I

INTRODUCTION

1.1 Introduction

The fundamental property of solid surface is wettability, which has aroused great interest due to its varied and potential applications. Many plants and insects are repellent to water, as they are covered with epicuticular waxes as protective layer. The so-called "Nelumbo effect" (Lotus effect) **[Barhlott W et al., and Neinhuis C et al.,1997]** has endured enormous interest in elemental research and rational applications over the past decade. When water tumbles onto the surface of nelumbo leaf, the droplet gets beaded up with the contact angle of 160° (Super-hydrophobic). The water droplet rolls off the leaves, gathering the dust particles along the way. In general, the leaves of (lotus) consists of two level roughness structure allowing the air to trap. High contact angle is obtained with this leaf-air composite surface, generating repulsive force which is sufficient for the water drop to form a globular shape. Varied methodologies have been reported to develop such artificial surfaces with self-cleaning, anti-icing property. Of all the factors, surface roughness and energy play a vital role in synthesizing non-wettable surfaces. The liquid-solid interface is striked by the surface energy due to the influence of attractive forces between the liquid and solid at the molecular scale level **[A. Steele et al., 2009].** Application include Strain-resistant textiles, self-cleaning traffic indicators, windshields of cars, and in microfluidic devices **[H.M.Shang et al., 2005 and G.Gu et al., 2006].**

1.2 Wettability properties and its theory

Wettability – a key role in developing surfaces with water-repellent, water- loving, oil-repellent, oil- loving. Such surfaces were developed and studied for various applications in the recent decades. Natural surface of lotus leaves (*Nelumbo nucifera*), rice leaves (*Oryza sativa*), butterfly wings, moth eyes, rose petals exhibited hydrophobicity and/or superhydrophobicity , which paved the way for the researchers to succeed in blooming out such artificial hydrophobic or superhydrophobic surfaces as reported by [**Lin Feng et al.,2002]** The surface is said to be hydrophobic or super-hydrophobic, when the water drop on the surface forms a perfect sphere or a small tilt over the surface, making the water droplet to roll-off along the surface. These abilities, formations were designed only with certain noted properties of adhesion, Van-der waals interaction, surface energy materials, surface roughness, wettablity etc., **[Hua Zhou et al., 2018].** To create such surfaces, many technologies have been developed from bulk systems to quantum dots.

“Wetting property of material receives huge notice from primitive and application point of view. This plays a crucial role in many industrial processes, such as lubrication, liquid coating, spray quenching etc. High-technology materials have been indentured to obtain such applications with the properties related to wettablility such as adhesion, anticorrosion, lubrication, friction, wear resistance, biocompatibility, catalysis, antifouling etc. The wetting properties of solid surfaces with copious polar and non-polar solvents acquire more attention in recent decades because of their widened demand in varied fields of applications”.

“The study involves the measurement of contact angle, which measures the droplet through the intercession of three phases such as solid, liquid and vapour, noted as water contact angle (WCA). With young’s equation as the primary model, the three interfacial free energies such as solid-vapor, liquid-vapor and solid-vapor are related **[T.Young., 1805].** Application of this equation is constrained to a surface that is taut, flat, insoluble, non-reactive and chemically equivalent and the surface is presumed to have no contact angle hysteresis. On the surface, contact angle of a liquid drop can be evoked by the following young's equation:

$$\text{Cos}\theta_Y = \frac{\Upsilon_{SG} - \Upsilon_{SL}}{\Upsilon_{LG}}$$

Where Υ_{SG} is the surface tension coefficient of solid-gas interface, Υ_{SL} is the coeffiecient of solid-liquid interface and Υ_{LG} is the coefficient of liquid-gas interface. For smooth surfaces the contact angle θ lies in the horizon $0^\circ < \theta < 90^\circ$ and has well wetting property making the liquid flatten over a large area of the surface, (i.e) the solid surface attracts the liquid and is termed as hydrophilic. The contact angle for rough surface lies in the horizon $90^\circ < \theta < 180^\circ$ and has non-wetting property, the liquid minimizes its contact with the surface. The solid surface repels the liquid forming a liquid droplet and denoted as hydrophobic. **[Robin H A Ras, Abraham Marmur; 2017]**

It can be seen that the liquid flows over the surface for low contact angle values, whereas for surface with higher contact angle values, it shows less spreading or the droplet gets beaded up. The surface gets wetted by the liquid for the contact angle less than 90° and non-wetting of the surface is noted if the contact angle is greater than 90º, as the liquid clings to the surface. Static angles and Dynamic angles are the two types of contact angles. In case of static angle, the three phase boundary is not moving and the droplet stands on the surface. These angles are utilized in quality control of surfaces and in research and product development. These contact angle measurements have great applications in the sectors like printing to oil recovery, even from coatings to implants.**[Toshiya Wantanbe et al.,2009]**

The reliability of suspension and emulsion were steered by the forces between the particles. Due to Brownian movement in dispersion, frequent encounters between the particles occur resulting in permanent contact of the particles. The force between the colloidal particles based on the Van der waals London interaction along with the double layer interaction. The interrelation between two particles in terms of potential curves have been investigated by Hamaker. Negative part is due to Van der waals London interaction and the positive derivative is adequate to exceed the interaction by preventing agglomerization. The types of forces between the particles are Van-der Waals Force and Electrostatic Force.

Van der Waals Force

"All atoms can be thought of as fluctuating dipoles because the electrons surrounding the nucleus do not form a uniform barrier or screen. The average distribution of charge around a molecule may be symmetrical; thus there is no net dipole moment. However electron move about so that at any instant of time, the distribution will be probably distorted and a small dipole moment will exist. The resultant attractive force between atoms is known as Van der Waals force. This force is proportional to the polarizability of the atom and inversely proportional to the sixth power of the distance between two atoms **[H C Hamker., 1936]**. There are three kinds of interactions contributing to the Van der Walls forces: 1. interactions between permanent dipoles, 2. interactions between induced and permanent dipoles and 3. interactions between induced dipoles (London force). The long range attractive interactions between colloidal particles originate from London force. Although the net permanent dipole moment may be zero, the induced interaction can produce a net attraction. Since the particles in a colloidal system are large compared to atomic dimensions, macroscopic interactions are the summations of the pair wise interactions of the constituent molecules in the individual particle. Therefore, the scaling of Van-der Waals force depends on the geometry of the particles involved".

Electrostatic Forces

"The electrostatic interaction between two colloidal particles is a consequence of charge carried by the particles. All colloidal particles acquire a charge when dispersed in an electrolyte solution, by adsorption of ions from solution onto the particle surface, by ionization of ionisable groups on the particle surface or by selective ion dissolution from the particle surface. The charged particle surface attracts ions of the opposite sign. This attraction is so strong that some of the counter ions are tightly bound to the particle surface. The counter ions also experience the attractive force, which is exerted by the bulk solution and is caused by the thermal motion. As a result of these two opposing effects, electrostatic attraction and thermal motion, a diffuse layer of ions build up so that at a distance from the particle surface it appears to be electrically neutral. The tightly bound and diffuse layers are known as electrical double layer".

Wettability of any solid surface decreases with increase in the contact angle of the liquid. An atom at the surface lacks one part of surrounding atoms, eventhough the atom in solid is surrounded by other atoms or ions. Therefore, the entire interactions from other atoms or ions at the surface atoms are discrete from that in a bulk solid, and this is the qualitative origin of the surface or interface energy **[Akira Nakajima, 2011]**

In recent years, non-wettable surfaces with higher contact angles and facile sliding of drops, called superhydrophobic (θ >130°) has received immense attention. The wettability of the solid surface is a facet property of materials which depends both on surface roughness and energy, by the way ignoring the effects of surface stain or the adsorption of molecular substances.

Authentically, in sol-gel process, metal alkoxides have been utilized which readily undergoes catalyzed hydrolysis and condensation to form nanoscale oxide or hydroxide particles. Variety of materials have been used to fabricate hydrophobic surfaces by sol-gel process. The sol can be applied either directly or combined with fillers such as silica nanoparticles. The resulting surface property depends on how the sol was prepared and surface functional groups of the resulted gel. In most of these appraisals, no post-process hydrophobization was used for the achievement of hydrophobicity since the low surface energy materials were used in the sol–gel and spin-coating process.

1.3 Thin Film Technology

The behavior of thin film with bulk materials varies rapidly, eventhough their chemical compositions are same, they differ in their physical properties and texture, especially incase of surface-properties and thermo-mechanical stresses.

Thin film technology has received more attention in the present era, as the technology is simple, cost-effective and has wide applications in the area of electronic industries, space science, solar energy devices, sensors, hybrid circuits. A layer of material varying from snippets of nanometer to various micrometers in thickness tend to be known as thin film, with a high surface-to-volume ratio. As a specialized technology, thin film technology comes as a reference to layers deposited by some type of atom by atom process rather than to layers produced by laying down relatively large particles.[**A.Goswami, 2003].** Such films were used in wafer fabrication, which can be a resistor, a conductor, an insulator,or even a semi-conductor.

The name thin film itself indicates that it is a layer with high surface-to-volume ratio. The absolute condition for the film formation requires the deposition of material, atom by atom (molecule by molecule) and layer by layer. Thin films both amorphous and crystalline are very important in modern technology. For instance, they may be used for protective coating on materials and they play a key role in the miniaturization of components on electronic devices. In thin films the material is coated using chemical bath method, vapour deposition method etc. Polymer is used for coating because their ability to withstand stress, strain exerted by different kinds of exposure in aggressive environment. They protect the metallic, concrete and other structures from corrosion, erosion and aesthetic retention. Thin films have wide application and are used in opto-electronic devices, glass, sensors, solar energy utilization, optical & superconducting material films, computer elements with high memory and hybrid circuits.

The characteristic of thin films vary from bulk materials with similar chemical composition in varied ways. These thin films are sensitive to surface properties and thermo-mechanical stresses whereas bulk materials are not.[**A.Goswami, 2003, Antony R.West ,2014**]

The virtue of thin films are influenced by the nature of its adhesion and conformal coverage of the underlying layer, residual or intrinsic stresses after deposition, and even the existence of surface imperfections such as pinholes. The adhesion of a thin film to the substrate or underlying layer is of great concern in clinching the reliability of the thin film. A thin film that is primarily clinging to the underlying layer but lifts off after the device is subjected to thermo-mechanical stresses result in field failures. Regardless of the deposition process, thin films always end up with an innate stress which can either be tensile or compressive. High residual stresses can lead to adhesion problems, corrosion, cracking, and deviations in electrical properties. Thus, conventional deposition is expository to minimize innate stresses in thin films. **[Leon I. Maissel].**

1.4 Surfaces

Wettability of solid surface by liquid is one of the most vital material property. Surface wetting is relevant characteristics for diverse materials, comprising paper, board, cotton fabrics etc., **[Hannu teisala et al., 2014]**. “Surface of materials strongly alter the functional properties such as optical, acoustic, mechanical, electronic and biological properties of materials, particularly at the micro/nano scale. The chemistry of solid surface determines whether the surface has a tendency to repel or to get wetted by a liquid. With young’s equation , the wetting of ideal, homogenous and smooth surface can be evaluated. Wenzel and

Cassie-Baxter introduced wetting theories for rough surfaces. Though a surface appear macroscopically smooth, there typically exists micro-, nano-and molecular-level roughness. Wenzel regime represents the state where the surface is completely wetted by the liquid and the state where the air gets entrapped on the substrate and the liquid wets the top area of the surface is Cassie-Baxter regime**.[Robert N Wenzel, 1936; A. B. D Cassie and S. Baxter,1944]** The Wenzel equation describing the complete wetting state on rough surface,

$\text{Cos}\ \theta_W = r\ \text{Cos}\ \theta_Y$

$\theta_W =$ Wenzel's Contact Angle on the rough surface, r = The actual wetted area divided by the projected wetted area of the surface, θ_Y = Young's Contact angle

The Partial wetting of the rough surface was given by Cassie-Baxter equation,

$\text{Cos}\ \theta_{CB} = r_f\ f \cos\theta_Y + f - 1$

θ_{CB} = Cassie-Baxter Contact angle on the rough surface, r_f = actual wetted area divided by the projected wetted area of the surface, and f is the fraction of the projected area of the surface that is wetted by the liquid.**Fig.1.1** represents the young's regime, **Fig. 1.2 (a)** and **(b)** represents the Wenzel and Cassie-Baxter regime.

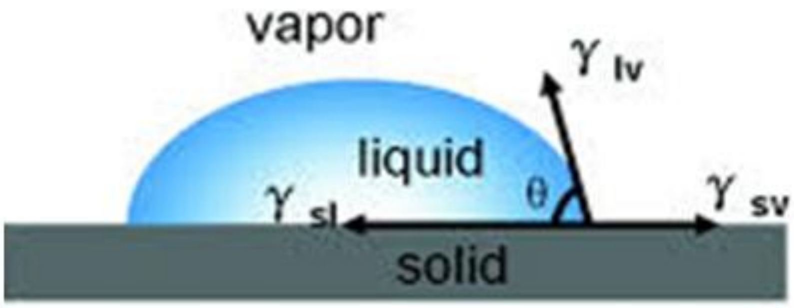

Fig. 1.1 Young's regime

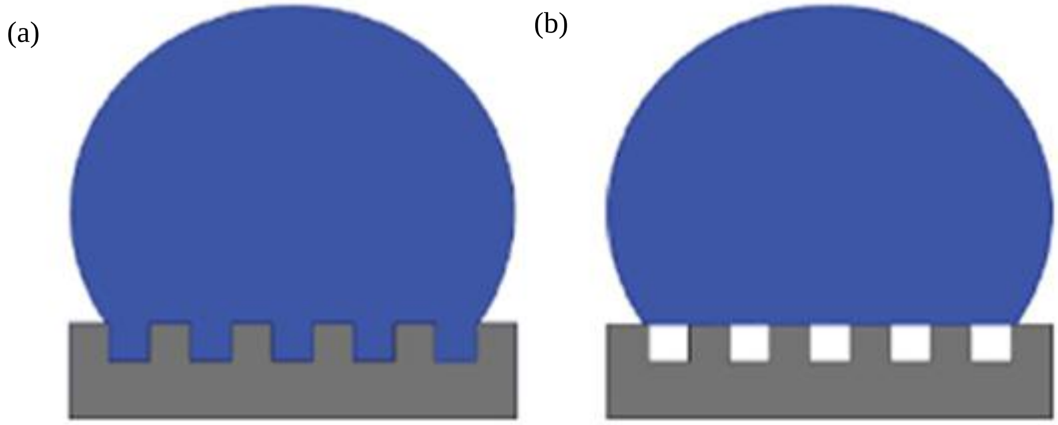

Fig.1.2 (a) Wenzel regime and (b) Cassie-Baxter regime

Depending on the surface, whether it is smooth or rough, the wettability and/or repellency against the liquid can be evaluated. This further depends on the chemical composition of the surface and even on the properties of the liquid. The surface where the liquid spread over the surface is Hydrophilic surface,the contact angle will be less than 90°. The surface where the liquid gets beaded up or gets clinged is Hydrophobic and/or Super-hydrophobic surface". For Hydrophobic surface the contact angle will be higher than 90° but lesser than 130°. In case of Super-hydrophobic surface, the contact angle exceeds 130°. In case of oil affinity and/or repellency, this can be classified as Oleophilic, Oleophobic and Super-oleophobic.

1.4.1 Hydrophilic Surface

Hydrophilic surfaces are water-loving surfaces (i.e) they have affinity towards water. The solid surface is ideal, smooth, and homogeneous. It leads to to the simple but qualitative definition of hydrophilic surfaces- *"like spreads on like"* or *"polar spreads on polar".* The substance (molecules, ions) on the surface are readily soluble in water. The Hydrophilic surfaces are those having polarity, where the surface molecules or their chemical groups have an electric dipole or multipole moment.

When the water contact angle on a hydrophilic surface is <10º, water thus spreads almost perfectly over the solid, and the surface is often termed as superhydrophilic. Roughness of a solid surface can enhance the surface wettability against liquid. The wettability of superhydrophilic surface is normally high due to the low surface roughness. The contact angle of such surfaces gets reduced to 0º **[Cheng Piao et al.,2011].**

1.4.2 Hydrophobic Surface

The hydrophobic molecules, when dispersed in water, are either repelled from it towards the water surface or aggregate into micellar structures, they dissolve easily in an nonpolar solvent, whose molecules are hydrophobic. The Hydrophobic property results due to the absence of any permanent or induced electrical dipole of the molecule and/or lack of ability to form hydrogen bonds. Hence, the interaction between hydrophobic molecules and water is only with London dispersion force. The contact angle value for hydrophobic surfaces will be more than 90°. For such surfaces, the surface free energy will be lower and the surface roughness will be higher. Only when the surface roughness is higher, the liquid gets clanged between the solid surface and trapped air grooves.

In thermodynamic point of view, solid/liquid system which is free of any chemical reaction, minimizes its free energy realized with the help of physical interactions. The hydrophobic molecule suspends in a polar medium (water), the medium will repel the molecule because neither polar nor hydrogen bonds can develop. On the other hand, water molecules form hydrogen bonds between themselves. Free energy (ΔG) associated with mixing non-polar molecules with water, which depends on both the entropy ΔS and enthalpy ΔH changes in the system, where $\Delta G = \Delta H - T\Delta S$. The entropy decreases because the water molecules lose translational and rotational mobility around the non-polar molecules (hydrophobic) **[Robin H A Ras, Abraham Marmur; 2017].** The enthalpy changes are important in water-water hydrogen bond formation around the non-polar molecule. The hydrophobic effect does not depend much on the temperature increase because both the enthalpy and entropy increase compensate their changes.

“Hydrophobic surfaces depends on the angle made by the surfaces. In the case of liquid resting on a solid surface in a gaseous environment, the contact angle can be defined as the angle formed by the liquid at the gas, liquid, solid boundary. Due to the high surface tension of the water, it tends to form spherical droplets on surfaces, so as to reduce its area and thus energy. The contact angle is thus generally large, although this depends on the surface material. Due to its high surface tension, water has a high capacity for bonding if the surface is right **[Chengyu Wang et al., 2011 and Nils O Petersen., 2017]**.The idea of hydrophobicity has come from nature itself. One of the most notable surfaces is Lotus leaf. The cause of self- cleaning properties in lotus leaf is due to the hydrophobic water repellent double structure nature of the surface. This enables the contact area and the adhesion force between surface and droplet to be significantly reduced and results in a self- cleaning process allowing water to readily roll off the leaf and remove dust deposits on the way **[Prathapan Ragesh et al., 2014]**. Such Hydrophobic surfaces can be prepared or developed with low surface chemistry materials. With higher surface roughness, water droplets gets clinged to the surface, which is due to the adhesion effect on the surface. The Lifshitz theory of Van der Waals interaction can be used to explain the attraction between two uncharged macroscopic surfaces across air or water **[J.Vial et al., 1991].** These surfaces has wide application for anti-dust, self-coating, anti-fog coatings”.

1.4.3 Super-Hydrophobic Surface

Super-hydrophobic surfaces possess extraordinary water repellency properties, due to their low surface energy chemistry and specific nano- and microscale roughness, are of great interest as it has variety of applications ranging from self-cleaning surfaces to microfluidic devices. Superhydrophobic surfaces get great acceptability in the modern scientific world due to the advent of new nano-material fabrication techniques. If a surface is made hydrophobic and then patterned with structure to provide roughness, a drop may be able to remain on top of the microstructure, forming air-liquid interfaces **[Minglin Ma and Randal M.Hill.,2006].** This drop will have greater mobility and a higher contact angle than a drop in the wenzile regime. On natural superhydrophobic surfaces of lotus leaves, where the mobility of water droplets resulted in self-cleaning effect or in case of rose petals, where the droplets firmly adhere to the surface. In common these surfaces have high static and high advancing contact angle. **[Thierry Darmanin and Frederic Guittard., 2015].** The receding contact angle and droplet adhesion varies a lot depending on the chemical and physical nature of the surface. In addition, the anti-wetting properties are confirmed with contact angle hysteresis (CAH) and sliding angle. The surfaces with contact angle greater than 130º is known as superhydrophobic surfaces. One of the more popular applications of these type of structure is their so called “self-cleaning” capability. The highly-mobile water droplet on superhydrophobic surfaces tend to pick up dust particles as they roll off the surface. This effect has many applications in coating, paints, self-cleaning, oil-water separation, water proof textiles, anti-ageing, anti-fog coatings and even in microfluidic devices **[Harinarayanan Puliyalil et al., 2015]**

To fabricate hydrophobic/ super-hydrophobic surfaces, many methods and materials have been used. Low surface materials such as siloxanes or fluoropolymers has big attraction in developing hydrophobic chemistry on artificial superhydrophobic surfaces. However , moderate low surface materials can also be used. With surface roughness, hydrophobic-hydrophilic surfaces can be developed depending on the surface-chemistry. High surface energy also enhances the non-wettable surface. Methods such as templating, plasmaetching, spin-coating, sol-gel method, dip coating, layer-by-layer deposition can be used to obtain surfaces.

1.5 Application

Non-wettable surface has wide applications in recent decades and has made researchers to develop structures innovatively resulting in hydrophobic/superhydrophobic surfaces. Self-cleaning glass can be used in other electronic devices such as laptop, mobiles, camera, which often get contaminated by dirt. Even in underwater photography, this type of glass plays a vital role. Water-repellent textiles, self-cleaning solar panels, Marine vessels and oil rigs are few miscellaneous applications, where such non-wettable surfaces are important.

1.6 Objective of the Research Work

- The foremost purpose of the current research work is to deposit Hydrophobic/Super hydrophobic surfaces with low surface energy materials.
- Analyzing the surface for applications related to self-cleaning, water-proof coatings and for oil-water separation.

1.7 Methodology of the Research Work

- ✓ Chapter I is enriched with the introduction of thin films, wettability, and the properties based on wettability.
- ✓ Chapter II deals with the Literature Review, of hydrophilic, hydrophobic and superhydrophobic surfaces.
- ✓ In Chapter III the methods and materials used to fabricate hydrophobic/superhydrophobic surfaces , the chemistry beyond surfaces and the methods utilized were discussed.
- ✓ The characterization and analysis of the prepared films were interpreted in Chapter IV,the reason for obtaining hydrophobic/superhydrophobic surfaces,

their surface roughness, morphology, presence of chemical constitutents were explored.

- ✓ Summary of the research work was included in Chapter V.