite the reaction products and it may generate flammable hydrogen with alkali metals and hydrides.
- Tetraethoxysilane is the main precursor material for the synthesis of zeolites and silicon dioxide, which is used in semiconductor industry. It is widely used as cross linking agents in silicon polymers and in aerogel preparations.

3.4.2 MTMS

Methyltrimethoxysilane or Trimethoxy(methyl)silane is an organosilicon compound. The colourless free-flowing liquid was prepared from methyltrichlorosilane and methanol, which is a crosslinker in the preparation of polysiloxane polymers.

$$CH_3SiCl_3 + 3\ CH_3OH \rightarrow CH_3Si(OCH_3)_3 + 3\ HCl$$

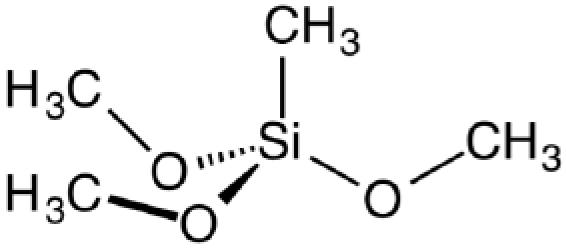


Fig. 3.9 Structure of MTMS

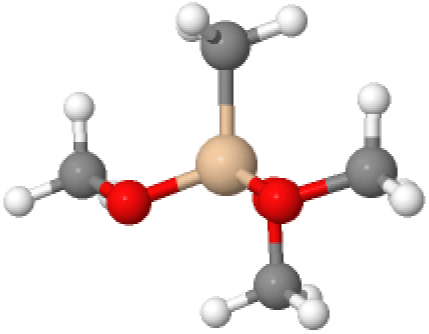


Fig.3.10 3D structure of MTMS

Properties

Chemical Formula	-	$C_4H_{12}O_3Si$
Appearance	-	Colourless liquid
Molecular Weight	-	136.222 g/mol
Density	-	0.955 g/cm^3

- Colourless free-flowing liquid
- The tetrahedral structure described as sp^3 hybridized and idealized by point symmetry.
- Hydrolysis of MTMS proceeds both under acidic and basic conditions. Under acidic conditions, rates of successive hydrolyses for MTMS decreases with each step and vice-versa for basic condition.
- MTMS was preferred for fabrication of hydrophobic coatings as this organic alkoxide methyl-trimethoxy-silane (MTMS), $CH_3{-}Si(OCH_3)_3$, provides control over the degree of cross-linking which allows the gelation with higher concentration of silicon precursors and thereby results in a less porous material and less shrinkage. MTMS based silica films has enhanced hydrophobicity was probably due to the decrease of hydrophilic Si–OH group along with the gradually completed condensation of silanol species.

3.4.3 PDMS

Polydimethoxysilane or Polydimethylsiloxane (PDMS) , belongs to a group of polymeric organosilicon compounds, commonly referred as silicones. PDMS with low polydispersity index and high homogeneity is produced by controlled anionic ring-opening polymerization of hexamethylcyclotrisiloxane. With this methodology, it is possible to synthesize linear block copolymers. PDMS is manufactured in multiple viscosities, ranging from a thin pourable liquid (n is very low) to a thick rubbery semi-solid (n is very high).

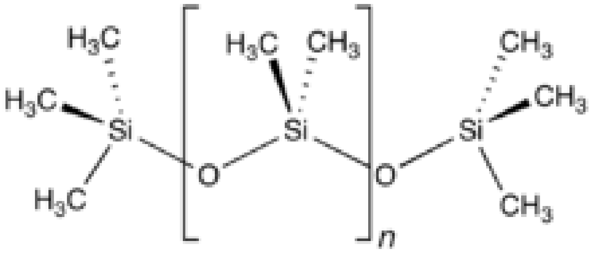


Fig. 3.11 Structure of PDMS

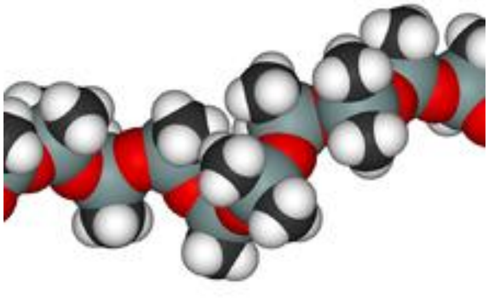


Fig. 3.12 3D Structure of PDMS

Properties

Chemical Formula	-	$(C_2H_5OSi)_n$
Appearance	-	Colourless liquid
Molecular Weight	-	1250 g/mol at n=13
Density	-	965 kg/m^3

- PDMS acts as Viscoelastic (i.e.,) at long flow times or at high temperature, it acts as viscous liquid whereas at short flow times or at low temperature, it acts like an elastic solid. The loading and unloading of a stress-strain curve for PDMS donot coincide.
- The time-dependent elastic deformation results from the long-chains of the polymer. It is relevant only when the cross-linking is present. If it is not present, PDMS cannot shift back to the original state even when the load is removed, resulting in permanent deformation. It is rarely seen in PDMS, since it is always cured with a cross-linking agent.
- It is Hydrophobic. Plasma oxidation can be used to study the surface behavior. The treatment with silanol, allows the water to wet the surface. On oxidizing the surface can be funtionalized with trichlorosilanes. With time, the recovery of surface's hydrophobicity is inevitable.
- Organic solvents diffuse PDMS and cause it to swell. The swelling ratio is roughly inversely related to the solubility parameter of the solvent. With chloroform, ether and THF, it swells to a large extent whereas with acetone, 1-propanol and pyridines, the material swells to a smaller extent.

3.5 Preparation of Solution

In the present research work, Polymer-Silane sols were prepared to develop hydrophobic thin films. Seven sets of solution were prepared with Polymer (PVDF, PMMA, PS) and Silane (TEOS, MTMS, PDMS). The molar ratios of the silanes and polymers were optimized. These proportions and rate of aging resulted in good and uniform coatings. The solutions were prepared with the help of Ultra-sonicator and annealed at different temperatures. The sets of solution were listed below,

Set – I - TEOS + Polymer

Set – II - MTMS + Polymer

Set – III - PDMS + Polymer

Set – IV - TEOS + MTMS + Polymer

Set – V - TEOS + PDMS + Polymer

Set – VI - MTMS + PDMS + Polymer

Set – VII - TEOS + MTMS + PDMS + Polymer

- **Set – I [TEOS + Polymer]**

The Set – I solutions were prepared with TEOS and Polymers [PVDF, PMMA and PS]. TEOS sol and Polymer sols were prepared separately. 1 ml of TEOS was mixed with 10 ml of ethanol and 0.5 ml of HCl was added as catalyst. The mixture was kept in ultra-sonicator for 1.5 hours and noted as Sol A. In case of polymer sol, all the polymer solutions were prepared separately. 1g of PVDF was dissolved in 15ml of DMF and sonicated for 45 minutes which is noted as Sol B. 0.6g of PMMA and 0.6g of PS were dissolved in 10ml of Toluene each, noted as Sol C and D respectively. TEOS solution was mixed to all the three polymer sols and they were noted as Sol AB, Sol AC and Sol AD and were kept for 12 hours, 15 hours and 18 hours of aging respectively.

- **Set – II [MTMS + Polymer]**

The Set – II solutions were prepared with MTMS and Polymers [PVDF, PMMA and PS]. MTMS sol and Polymer sols were prepared separately. 0.4ml of MTMS was mixed with 5ml of ethanol and 0.2 ml of HCl had been added as catalyst. The mixture was sonicated for 30 minutes, noted as Sol A. All the three polymer solutions were prepared separately and noted as Sol B, Sol C and Sol D. 1g of PVDF was dissolved in 15ml of DMF (Sol B) and sonicated for 45 minutes. 0.6g of PMMA (Sol C) and 0.6g of PS (Sol D) were dissolved in 10ml of Toluene each. Sol A was mixed to all the three polymer sols and they were noted as Sol AB, Sol AC and Sol AD and kept for about 2 hours, 12 hours and 15 hours of aging, respectively.

- **Set – III [PDMS + Polymer]**

The Set – III solutions have been prepared with PDMS and Polymers [PVDF, PMMA and PS]. Preliminarily all the three polymer sols were prepared separately. 0.5g of PVDF was dissolved in 10ml of DMF using sonication for 45 minutes. 0.6g of PMMA and 0.5g of PS were dissolved in 10ml of Toluene and sonicated for 30 minutes. The prepared sols were denoted as Sol A, Sol B and Sol C. 0.2ml of PDMS was added drop-wise to all the solutions and sonicated for 10 minutes to get homogenous solution. Sol A was aged for about 12 hours whereas Sol B and Sol C were aged for 3 and 4 hours respectively.

- **Set – IV [TEOS + MTMS + Polymer]**

The Set – IV solutions have been prepared with TEOS, MTMS and Polymers [PVDF, PMMA and PS]. Initially, all the three polymer sols were prepared separately. 0.5g of PVDF was dissolved in 10ml of DMF using sonication for 45 minutes. 0.5g of PMMA and 0.6g of PS were dissolved in 10ml of Toluene and sonicated for 30 minutes. The prepared sols were denoted as Sol A, Sol B and Sol C. 0.2ml of TEOS and 0.1ml of MTMS were added drop-wise to each sol and all the solutions were sonicated for 15 minutes to get homogenous solution. The sols A,B and C were aged for about 10 hours, 6 hours and 8 hours respectively.

- **Set – V [TEOS + PDMS + Polymer]**

With TEOS, PDMS and Polymers [PVDF, PMMA and PS], Set-V solutions were prepared. The polymer sols were prepared separately. 0.5g of PVDF was dissolved in 10ml of DMF using sonication for 45 minutes. 0.5g of PMMA and 0.6g of PS were dissolved in 10ml of Toluene and sonicated for 30 minutes. The prepared sols were denoted as Sol A, Sol B and Sol C. 0.2ml of TEOS and 0.2ml of PDMS were added drop-wise to each sol and all the solutions were sonicated for 15 minutes to get homogenous solution. The sols A, B and C were aged for about 10 hours, 5 hours and 6 hours respectively.

- **Set – VI [MTMS + PDMS + Polymer]**

With MTMS, PDMS and Polymers [PVDF, PMMA and PS], Set-VI solutions were prepared. The polymer sols were prepared separately. 0.5g of PVDF was dissolved in 10ml of DMF using sonication for 45 minutes. 0.5g of PMMA and 0.6g of PS were dissolved in 10ml of Toluene and sonicated for 30 minutes. The prepared sols were denoted as Sol A, Sol B and Sol C. 0.2ml of MTMS and 0.2ml of PDMS were added drop-wise to each sol and all the solutions were sonicated for 15 minutes to get homogenous solution. The sols A, B and C were aged for about 10 hours, 5 hours and 6 hours respectively.

- **Set – VII [TEOS + MTMS + PDMS + Polymer]**

With TEOS, MTMS, PDMS and Polymers [PVDF, PMMA and PS], Set-VI solutions were prepared. The polymer sols were prepared separately. 0.5g of PVDF was dissolved in 10ml of DMF using sonication for 45 minutes. 0.5g of PMMA and 0.6g of PS were dissolved in 10ml of Toluene and sonicated for 30 minutes. The prepared sols were denoted as Sol A, Sol B and Sol C. 0.2ml of TEOS, 0.2ml of MTMS and 0.2ml of PDMS were added drop-wise to each sol and all the solutions were sonicated for 15 minutes to get homogenous solution. The sols A, B and C were aged for about 8 hours, 4 hours and 5 hours respectively.

3.6 Substrate Cleaning

Glass slides of 1mmx1mmx1mm were used as the substrates for coating. The substrates were cleaned before coating. Preliminarily, the substrates were soaked in soap solution, HCl, HNO_3 and finally in distilled water with time interval of half an hour. The cleaned slides were dried in hot air oven for two hours at 60°C.

3.7 Deposition Techniques

Deposition process include Physical vapour deposition (PVD) and Chemical Vapour deposition (CVD) depending on the principle causing film deposition. The physical process includes evaporation and sputtering, the chemical process include plating, sol-gel and chemical vapour deposition.Physical vapour deposition, is one of the approaches to fabricate thin film on substrates, in which the physical processes such as evaporation, collision of ions or sublimation on a target.The transfer of atoms from a solid or molten source onto the subatrate was involved. In case of Chemical vapour deposition, chemical reaction takes place on the substrate surface or in the surroundings of the substrate. It also can be defined as a system in which combination of gases reacts with the substrate surface at a relatively great temperature, leads to the decay of certain constitutents and the fabrication of a solid film by depositing metal or composite on the substrate **[Dler Adil Jameel et al., 2005 and Guozhong Cao et al., 2004].**

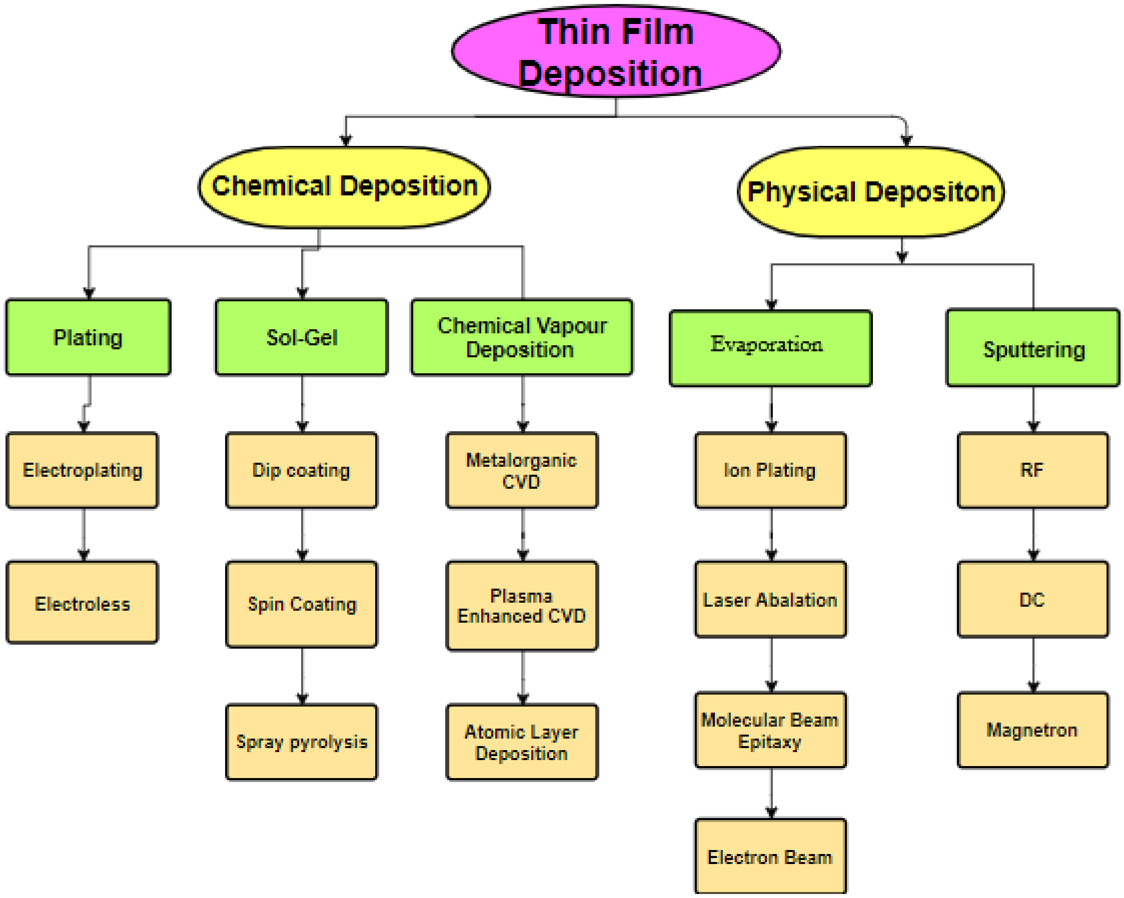


Fig. 3.13 Schematic representation of Thin-film deposition Techniques

3.8 Deposition Technique adopted in this study

3.8.1 Sol-Gel method

Sol-gel method falls under the category of chemical deposition technique. In this process, there involves the transition of a system from a liquid “sol” (colloidal) into a solid “gel” phase. With sol-gel process, ceramic or glass materials can be coated in wide variety of forms, includes thin film coatings, ceramic fibres, micro porous inorganic membranes and aerogel materials. A “sol” is a dispersion of the solid particles in a liquid where only the Brownian motion suspends the particles. Suspension of the particles of linear dimension between 1nm and 1μm are called colloids which are formed by hydrolysis and polycondensation reactions of metal alkoxides (i.e.,) precursors. A precursor is a compound that participates in chemical reaction to produce another compound. Numerous metal organic precursors including alkoxides, carboxylates, diketonates and various organic salts are used to form initially metal complexed solutions but from commercial viewpoint, alkoxides of most metals can be synthesized and are convenient starting materials with respect to availability and cost.

A “gel” is a state where both liquid and solid are dispersed in each other which presents a solid network containing liquid components. A gel is a porous three dimensionally interconnected semi-solid network that expands in a stable fashion throughout a liquid medium and limited by the size of the container. A gel is said to be colloidal if the solid network is prepared using colloidal sol particles. The liquid is present between the mesh of the solid network that composes the gel that does not flow out spontaneously and is in thermodynamic equilibrium with the solid network.

The sol-gel method consists of the following steps,

a) The desired colloidal particles gets dispersed in a liquid to form a sol.

b) The deposition of sol solution produces the coatings on the substrates by spraying or dipping or spinning. The particles in the sol are polymerized through the removal of establishing components and produce gel in a state of continuous network.

c) The final heat treatment pyrolysis the remaining organic or inorganic components.

Sol-Gel process has more advantages than other methods for film deposition and the advantages are:

- Ambient temperature requirement.
- An economical method.
- Coating of large surface is very easy.
- Capable of making small thickness films.
- Produce thick coating to provide the corrosion protection performance.
- Easily shape material into the complex geometries in the gel state.
- Ability to precisely control the microstructure of the deposited film like surface area, volume and size of the pores

3.8.2 Spin-coating Technique

The basic principle of spin-coating process is that the substrate spins around an axis which is perpendicular to the coating area. An amount of solution is kept on the subatrate and rotated at high speed in order to spread the fluid by centrifugal force. After the evaporation of the solvent, thin, homogenous film is formed. The film thickness depends on the spin speed rate and spin time. To ensure the film uniformity, the drying rate should be less. A supplementary drying step is sometimes necessary after the high-speed spin step to further dry the film without substantially thinning it. The spin coating unit **(SCU2007A – Apex instruments)** was used, which is shown in the **Fig.3.14**.

Fig.3.14 Spin-coating Equipment

The spin-coating technique can be carried out in four steps,

(i) Deposition of the sol
(ii) Spin up
(iii) Spin off and
(iv) Gelation by solvent evaporation.

The first two are commonly sequential, but spin-off and evaporation usually overlap. Stage 3 (flow controlled) and stage 4 (evaporation controlled) are the two stages that have the most impact on final coating thickness.

Spin-coating stages

(i) An excess of liquid is dispensed on the surface during the deposition stage.

(ii) In the spin up stage, the liquid flows radially outward, driven by centrifugal force.

(iii) In the spin off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin off slows down, because the thinner the film, the greater the resistance to flow, and because the concentration of the nonvolatile components increases raising the viscosity.

(iv) In the fourth stage, evaporation takes over as the primary mechanism of thinning.

Deposition :

In this stage, solution was allowed to fall on rotating substrates from micro syringe and the substrate is accelerated at the desired speed. Spreading of the solution takes place due to centrifugal force. This is the stage of delivering an excess of liquid to be coated on the surface of the substrate, where a portion of the substrate is immediately covered or “wetted”. In this stage liquid can be deposited in different ways, such as (a) as a bolus at the center or around the perimeter of hole if the center has been cut out, the liquid then spreads over the rest of the disk, or (c) as a continuous stream at the center, or all the way around the inner perimeter, the liquid then flowing outward over the entire slot.

Spin-up :

Spin up occurs when the substrate is accelerated up to its final, desired, rotation speed. This stage is usually characterized by aggressive fluid expulsion from the wafer surface by the rotational motion. Because of the initial depth of fluid on the wafer surface, spiral vortices may briefly be present during this stage; these would form as a result of the twisting motion caused by the inertia that the top of the fluid layer exerts while the wafer below rotates faster and faster. Eventually, the fluid is thin enough to be completely co-rotating with the wafer. Ultimately, the wafer reaches its desired speed and the fluid is thin enough that the viscous shear exactly balances the rotational acceleration.

Stable fluid outflow :

The third stage occurs when the substrate is spinning at a constant rate and fluid viscous forces dominate fluid thinning behavior. This stage is characterized by gradual fluid thinning. As the coating thickness is reduced, uniform fluid thinning takes place. Edge effects are often seen because the fluid flows uniformly outward, but must form droplets at the edge to be flung off. Thus, depending on the surface tension, viscosity, rotation rate, etc., there may be a small bead of coating thickness difference around the rim of the final substrate. If the liquid exhibits Newtonian viscosity (i.e. is linear) and if the fluid thickness is initially uniform across the wafer (albeit rather thick), then the fluid thickness profile at any following time will also be uniform.

Evaporation :

When spin-off stage ends the film drying stage begins. During this stage centrifugal out flow stops and further shrinkage is due to solvent loss. This results in the formation of thin film on the substrate. The fourth stage is when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior. In this, the rate of evaporation depends on, the difference in partial pressure (actually chemical potential) of each solvent species between the free surface of the liquid layer.

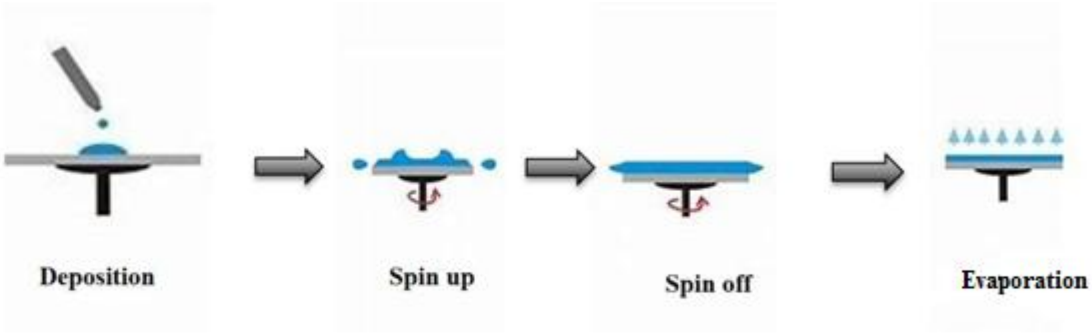


Fig. 3.15 Spin-coating technique

Advantages :

- Spin coating has many advantages in coating operations with its biggest advantage being the absence of coupled process variables. Film thickness is easily changed by changing spin speed, or switching to a different viscosity photoresist. But among the alternative coating techniques, many have multiple coupled parameters, making coating control more complex.
- Another advantage of spin coating is the ability of the film to get progressively more uniform as it thins, and if the film ever becomes completely uniform during the coating process, it will remain so for the duration of the process.
- Economically effective and fast operating system.
- Such techniques were widely used in the manufacture of integrated circuits, optical mirrors, magnetic disk for data storage, device for solar cells, detectors,

sensors, DVD, CD-ROM, insulating layers for microcircuit fabrication such as polymers, etc., **[Niranjan Sahu et al., 2009]**

3.9 Thin film preparation

The solutions were prepared with appropriate proportion of polymer-silane compositions. The prepared sols were aged at different time duration. Later, the aged sols were coated on glass substrates by Sol-gel and Spin coating techniques. Hydrolysis and condensation of silane with polymer modifies the surface of the substrate resulting in the development of hydrophobic/superhydrophobic films. All the films were coated at different rate of speed using spin-coater. The coated films have been annealed at different temperatures with ramping rate of 1°C/min.

The thickness of the films were calculated by Gravimetric method. The rate of speed, thickness and annealing temperature were listed in table. 3.2.

Table.3.2 Deposition method for Polymer-silane films

S.No	Sample	Sol-gel	Spin-coating	Annealing temperature
1.	TEOS/PVDF	Sol-gel		100° C
2.	TEOS/PMMA	1000 rpm		100°C
3.	TEOS/PS	1000 rpm		100°C
4.	MTMS/PVDF	Sol-gel		90°C
5.	MTMS/PMMA	1500 rpm		100°C
6.	MTMS/PS	1300 rpm		100°C
7.	PDMS/PVDF	Sol-gel		100°C
8.	PDMS/PMMA	1200 rpm		90°C
9.	PDMS/PS	1000 rpm		80°C
10.	TEOS+MTMS/PVDF	Sol-gel		100°C
11.	TEOS+MTMS/PMMA	1500 rpm		90°C
12.	TEOS+MTMS/PS	1300 rpm		90°C
13.	TEOS+PDMS/PVDF	Sol-gel		90°C
14.	TEOS+PDMS/PMMA	1000 rpm		90°C
15.	TEOS+PDMS/PS	1200 rpm		90°C
16.	MTMS+PDMS/PVDF	Sol-gel		90°C
17.	MTMS+PDMS/PMMA	1000 rpm		90°C
18.	MTMS+PDMS/PS	1200 rpm		90°C
19.	TEOS+MTMS+PDMS/PVDF	Sol-gel		90°C
20.	TEOS+MTMS+PDMS/PMMA	1200 rpm		90°C
21.	TEOS+MTMS+PDMS/PS	1400 rpm		90°C

Thus, Polymer-silane solutions were prepared and coated on the glass substrates. The coated substrates were dried and characterized by FTIR analysis, Contact angle measurement, Surface roughness analysis, Surface morphology analysis, and also optical and thermal stability has been analysed and are discussed in the next chapter.