Development of Coatings for The Prevention of Contamination, Water Wetting, and Ice Formation

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Certificate

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ABSTRACT

The modification of glass for prevention of contamination has been a subject of active research in materials science. The key property to attain this feature is the self-cleaning in glass. Self-cleaning can occur via different mechanisms, such as hydrophobic, hydrophilic, and hydrophilic mechanism coupled with photocatalysis. Self-cleaning has been gaining a lot of attention in the academic as well as commercial sectors mainly due to the immense variety of its potential applications, which include daily-life as well as industrial and high-tech uses, such as self-cleaning windows, windshields, exterior paints for building, roof tiles, textiles, and drag reduction in fluid flow etc. A lot of research has been ongoing for the development of self-cleaning glass by application of superhydrophobic material on the surface of glass. In this work, formation of hydrophobic coating on glass substrates was carried out via sol-gel thin-film synthesis route, with the use of Triethyl orthosilicate as the starting precursor. Attempts to increase the hydrophobicity of silica films by surface modification using Trimethyl silane. Effects of surface modification through introduction of varying amounts of CTAB was also studied. In order to enhance the strength and durability of the coatings while retaining super hydrophobicity, the silica films were reinforced with small amounts of multi-walled carbon nanotubes (MWCNTs), and its effects on wetting characteristic and morphology of the films were studied. To overcome the problem of adhesion and durability of the films, another method was explored, which utilized colorless epoxy resin to adhere silica particles onto the substrate surface. The morphology of the films prepared was analyzed using Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). To characterize the wettability of the films, contact angle measurements were carried out using Drop Shape Analyzer. The contact angles of silica modified surfaces were observed to approach 95^o.

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CHAPTER 1

INTRODUCTION

The use of glass for domestic as well as commercial applications has become quite common in today’s world. The widespread utility of glass in buildings, houses, windshields of automobiles, roofing and building glasses, traffic indicators, and optical components poses a problem regarding the maintenance of glass. Cleaning the remote portions and huge glass windows and walls can be quite challenging and may require significant amount of resources. Furthermore, due to the issue of global warming, extreme weather has become more frequent in many regions of the word. Hence, frost formation has become an alarming problem affecting our daily lives in several ways. Quite a few deicing methods have been already developed, for instance, electrothermal heating, mechanical removal, and chemical modification. [1]. However, these methods are generally expensive, inefficient, and may be detrimental to the environment[2]. The wettability of a solid surface has attracted considerable attention in recent years because of the wide applications in anti-freezing, anti-contamination, and self-cleaning devices.

For such applications, super anti-wetting surfaces with static water contact angle higher than 150^o and a sliding angle less than 10^o gained a lot of research interest in academic and industrial research domains. In 1997, Barthlott and Neinhuis showed that the self-cleaning property of lotus leaves was due to their specialized surface morphology and hydrophobicity[3]. Since then, attention towards super-hydrophobicity has increased immensely. Anti-wetting induces self-cleaning, which keeps the surface contamination-free and frost-free while water beads up and rolls over these surface entrapping dirt and particulates. Anti-wetting property of the surface is greatly dependent on its surface energy. Generally, the extent, to which water wets a surface, is governed by the balance of surface free energy and roughness. Hydrophobicity is induced by the combination of low surface energy and rough structures. [4-6]

Hierarchical micro and nanostructures can be used to construct rough surfaces, whereas surface energy can be minimized by tailoring the chemical composition of the surface. [7] Moreover, for the practical applications mentioned previously (such as glass walls and windows), optical transparency, in addition to hydrophobicity, is also an essential requirement[8, 9]. Many transparent superhydrophobic surfaces have been synthesized recently, and promising results have been obtained [10].

Among the many materials used, silica-based coatings have proven to carry significant potential for such applications. The interest in silica films during recent years is due to their unique properties such thermal and oxidative stabilities, chemical and corrosion resistance, low refractive index, antireflective properties, resistance to bacterial growth, etc. These films have numerous high-tech applications in various areas of technology, such as aerospace, solar cell systems, optics, microelectronics, automotive industries and engineering. [11] Glass coated with silica using tetraethyl orthosilicate (TEOS) as the silica source can make the glass surface hydrophobic and has a self-cleaning effect. [12, 13] Several techniques have been employed in order to develop coatings for commercial applications, such as, chemical vapor deposition, sputtering, deposition layer, plasma treatment, sol-gel process.

For numerous applications, the sol-gel method has proven to be one of the most suitable and beneficial processing routes to produce amorphous or crystalline oxide coatings [14] Sol–gel derived coatings have been found to be very versatile due to the ease of solution based processing and the synthesis flexibility, which can be used to obtain good compositional control and control over optical properties of thin films. [15, 16] Sol-gel derived silica coatings have exhibited comparable or even superior properties, such as homogeneity, purity, easy processing and ability to coat large substrates and substrates with complex geometries, compared to coatings prepared by other techniques. [11] Even though the development of optically transparent superhydrophobic films has been a rather active research domain over the recent years, many important features still have a lot of room for improvement. Frequently faced issues are getting notable attention, such the durability and robustness of the hydrophobic films, and restriction imposed in case of large-scale preparation and widespread application, due to the limitation of available substrates, costly apparatus, complicated chemical synthesis procedures, and strict conditions in many available techniques. [8, 17, 18]

In this work, a study of effects of varying amounts of Tetraethyl orthosilicate (TEOS) on the wettability and film morphology of transparent hydrophobic silica films synthesized via sol-gel process has been conducted. Moreover, efforts have been made to develop a facile fabrication method for development of superhydrophobic surfaces with adequate durability, robustness, complete optical transparency, and low sliding angle. Apart from synthesis based on TEOS, Trimethyl silane (TMS) and CTAB surfactant as co-precursors were also added to enhance the properties of the film. In order to increase the hydrophobicity and robustness of the films, silica films were reinforced with MWCNTs, and the nanocomposite film obtained showed improved hydrophobicity with negligible effects on optical transmission.

CHAPTER 2

LITERATURE REVIEW

2.1 Self-Cleaning

Self-cleaning glass refers to glasses with surface having the characteristic of removing any type of contamination or foreign particle from itself. Self-cleaning is a key feature necessary for prevention of surface contamination without the utilization of external sources. The idea of self-cleaning is not necessarily new, and the basis for this idea is the various self-cleaning phenomena existing in nature. The self-cleaning mechanism is mainly carried out by three mechanisms; super hydrophilic, photocatalytic, and superhydrophobic phenomenon.

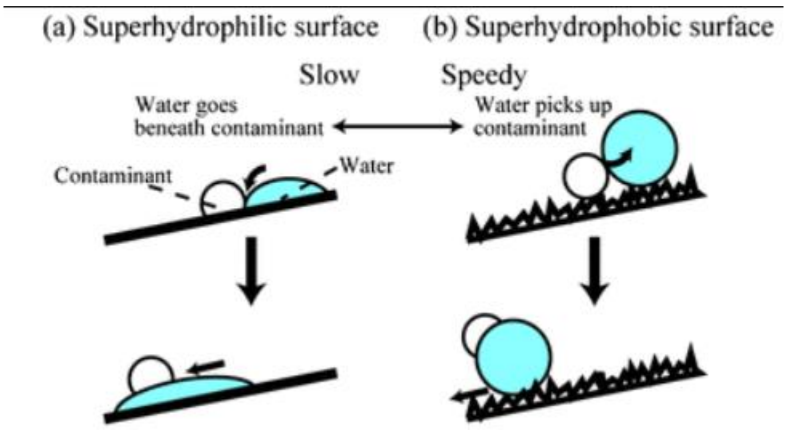


Fig 2.1 Self-cleaning mechanisms of super hydrophilic and superhydrophobic surfaces

2.1.1 Mechanism of self-cleaning

Super hydrophilic property of a material allows the surfaces to clear away most foreign contaminants. This mechanism differs greatly from the cleaning phenomenon observed in case of superhydrophobic surfaces. Super hydrophilic self-cleaning surfaces enable the water to spread out to a high extent on the surface, and get between the dirt particles and surface, resulting in occurs because water on the surface is able to spread out to a great degree (extremely low water contact angles) to get between any fouling debris and the surface to wash away the debris. The mechanism has been shown in Fig-[ ] (a).

An example of this phenomenon existing in nature would be the Nepenthes carnivorous pitcher plants, in which the water completely spreads on the surface, with contact angle close to zero. This causes the formation of film of water, making the surface slippery. [19] . The absence of wax crystals and microscopic roughness enhance the hydrophilicity and capillary forces, in doing so, water can swiftly wet the surface of rim. [20]

2.1.1.1 Photocatalysis

The self-cleaning surfaces which operate on this mechanism do not completely rely on the flow of water. They burn or decompose the dirt particles when exposed to light. This phenomenon is termed as "photocatalysis". One of the most commonly used self-cleaning products, titanium dioxide, utilizes this unique self-cleaning mechanism that combines an initial photocatalytic step and subsequent superhydrophilicity. A titanium dioxide coating, typically on glass windows, when exposed to UV light, will generate free electrons that will interact with oxygen and water in the air to create free radicals. These free radicals will in turn breakdown any fouling organic matter deposited on the surface of the glass. Titanium dioxide also changes the normally hydrophobic glass to a super hydrophilic surface. Thus, when rainfall occurs, instead of water beading up on the window surface and instantly falling down the glass, rain drops will rapidly spread out on the hydrophilic surface. The water will then move down the surface of the window, as a film rather than a droplet, essentially acting like a wiper to remove surface debris.

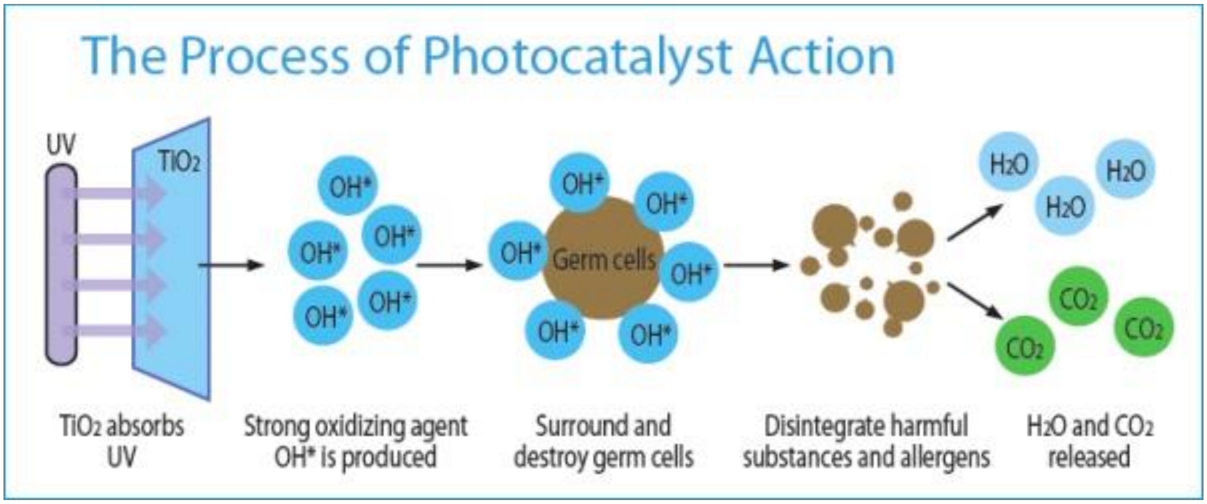


Fig 2.1.1.1 Photocatalysis

2.1.1.2 Super hydrophobicity

Super hydrophobic surfaces repel water and are generally characterized by an apparent water contact angle greater than 150^{o}, and sliding angle less than 10^{o}. Super hydrophobicity is promoted by low surface free energies coupled with adequate roughness. Lotus leaf is one of the most well-known examples of superhydrophobic self-cleaning surfaces in nature. The high anti-wetting characteristic exhibited by lotus leaves has been a huge inspiration for scientists to initially conduct research regarding superhydrophobic phenomena. In fact, the term 'lotus effect' is still synonymous with superhydrophobic behavior.

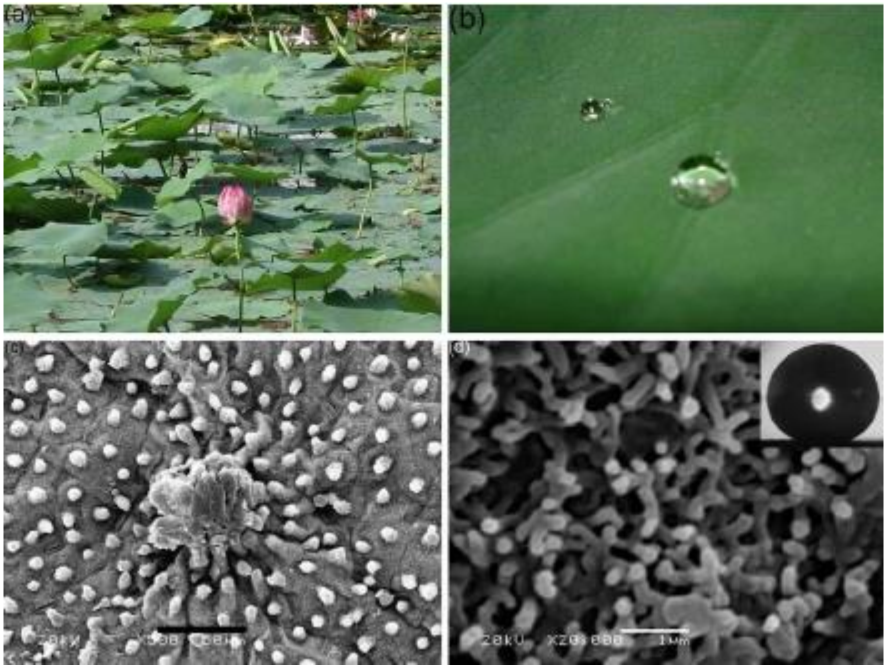


Fig 2.1.1.2 the photos of some lotus leaves (a) and of a water droplet on a lotus leaf (b) and the SEM images of lotus leaves with different magnifications (c and d). The inset of (d) is a water contact angle on a lotus leaf, with a value of 161 ◦ ± 2 ◦

The mechanism by which the surface cleans itself included the weak interaction of water droplet with the hydrophobic surface, which enables it to slide off the surface at a relatively small inclination angle. While sliding off, the dust or other particles stick to the droplet and the droplet slips off of surface along with the dirt. Since the surface has low energy, the dirt sticks to the droplet because the dirt-droplet interface would be more stable than dirt-solid surface. The mechanism is demonstrated in Fig-[2.1.1.2] (b). Due to anti-wetting characteristic, the water is prevented from staying onto the surface which also attributes to prevention of frost formation. Furthermore, if the dirty water falls onto the surface, it will simply roll off along with the dirt without staying long enough to evaporate.

The most common and relevant parameter describing the wetting property of a surface with respect to liquid water is the Young's equation, which describes the force balance between the interfacial tensions formed at the solid–liquid–vapor interfaces. According to this model, water drop will tend to wet a surface that has high surface energy chemistry and will tend to bead-up on a surface that has low surface energy chemistry. [21]

$$\cos \theta_{Y} = (\sigma_{sv} - \sigma_{sl})/\sigma_{lv}$$

θ_Y = Young's contact angle
σ_{sv} = surface tension (energy per unit surface) of the solid–vapor interface
σ_{sl} = surface tension of the solid–liquid interface
σ_{lv} = surface tension of the liquid–vapor intersface

Fig- Young's equation

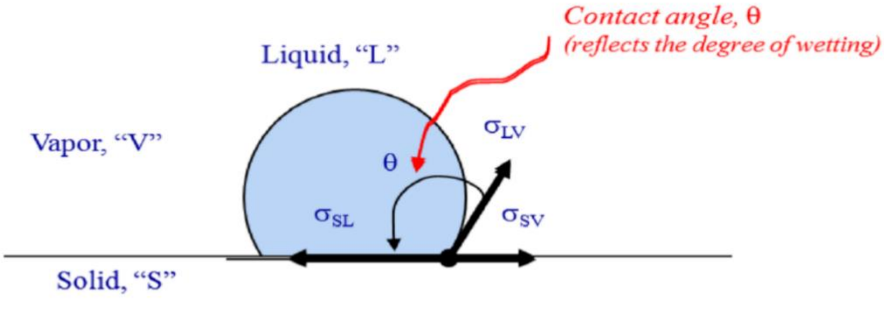


Fig- Force diagram of Young's equation and associated Contact Angle measurement

It is important to note that a water droplet that completely wets a surface will have a contact angle approaching 0°, while a droplet that doesn’t wet the surface at all will bead up into a spherical shape without being affected by gravity and will have a contact angle approaching 180°. The images in figure below show these conditions.

Fig 2.1.1.2 (e) Wetting

The effect of surface roughness and topographical features of hydrophobic surfaces on the increment in contact angle falls within two regimes, Wenzel, and Cassie-Baxter regimes. These models indicate an increase in contact angle with increasing surface roughness. However, the Cassie–Baxter state is obtained when there is a trapped air layer within the roughened or textured surface which causes the contact angle to increase, and the sliding angle to decrease. [22-24]

2.2 Deposition method for thin films

Various methods are available for thin film synthesis and deposition, some of which are enlisted below:

- Chemical Vapor Deposition (CVD)
- Sputtering
- Atomic Layer Deposition
- Sol-Gel

2.2.1 Atomic Layer Deposition (ALD)

This is a reactive process, which is self-limiting in nature, and results in controlled layer-by-layer growth of the film. The precursors enter the reaction chamber separately, and after the introduction of each precursor, purging is done to remove the remaining unreacted precursor before the introduction of second precursor. This process is quite sophisticated and expensive and is generally employed in case of sensitive high-tech applications.

This process generally utilizes repetition of following four sequential steps:

1. Introduction of first gaseous precursor into the reaction chamber where the substrate is placed.
2. Purging the chamber using an inert gas to remove the remaining precursor that didn't get adsorbed onto the surface.
3. Introduction of second precursor gas in the chamber which reacts with the molecules of previous precursor adsorbed onto the substrate.
4. Purging the chamber once again for the removal of the unreacted precursor before the deposition of another layer.

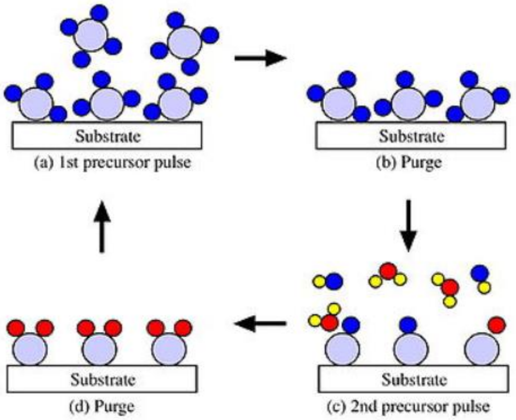


Fig 2.2.1 Mechanism and stages of Atomic Layer Deposition

2.2.2 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) [25] is parent to a family of processes whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface. The resulting solid material is in the form of a thin film, powder, or single crystal. The CVD process involves depositing a solid material from a gaseous phase; this is achieved by means of a chemical reaction between volatile precursors and the surface of the materials to be coated. As the precursor gases pass over the surface of the heated substrate, the resulting chemical reaction forms a solid phase which is deposited onto the substrate. The substrate temperature is critical and can influence the crystallinity of the film and occurrence of different reactions.

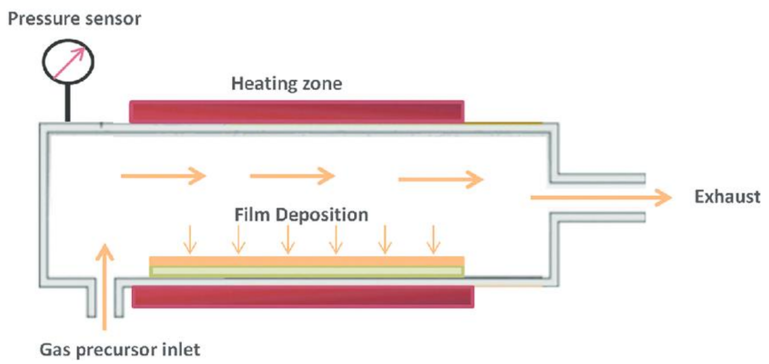


Fig 2.2.2 Schematic diagram of a chemical vapor deposition (CVD) system

2.2.3 Sol-Gel Method

The sol-gel method is a well-established procedure among solution reactions which involves the transition of the solution from “sol” (usually a colloidal liquid) to “gel” (a solid phase). Generally, the initial contents of the “sol” are inorganic metal salts or metal organic compounds, such as metal alkoxides. Sol–gel process is primarily subjected to certain reaction steps in order to yield the final metal oxide products. Those steps include hydrolysis, and condensation (and drying process, if the gel is to be converted to aerogel or xerogel). The formation of metal oxide involves different consecutive steps, initially the corresponding metal precursor undergoes rapid hydrolysis to produce the metal hydroxide solution, followed by immediate condensation which leads to the formation of three-dimensional gels.

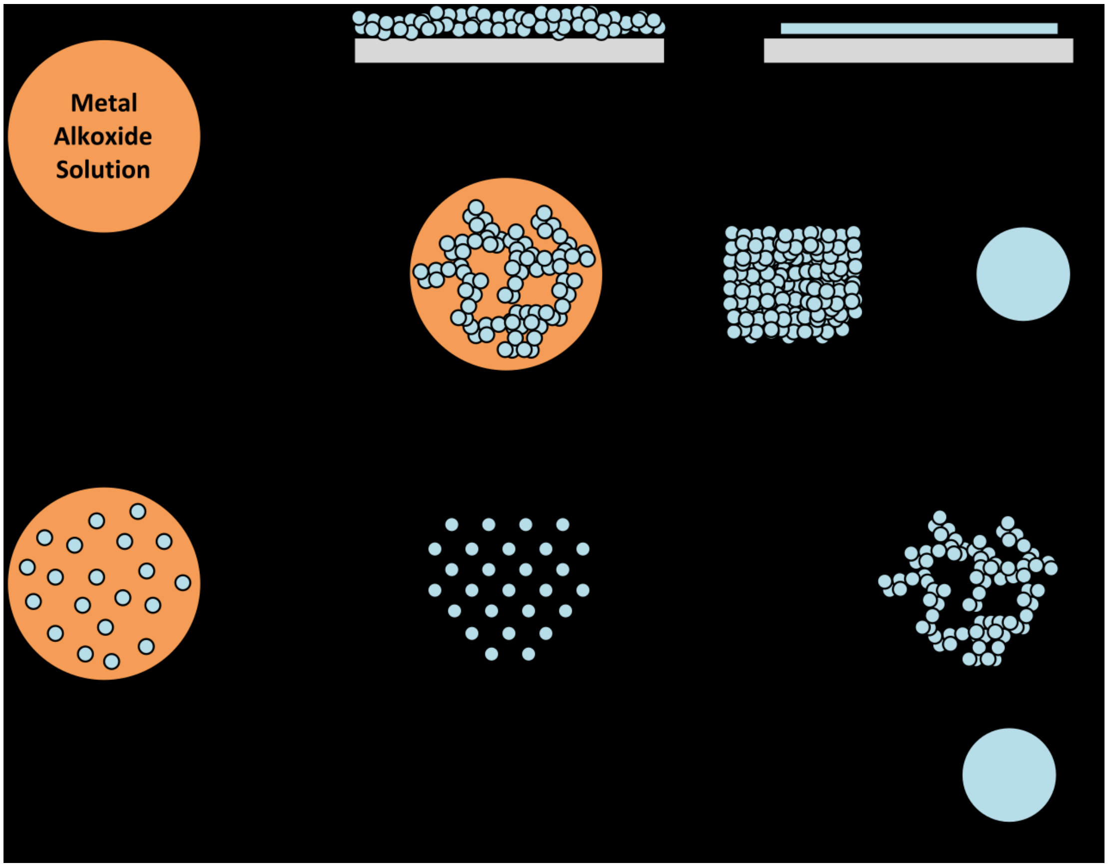


Fig 2.2.3 Schematic representation of the different stages and routes of the sol–gel process.

2.2.3.1 Sol-gel process for thin films and coatings

Thin film or coating deposition has been one of the earliest commercial applications of sol-gel technology. Recently, the thin film coatings synthesized via sol-gel process have been widely investigated for a number of applications, for example, as protective and optical coatings, passivation and planarization layers, sensors, high or low dielectric constant films, inorganic membranes, electro-optic and nonlinear optical films, electrochromic, semiconducting anti-static coatings, superconducting films, strengthening layers and Ferro-electrics.

Thin films (normally <1μm in thickness) formed by dipping or spinning utilize the least amount of precursors and processing times are also short.

2.2.3.2 Sol-gel process for development of super hydrophobic surfaces [26]

The sol-gel process has also been extensively used for manufacturing superhydrophobic surfaces from a variety of materials. In many investigations, due to the presence of materials with low surface energy in the sol-gel process, no alternative hydrophobizing process has been found better suited. For instance, Shirtcliff produced a porous sol-gel foam of Organo-trithoxysile that shows both superhydrophobic behavior and super hydrophilic behavior when exposed to high temperatures. Shang presented a method whereby transparent superhydrophobic surfaces were produced by modifying silicate-based films using fluorinated silanes instead of adding low-energy materials in sol. Moreover, Wu produced a ZnO-based surface in a microstructure using chemical processing. In that case, super hydrophobicity was obtained after coating using long-chain alkanoic acids.

Reaction mechanism [26]:

As discussed previously, sol-gel process undergoes a few reactions, which include hydrolysis and condensation. Since this particular work involves synthesis of silica films using TEOS as the starting precursor, the reactions occurring in this particular case will be discussed.

Fig 2.2.3.2 Simplified representation of the condensation of TEOS in sol gel process

2.2.3.3 Hydrolysis

The chemical formula for TEOS is given by $Si(OC_2H_5)_4$, or $Si(OR)_4$, where the alkyl group $R = C_2H_5$. Alkoxides are ideal chemical precursors for sol–gel synthesis because they react readily with water.

The reaction is called hydrolysis;

$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$

For complete hydrolysis, abundance of water is generally required, coupled with the use of a hydrolysis catalyst. In case of partial hydrolysis, resulting intermediate species such as $[(OR)_2{-}Si{-}(OH)_2]$ or $[(OR)_3{-}Si{-}(OH)]$ may also form as products of the reactions. [27]

2.2.3.4 Condensation

By definition, condensation reaction is the one that liberates a small molecule, such as water or alcohol. This type of reaction may continue to form larger silicon-containing molecules.

-Water condensation:

$n Si(OH)_4 \rightarrow n SiO_2 + 2n H_2O$

-Alcohol condensation:

$Si(OH)_4 + Si(OC_2H_5)_4 \rightarrow 2SiO_2 + 4C_2H_5OH$

2.2.3.5 Gelation

A gel is a porous, three-dimensionally continuous solid structure, which surrounds and supports a continuous liquid phase (i.e. “wet gel”). In sol–gel processes commonly used for the synthesis of oxide materials, gelation or gel formation is because of the covalent bonds generated between the sol particles. Gel formation can be reversible when other bonds are involved, such as van der Waals forces or hydrogen bonds.

Gelation is commenced in aqueous silicate systems due to pH changes, whereas the initiation of gelation is carried out by addition of water in case of alkoxide precursor systems (hydrolysis reactions to generate Si-OH groups).

2.2.3.6 Film Deposition

Three main techniques are normally used to apply a sol-gel coating on the surface of a substrate, namely, dip-coating, spray pyrolysis and spin-coating. Recently, a lot of work has been done on the development of spray coating, which is a more practical approach, and has potential for application of thin films on large walls, roofing, windows etc.

Dip coating

By this technique, the material from which the film is produced is put into solution, and then the substrate is progressively dipped into and is extracted from the solution at a controlled rate (Fig-). After the solvent evaporates, a thin and homogeneous film is produced. The thickness of deposited liquid film coatings depends on the coating solution properties such as density, viscosity, and surface tension, as well as surface withdrawal speed from the coating solution. The thickness of the film is generally bigger than that prepared by spin-coating with the same solutions.

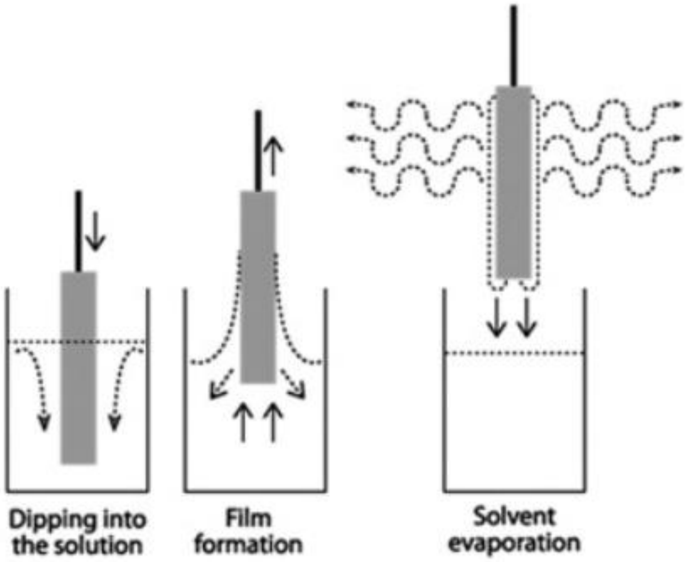


Fig 2.2.3.6 (a) Dip Coating Mechanism

Spin Coating

In the case of spin-coating, an amount of solution is placed on the substrate that is rotated at high speed in order to spread the fluid by centrifugal force (Fig-). After the evaporation of the solvent, a thin, homogeneous film is formed. As in the case of dip-coating, final film thickness and other properties will depend on the nature of the sol-gel coating (viscosity, drying rate, surface tension, etc.) and on the parameters chosen for the spin process. Higher spin speeds and longer spin times give birth to thinner films. Generally, a moderate spinning speed is recommended. The drying rate should also be slow in order to ensure film uniformity.

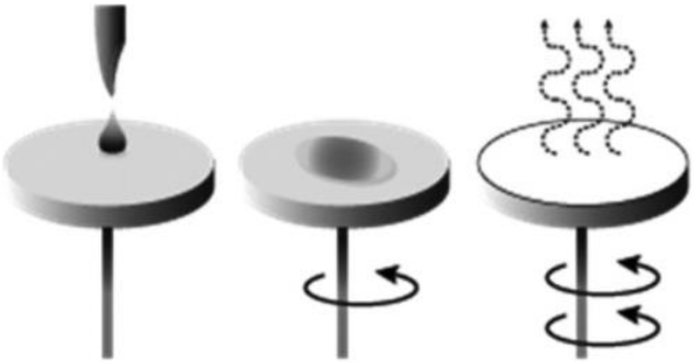


Fig 2.2.3.6 (b) Spin Coating Mechanism for the deposition of thin films synthesized by sol-gel method.

Spray Pyrolysis

The spray pyrolysis technique is a low-cost, non-vacuum required, way to synthesize materials in

the form of powders and films. In the case of films, they are usually deposited over a wide variety of substrates that can be easily adapted for large area deposition and industrial production processes.[28]

In spray pyrolysis, the reaction takes place from the vapor phase at moderate high temperature and can be performed in air for oxides. A solution of the dissolved precursor is sprayed in a vector gas as fine droplets onto a heated substrate. The solvent is evaporated or decomposes into gaseous products. The salt reacts to form a deposit generally based on oxide. The solution can also contain two reactive compounds and the temperature of the substrate allows the activation of the chemical reaction between the two compounds.

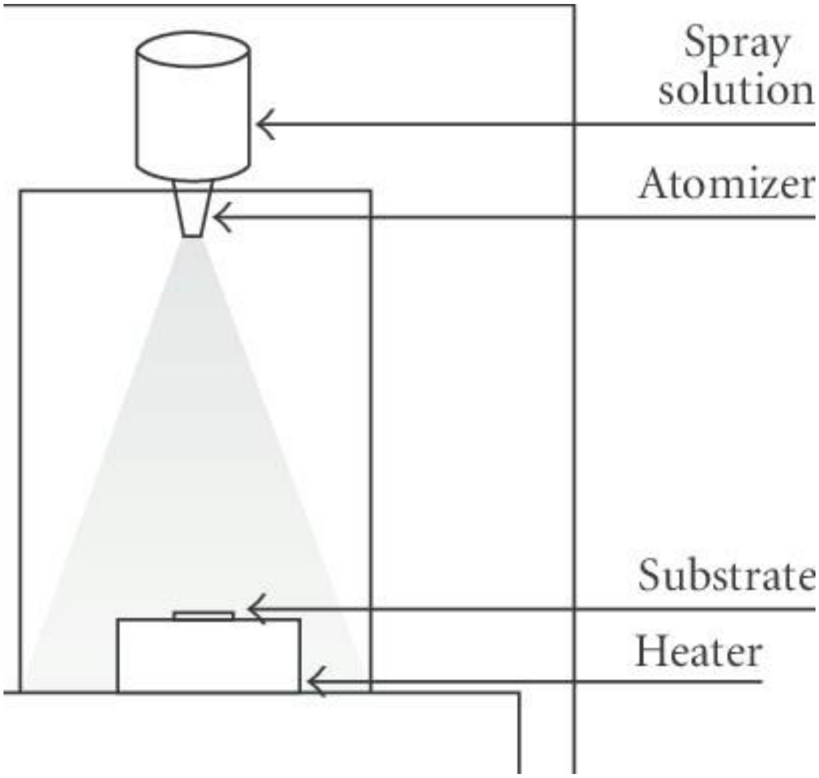


Fig 2.2.3.6 (c) Schematic representation of spray pyrolysis process for the deposition of thin films

2.3 Materials

Some of the materials being used to develop superhydrophobic coatings have been enlisted below. Silica films, being the choice of material for this study, have been discussed;

- Fluorine based films [29]
- Superhydrophobic Zinc Oxide coatings [30]
- Superhydrophobic Polymer Coatings [31]
- Graphene-Based Composite Coatings[32]

2.3.1 Silica based super hydrophobic coatings

Silica films exhibit excellent properties such as thermal and oxidative resistance and have the potential to fulfil the requirement to make durable superhydrophobic optical thin films. TEOS based silica hydrophobic films can be easily synthesized via sol-gel process, and an optimum compromise between surface roughness, optical transparency, contact angle, and durability can be obtained by tailoring the composition of the sol. Furthermore, such coatings are fluorine free, which makes the process environmentally favorable.

The hydrophilicity of silica films is due to the presence of a large number of Si–OH groups on surface of the films. Replacement of the Hs from the Si– OH groups by the hydrolytically stable Si–R groups through the oxygen bonds prevents the adsorption of water and hence results in hydrophobic silica surfaces.

2.4 Objectives

- Design of experimental methodology
- Development of coating by following the designed methodology
- Characterization of wettability and surface morphology of the coated substrate
- Applications and performance analysis of the prepared samples

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Experimental Details

Hydrophobic Thin Film for prevention of contamination, water wetting, and ice formation

Materials:

The substrate material used for the sample preparation were commercial microscopic glass slides. The chemicals used were Triethyl orthosilicate (TEOS) and Trimethyl silane (TMS) as silica precursors, Oxalic acid, methanol, and Ammonium hydroxide as catalyst for sol-gel reaction.

Method:

The synthesis of silica films involves the following four key steps:

1. Substrate pre-treatment for good adhesion of films
2. Preparation of silica sol
3. Coating the substrates with silica sol
4. Drying and annealing of the silica film.

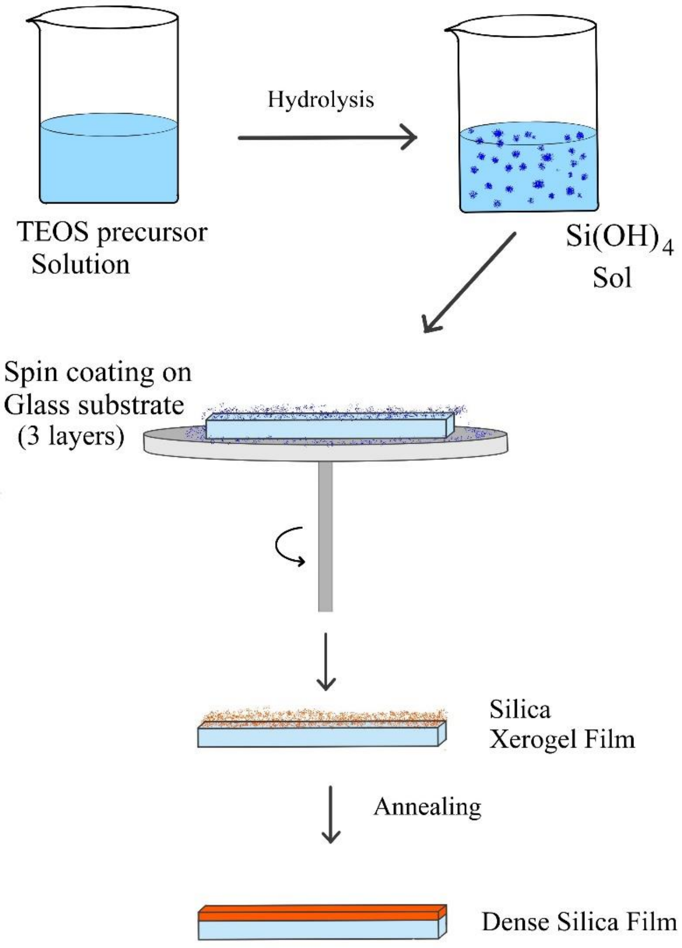


Fig 3.1 Schematic view of Sol-gel process for deposition of thin-film

Each step is further elaborated.

3.1.1 Substrate pre-treatment

The glass slides were immersed in 2 wt% chromic acid solution overnight and washed afterwards with a detergent. The substrates were then rinsed with acetone and dried in the laboratory oven at 60°C before the application of the film on their surface.

3.1.2 Solution preparation

Solution was prepared by first diluting TEOS in methanol. The acidic water (oxalic acid, 0.001 M) was added to this solution gradually while stirring (for about 15 min). In the second step, basic water (ammonium hydroxide, 8 M) was added to the solution gradually while stirring (for about 30 min), after 20 h of hydrolysis reaction. The resultant homogeneous sol was stored in airtight media bottle. The molar ratio of TEOS, methanol (MeOH), acidic water (0.001 M, oxalic acid), and basic water (8 M, NH4OH) was kept constant at 1:66.66:6.76:6.66.

Another solution with same composition as above was prepared, with the only difference being the molar ratio of TMS/TEOS being changed from 0 to 1.1.

3.1.3 Film deposition

The coating of sol onto the substrates was accomplished through spin coating methods, as well as spray pyrolysis technique. Three layers of silica sol were coated onto the substrate via spin coating. No particular protective environment was used for the deposition of silica films. Substrates were preheated for coating via spray pyrolysis.

3.1.4 Annealing

After the deposition of silica films onto the substrates, the substrates were annealed in the oven for 40 hours. The annealing temperature was kept 90^{o}C.

Annealing of thin films is important in order to improve the quality of the coating. Post-annealing mostly results in removal of crystalline defects, and improvement in crystallinity. It may also result in stress relief and relaxation and may also affect the interfacial bonding.

3.1.5 Hydrophobic nanocomposite coating

A minute quantity (0.01mg) of MWCNTS was added to a solution with same composition as above in order to modify the silica coatings and increase the hydrophobicity of the films. MWCNTs were dispersed in the sol by the addition of cetyltrimethylammonium bromide (CTAB) surfactant and stirred vigorously for an hour through probe sonication before coating onto the substrates via spin coating, the process elaboration of which has been done in chapter 2.

Reinforcing the silica film with MWCNTs can significantly reduce the wettability, since the structure of carbon nanotubes is very hydrophobic, and the addition of MWCNTs also result in relatively higher average surface roughness. Furthermore, CNTs, being very strong, can significantly impart strength and wear resistance to the coating and enhance its durability.

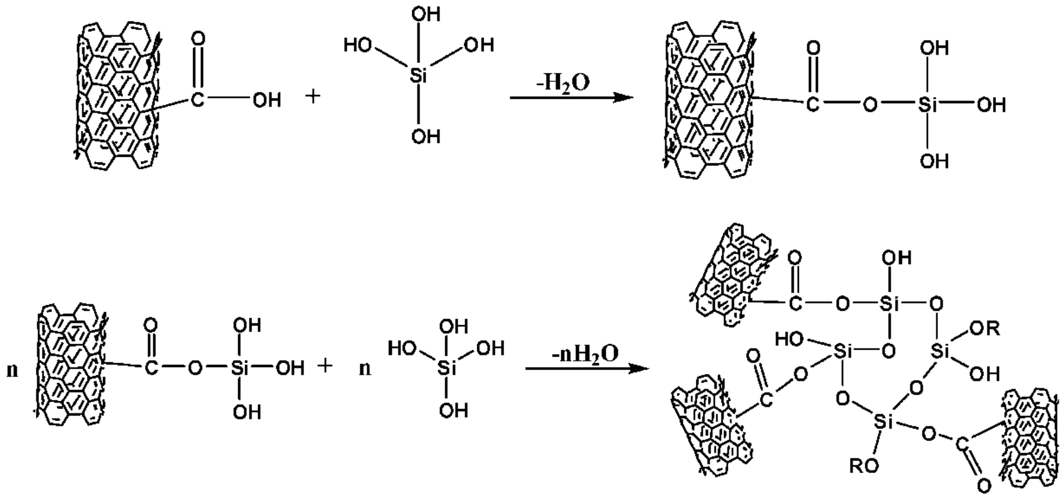


Fig 3.1.5 Schematic of CNT grafted silica nanocomposite thin film

3.2 Experiments Performed

1. Preparation of TEOS based silica films and their deposition onto glass substrates.

2. Preparation of silica film using TEOS and TMES as co-precursors, and deposition onto glass substrates.

3. Preparation of silica films using CTAB and TMES along with TEOS as co-precursors, and deposition onto the glass substrates

4. Preparation of MWCNTs reinforced Silica films using CTAB for dispersion of MWCNTs within the sol, and deposition onto glass substrates.

The different sol compositions used in the experiments have been listed below. All samples were annealed at 120^0C for 24 hours in heating oven.

3.2.1 Sol. Compositions

Sol	TMES: TEOS (vol%)	Methanol (vol %)	Water	Oxalic Acid 0.002 M (vol %)	NH_4OH (vol%)	Cetrimonium bromide (CTAB)	MWCNTs
A	0:1 (4%)	80%		8%	8% 8M	_____	_____
A1	0:1 (4%)	76%	4%	8%	8% 8M	_____	_____
A2	0:1 (4%)	80%	8%	_____	8% 8M	_____	_____
A3	0:1 (4%)	80%	_____	8%	8%	0.5 mg	_____
A4	0:1 (4%)	80%	_____	8%	8%	0.5 mg	0.01 mg
B	1:1 (4%)	80%	_____	8%	8% 8M	0.5 mg	0.01 mg
B1	1:1 (4%)	76%	4%	8%	8% 8M	0.1 mg	0.01 mg
B2	1:1 (4%)	80%	8%	____	8% 8M	0.2 mg	0.01 mg
B3	1:1 (4%)	80%	_____	8%	8% 8M	_____	_____
B4	1:1 (4%)	80%	_____	8%	8% 8M	0.5 mg	_____

Sol	TMES: TEOS (vol%)	Methanol (vol %)	Water	Oxalic Acid 0.002 M (vol %)	NH_4OH (vol%)	Cetrimonium bromide (CTAB)	MWCNTs
C	1.1:1(4%)	80%	_____	8%	8% 8M	0.5 mg	0.01 mg
C1	1.1:1(4%)	76%	4%	8%	8% 8M	0.1 mg	0.01 mg
C2	1.1:1(4%)	80%	8%	_____	8% 8M	0.2 mg	0.01 mg
C3	1.1:1(4%)	80%	_____	8%	8% 8M	0.5 mg	_____
C4	1.1:1(4%)	80%	_____	8%	8% 8M	_____	_____

3.2.2 Optimized Compositions

Sol	TMES:TEOS (vol%)	Methanol (vol %)	Oxalic Acid 0.002 M (vol %)	NH_4OH (vol%)	Cetrimonium bromide (CTAB)	MWCNTs
A	0:1 (4%)	80%	8%	8% 8M	_____	_____
B	1:1 (4%)	80%	8%	8% 8M	0.5 mg	0.01 mg
C	1.1:1(4%)	80%	8%	8% 8M	0.5 mg	0.01 mg

3.3 Characterization Tools

Surface morphology and contact angle measurements were carried out using the following imaging techniques:

3.3.1 Scanning Electron Microscope (SEM)

SEM is a tool designed to directly study the solid surfaces. It uses electron beam of focused electrons of relatively low energy as an electron probe, which scans over the surface to be analyzed. The surface should be conductive for the electrons to interact with it. The electron-surface interactions cause emission of electrons or photons, a fair amount of which are detected by the SEM detector. The signals generated disclose the information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

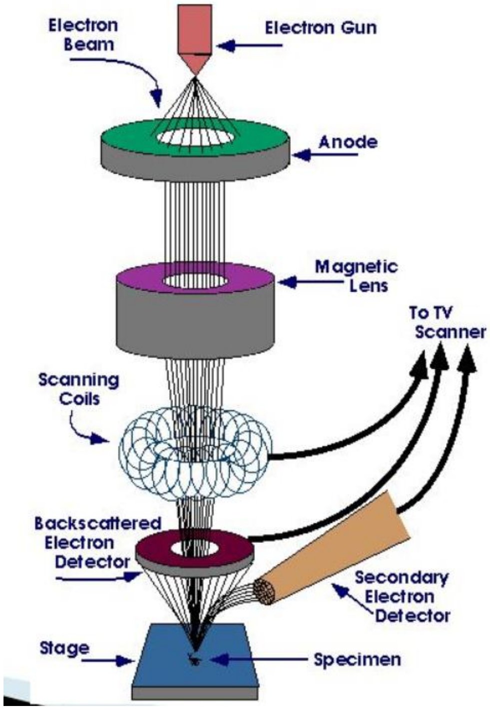


Fig 3.3.1 (a) Schematic representation of working of SEM

The typical working voltage of SEM is 10_20 kV, Spot size of 35_60 and working distance of 10mm.SEM produces very high magnified image of an object up to 300,000 X with the resolution up to nanometers.

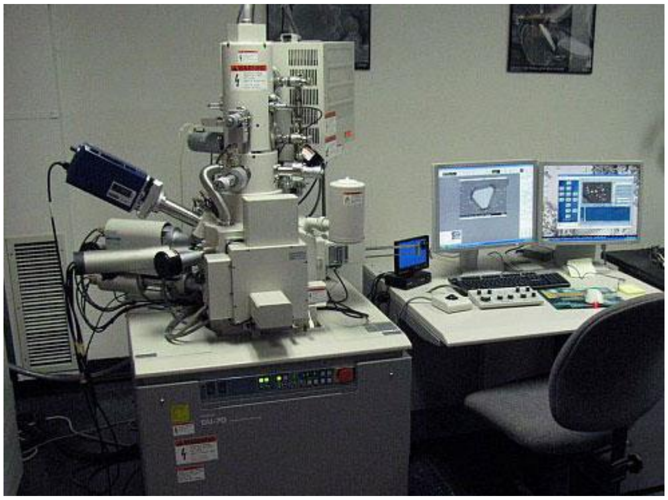


Figure 3.3.1 (b) SEM at NUST

3.3.2 Atomic Force Microscope

Atomic force microscopy is currently the most versatile and powerful microscopy technique for studying samples at nanoscale. It is multipurpose, as an atomic force microscope can not only image in three-dimensional topography, but it also provides various types of surface measurements to the needs of scientists and engineers. It is powerful because an AFM can generate images at atomic resolution with angstrom-scale resolution height information, with relative ease of sample preparation.

AFM is a type of scanning probe microscopy. The AFM has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples.

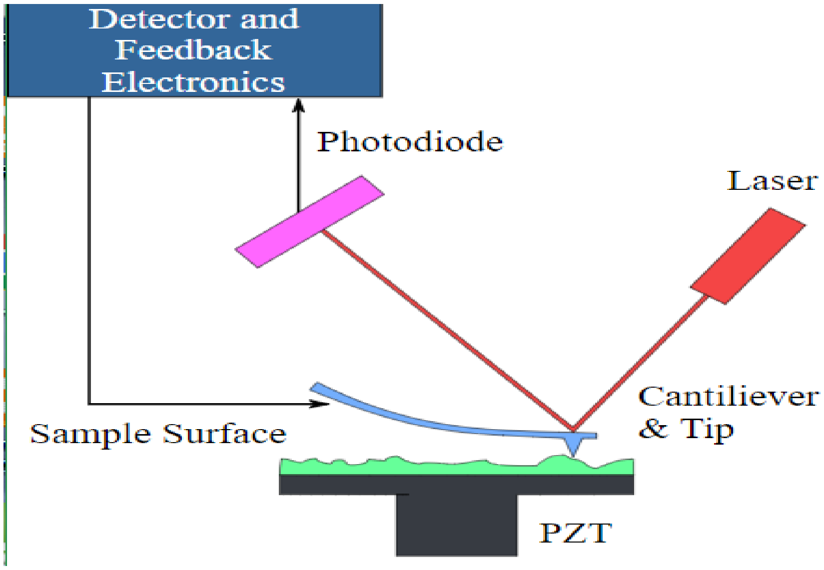


Fig 3.3.2 (a) Schematic Representation of working of AFM

A sharp tip is scanned over a surface using a feedback loop to adjust parameters needed to image a surface. Atomic forces are used to map the tip-sample interaction.

Atomic Force Microscopes use a laser beam deflection system where a laser is reflected from the back of the reflective AFM lever and onto a position-sensitive detector. It uses piezoelectric scanner to scan the tip across the sample and detector to maintain a constant distance between the tip and sample. AFM tips and cantilevers are typically micro-fabricated from Si or Si3N4. Typical tip radius is from a few to 10s of nm.

AFM model (JEOL JSPM 5200) was used in tapping mode for characterization of surface morphology and roughness of the silica-coated glass substrates.

Fig 3.2.2 (b) AFM (Scanning Probe Microscope) at SCME NUST

3.3.3 Drop Shape Analyzer, Krüss (ADVANCE)

Wetting of the substrate surfaces is best characterized by measurement of contact angle. One of the simplest methods for determination of contact angle is Drop Shape Analysis method. This method involves the measurement of contact angle using the image of a sessile drop at the points of intersection (three-phase contact points) between the drop contour and the projection of the surface (baseline).

Drop Shape Analyzer – DSA30 (Krüss) was used for the measurement of contact angle.

Fig 3.3.3 Drop Shape Analyzer – DSA30 (Krüss) at SCME NUST

3.3.4 X-Ray Diffraction

(XRD) is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample.

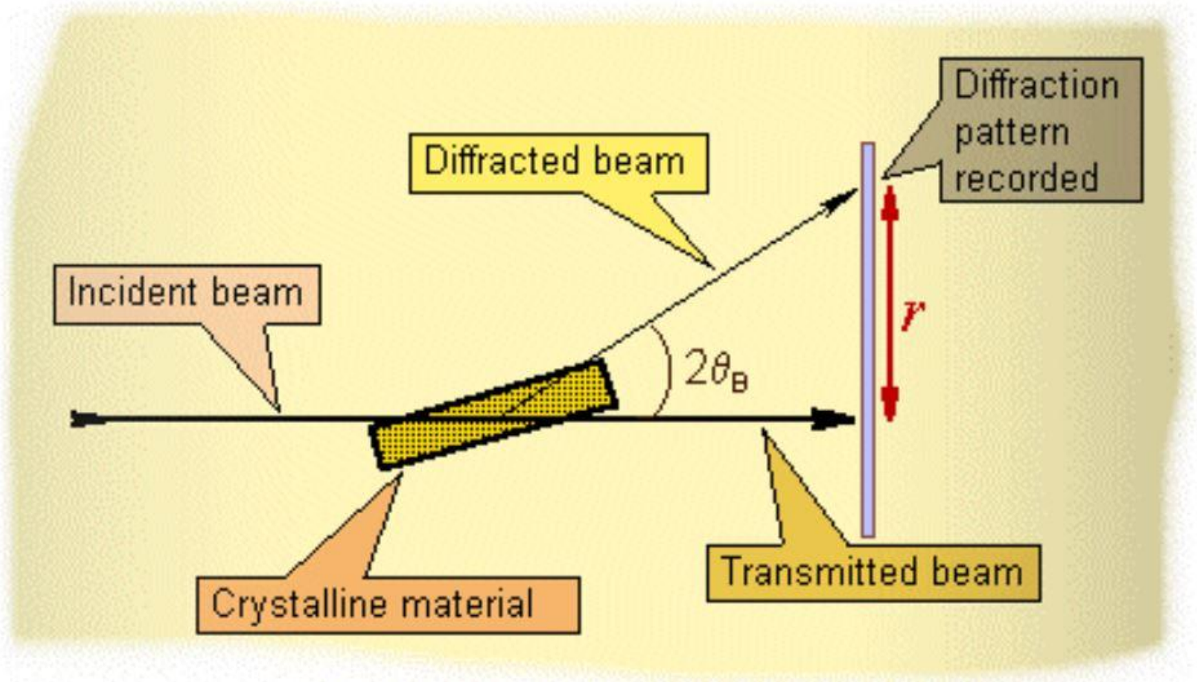


Fig 3.3.4 (a) Block diagram of mechanism and experimental setup of X-ray Diffraction

XRD's mechanism is based on the principle of diffraction angle measurement when x-rays leaves the sample that make certain pattern of peaks which are further evaluated by Bragg's law. William Lawrence Bragg introduced a law Fig 5.3: Block diagram of XRD mechanism 36 defining the space between atoms in a crystal to the angle at which x-rays are scattered by striking the crystal. Mathematical form of Bragg's law is:

$$n\lambda = 2d \sin \theta$$

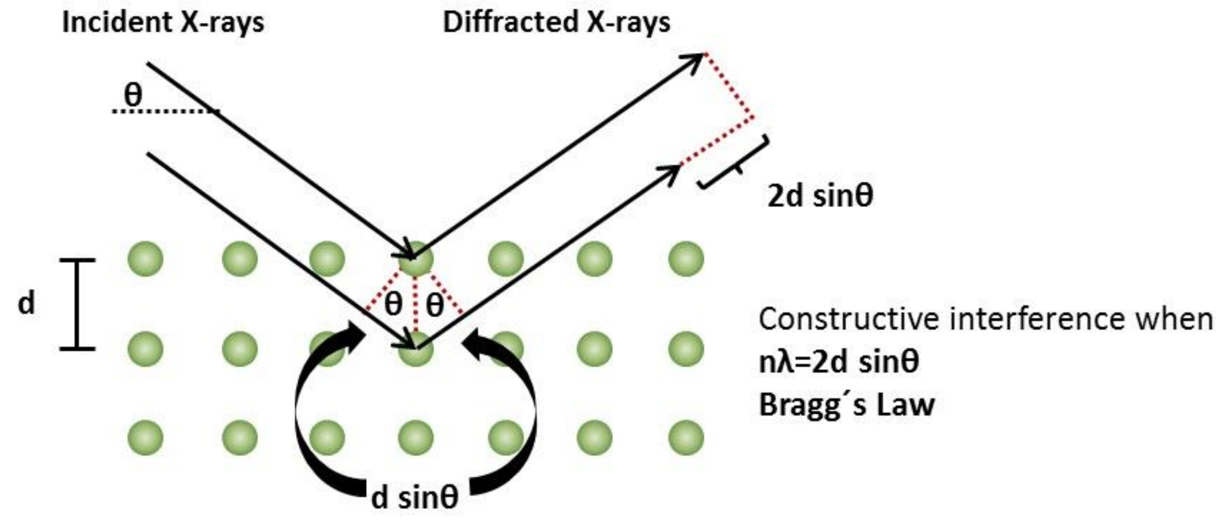
Where;

λ = wavelength of x-ray beam

d = spacing between crystal plane

θ = angle of x-rays scattering

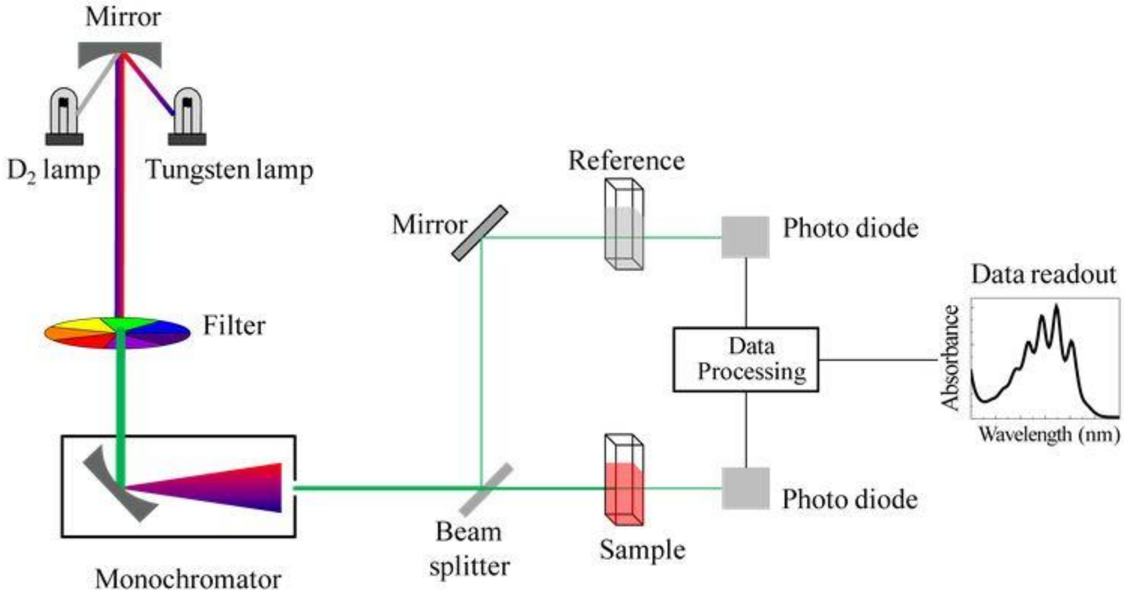
2θ = diffraction angle



3.3.4 (b) Schematic representation of Bragg’s Law; Principle of X-Ray Diffraction

3.3.5 UV – Vis Spectroscopy

Optical properties such as percent transmission, absorption, and reflectance can be determined using a spectrophotometer. A spectrophotometer involves collimated electromagnetic (EM) radiations from ultraviolet (UV) to the far infrared region (IR) range of the electromagnetic spectrum that are incident onto the specimen. The intensity of the transmitted beam is computed over range of the wavelength of incident radiations. Parameters are wavelength (λ) of incident beam, its energy (hν), and the wavenumber (WN). The most common unit for wavelength is nanometer. A spectrophotometer measures intensity as a function of λ of the light source.



3.3.5 Schematic representation of working and experimental setup of UV-Vis Spectrophotometer

CHAPTER 4

RESULTS

4.1 Scanning Electron Microscopy (SEM)

SEM analysis was done to inspect the surface morphology and uniformity of the thin films deposited by spin coating technique. The images show the uniform coverage of the films. The nanostructures and features are due to the deposited colloidal silica sol, which densified after annealing. Certain texture and porosity arise due to the densification of film, and evaporation of solvent and other non-desirable products during post heat treatment.

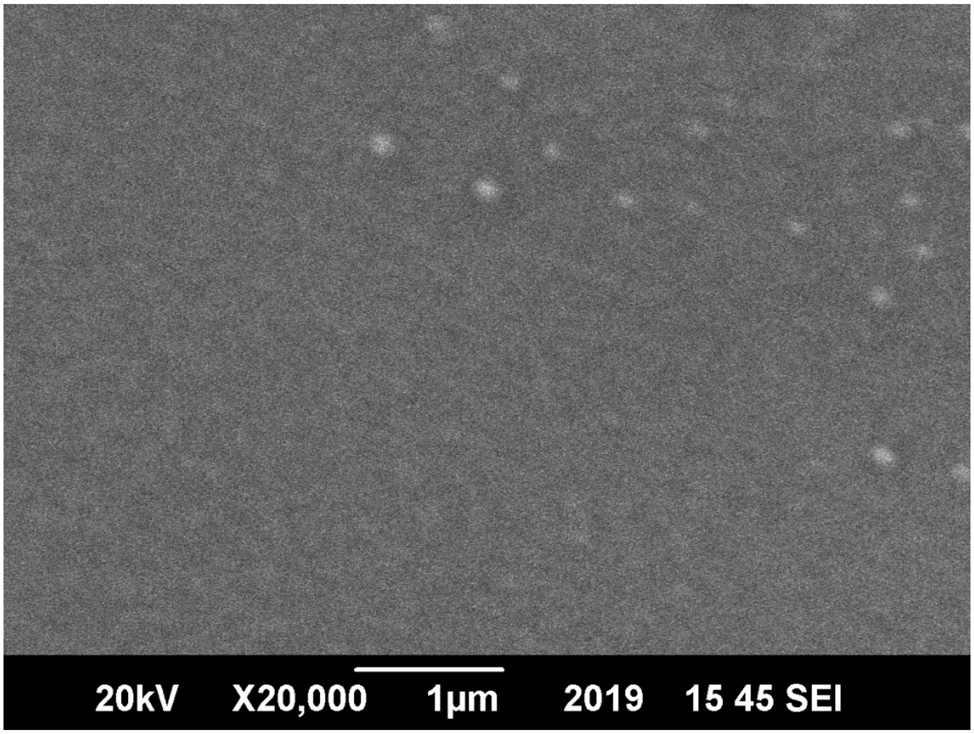


Fig 4.1 (a) SEM image of TEOS based silica films

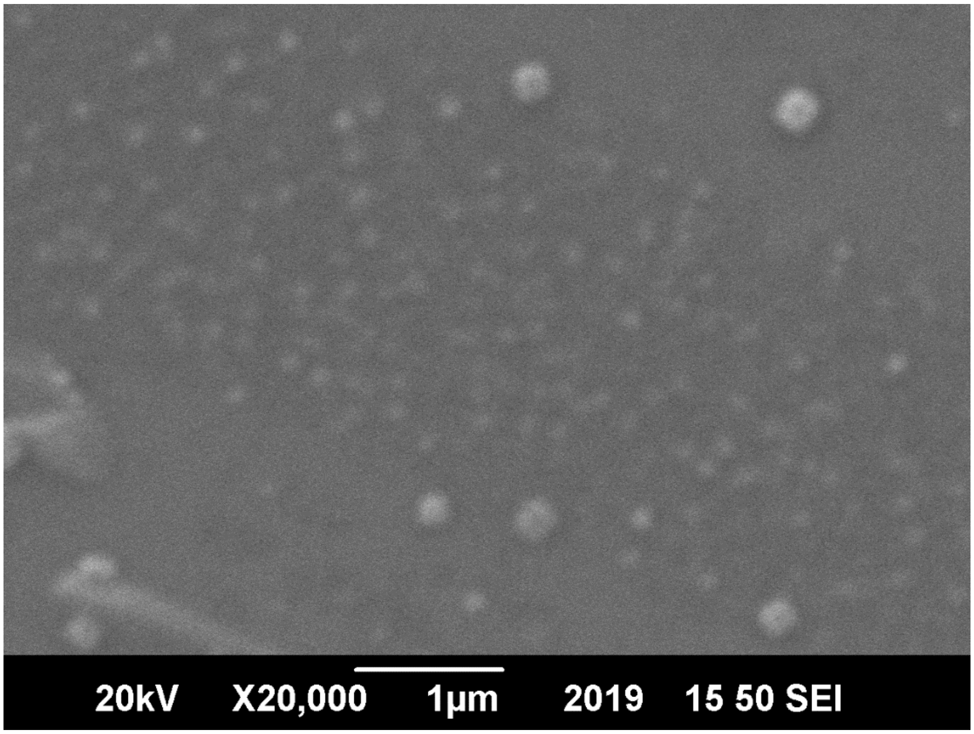


Fig 4.1 (b) SEM Image of TMES/TEOS (1:1) based silica films modified with MWCNTs

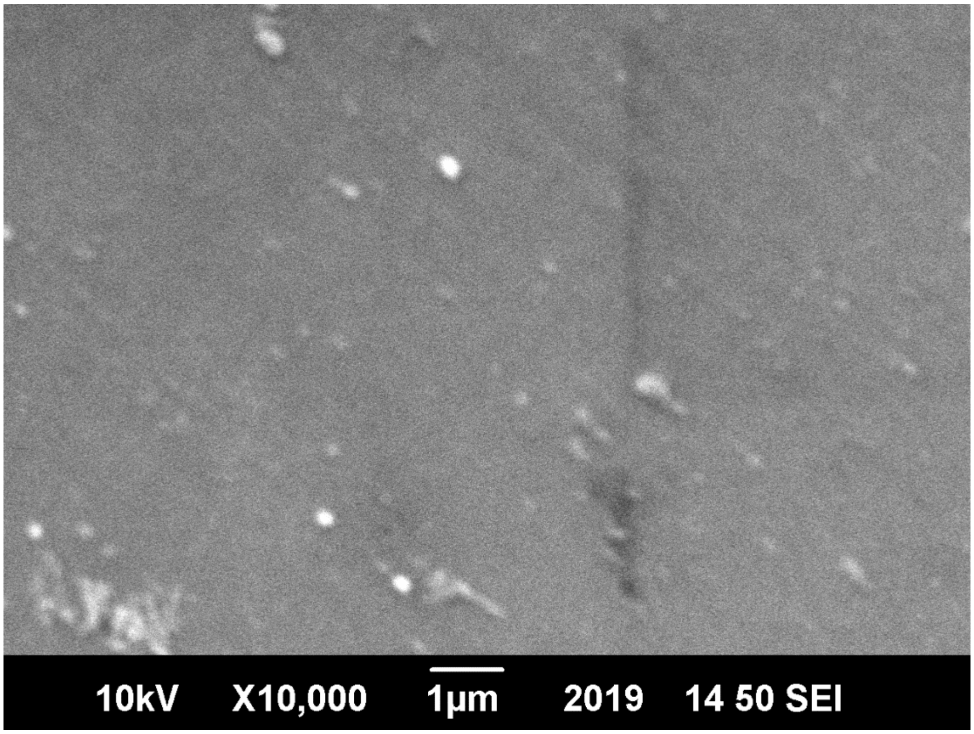


Fig 4.1 (c) SEM Image of TMES/TEOS (1.1:1) based silica films modified with MWCNTs

4.2 Atomic Force Microscopy (AFM)

AFM was used to check the surface topography and roughness of the coatings. 2 x 2 µm images were taken and the root mean square roughness of the surface was measured which has been summarized below;

Sample Composition	Average Roughness	Root Mean Sq. Roughness
Sol. A	R_a= 0.332 nm	R_q= 0.599 nm
Sol. B	R_a= 0.969 nm	R_q= 1.28 nm
Sol. C	R_a= 0.906 nm	R_q= 1.60 nm

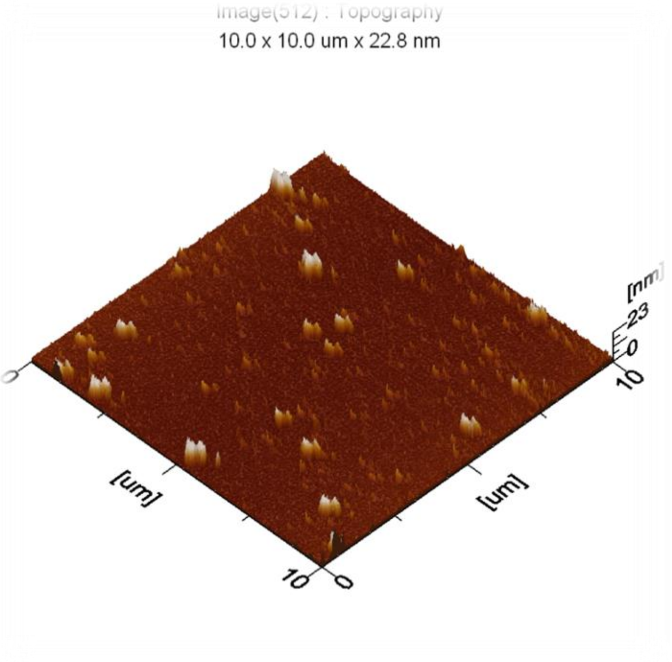


Fig 4.2 (a) 3D AFM image showing topography of TEOS based silica thin films

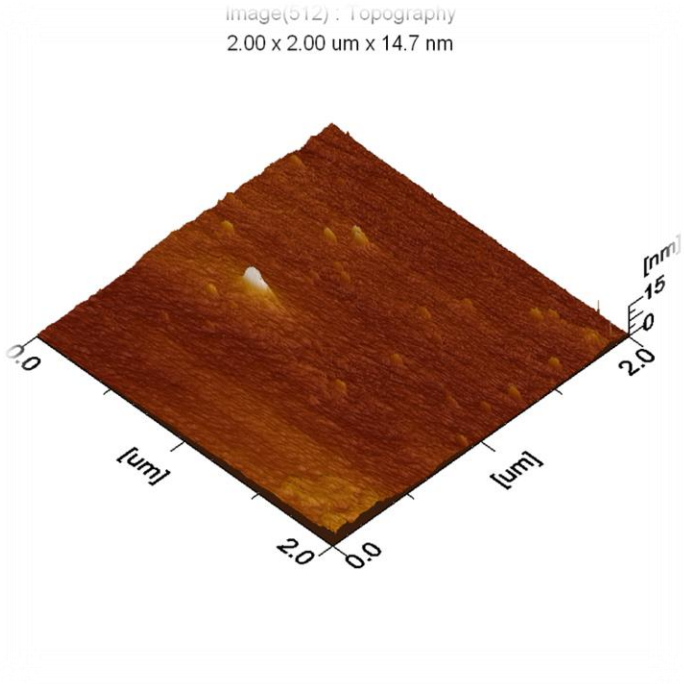


Fig 4.2 (b) 3D AFM Image showing topography of TMES/TEOS (1:1) based Silica thin films

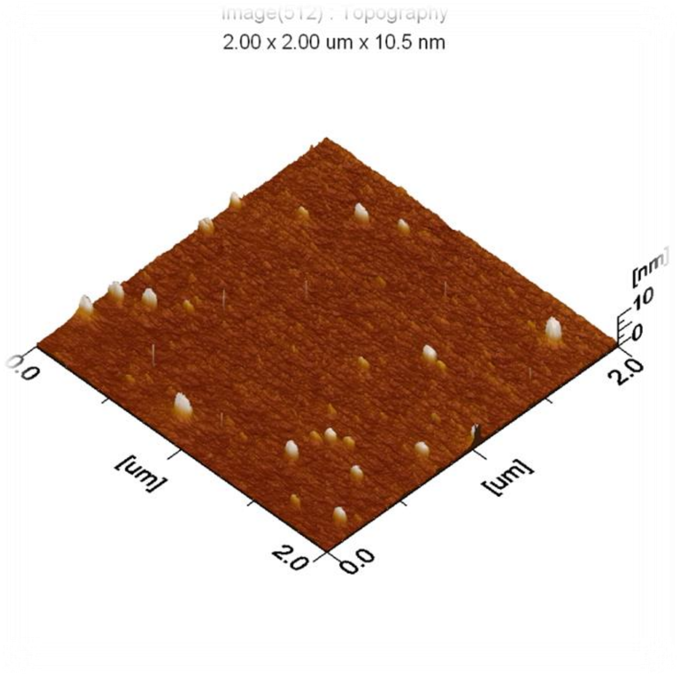


Fig 4.2 (c) 3D AFM Image showing topography of TMES/TEOS (1.1:1) based Silica

4.3 Drop Shape Analysis via Sessile Drop Method

Balance between surface energy, surface tension and substrate energy gives rise to its contact angle with the surface. Contact angle measurement was done by Drop Shape Analyzer – DSA30. Angles less than 90º correspond to a hydrophilic surface whereas greater than 90º indicate decreased wettability and a more hydrophobic nature. The contact angles of a water droplet with the thin films have been shown as images and graphs below**.**

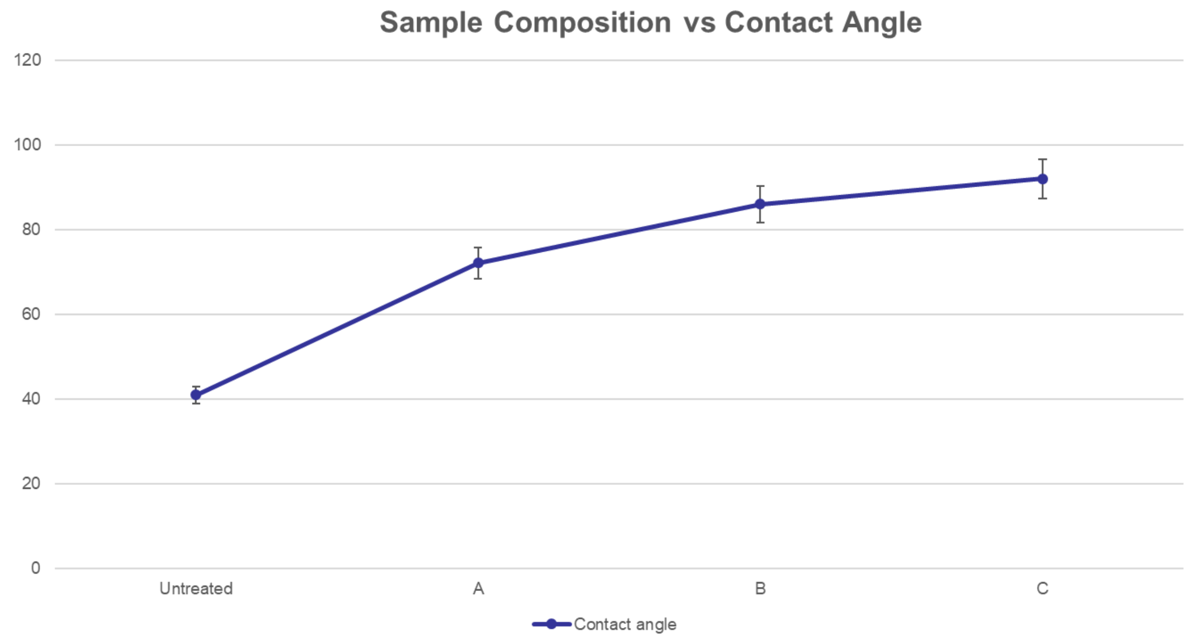


Figure 4.3 (a): Graph for contact angle for different samples

Fig 4.3 (b) Contact angle of water drop on untreated soda lime glass substrate

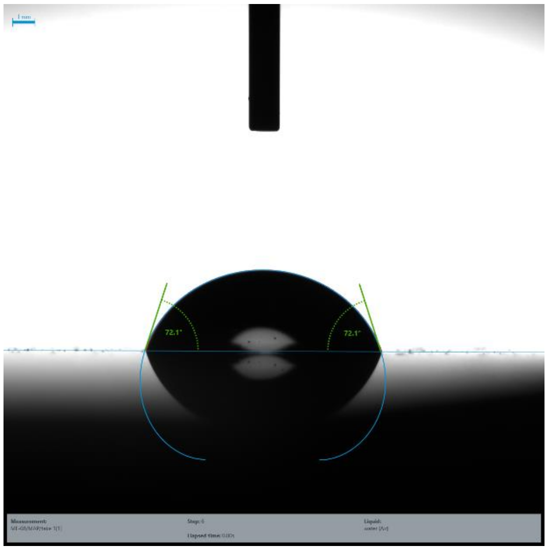


Fig 4.3 (c) Contact angle of water drop on glass modified by TEOS based silica coating

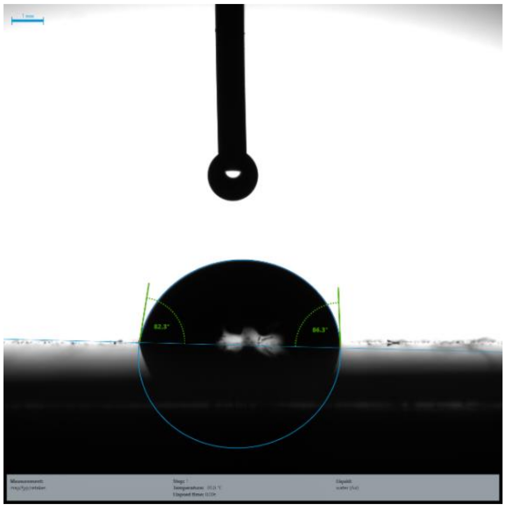


Fig 4.3 (d) Contact Angle of water drop on glass modified by TMES/TEOS (1:1) based Silica coating 1

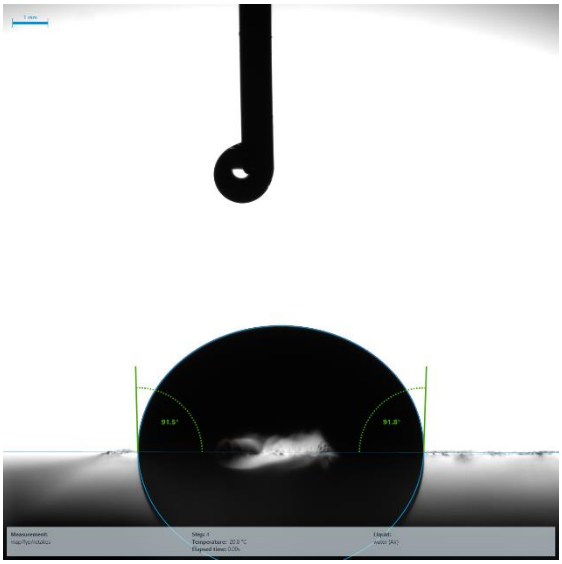
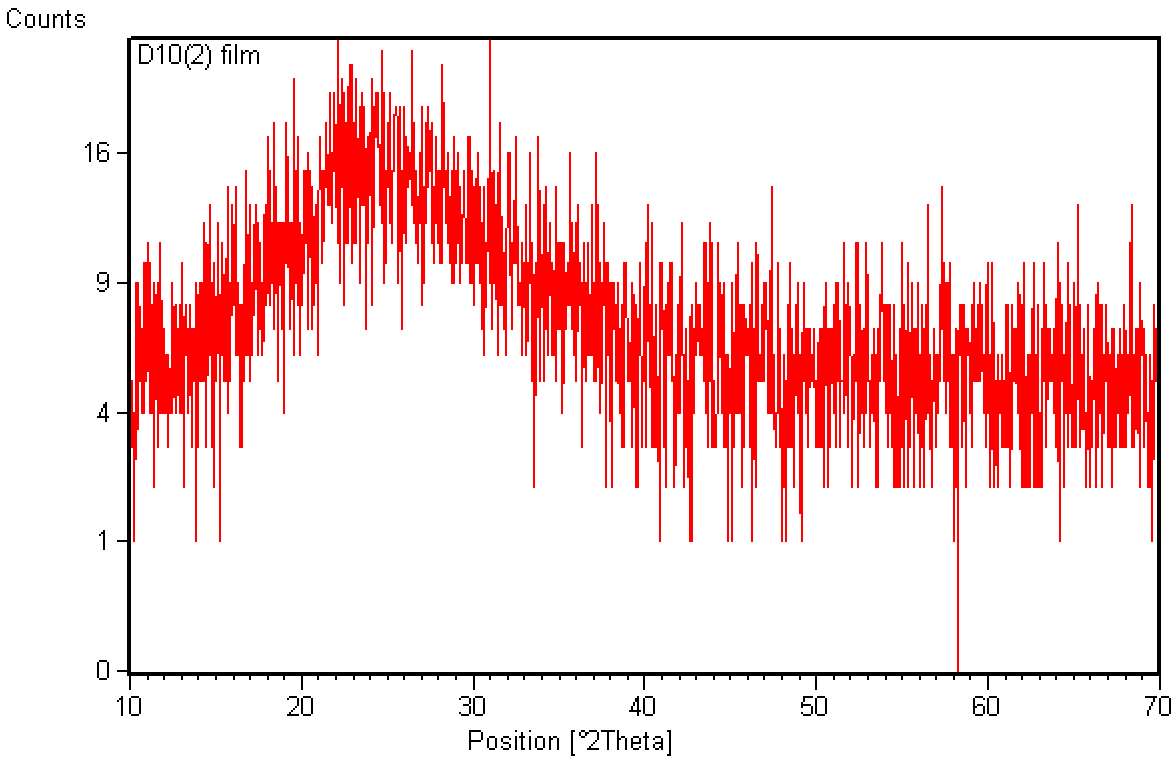


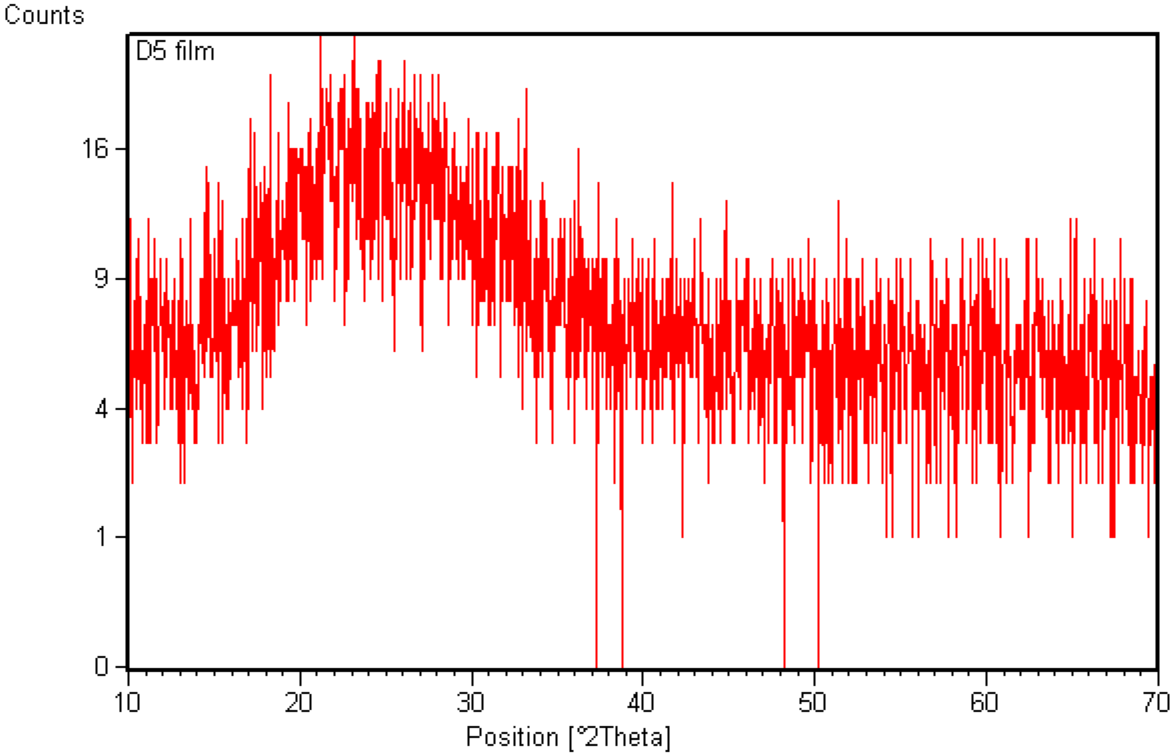
Fig 4.3 (e) Contact Angle of water drop on glass modified by TMES/TEOS (1:1) based Silica coating 2

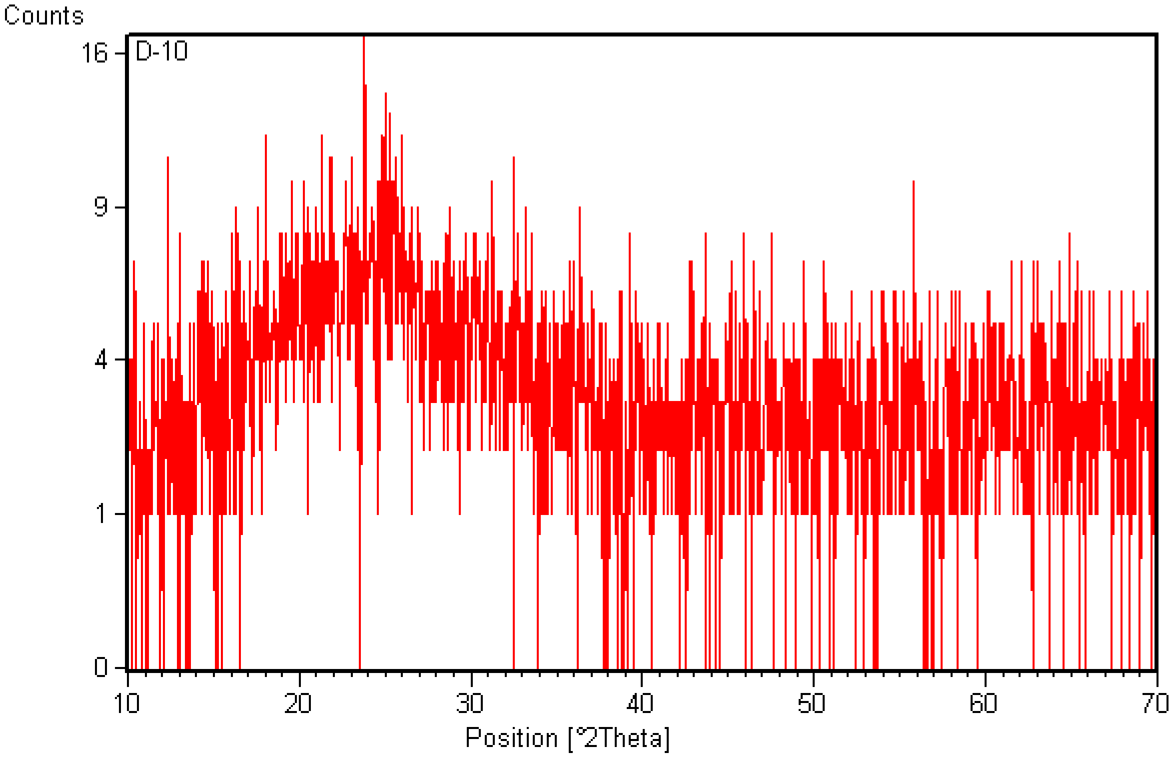
4.4 X-Ray Diffraction Analysis

A crystal is composed of periodically arranged atoms in a 3D space. On the other hand, amorphous materials do not possess that periodicity and atoms are randomly distributed in 3D space. The scattering of X-rays by atoms is the point to be considered in that case. When there is periodic arrangement of atoms, the X-rays will be scattered only in certain directions when they hit the formed lattice planes (formed by atoms). This will cause high intensity peaks. In case of amorphous material, X-rays will be scattered in many directions leading to a large bump distributed in a wide range (2 Theta) instead of high intensity narrower peaks.

The silica films synthesized through the above-mentioned experiments are amorphous, as indicated by the XRD results below.




Counts
D5 film
16
9
4
1
0
10
20
30
40
50
60
70
Position [°2Theta]


Counts
D-10
16
9
4
1
0
10
20
30
40
50
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70
Position [°2Theta]

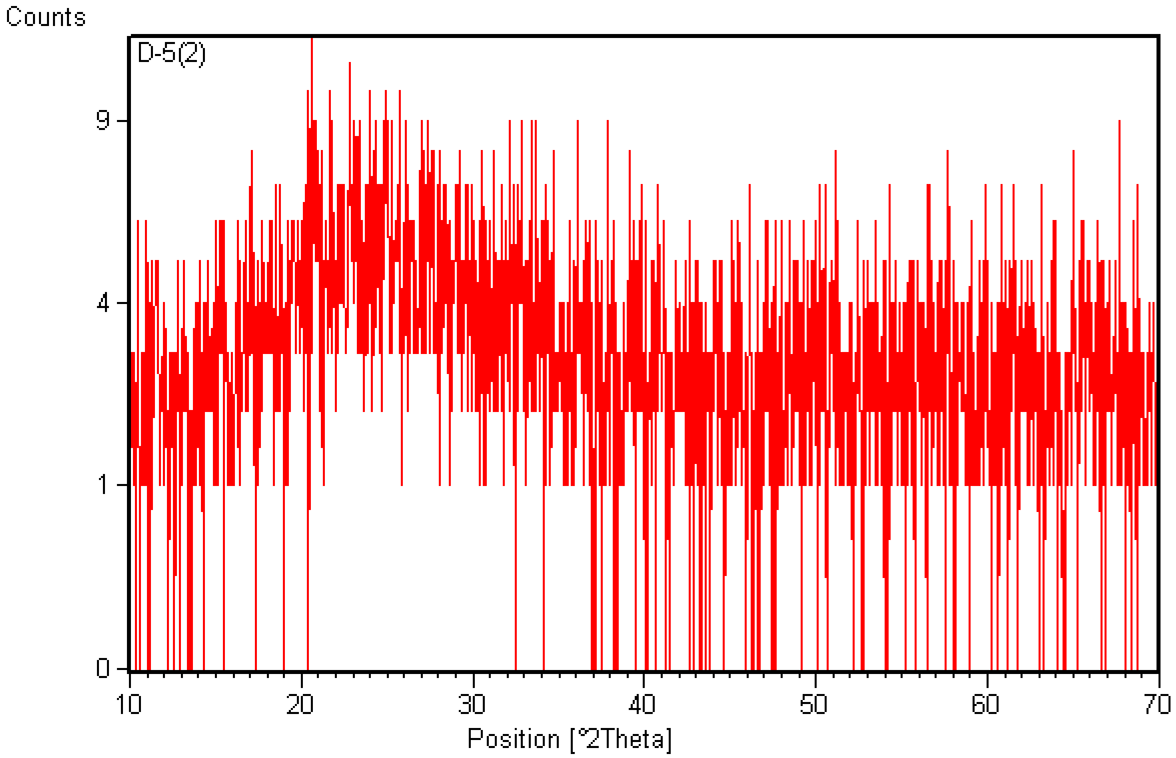

Fig- 4.4 (a), (b), (c), and (d) XRD graphs of silica thin films coated via spray pyrolysis technique.

4.5 Optical Properties

4.5.1 Optical transparency

The UV-Vis spectrophotometric analysis showed that the thin films formed are highly transparent. The transmission and absorption data shows high transparency (>90°C) for the optimized samples. Absorption spectrum against wavelength have been plotted, which shows that the visible region (400nm – 700nm) has not been absorbed.

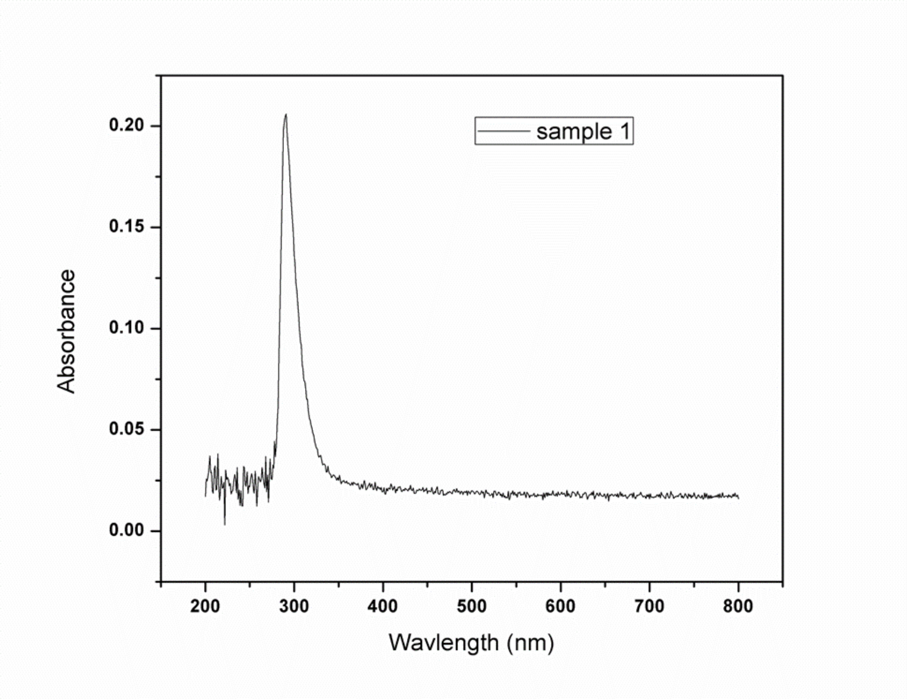

Fig 4.5.1 (a) 1

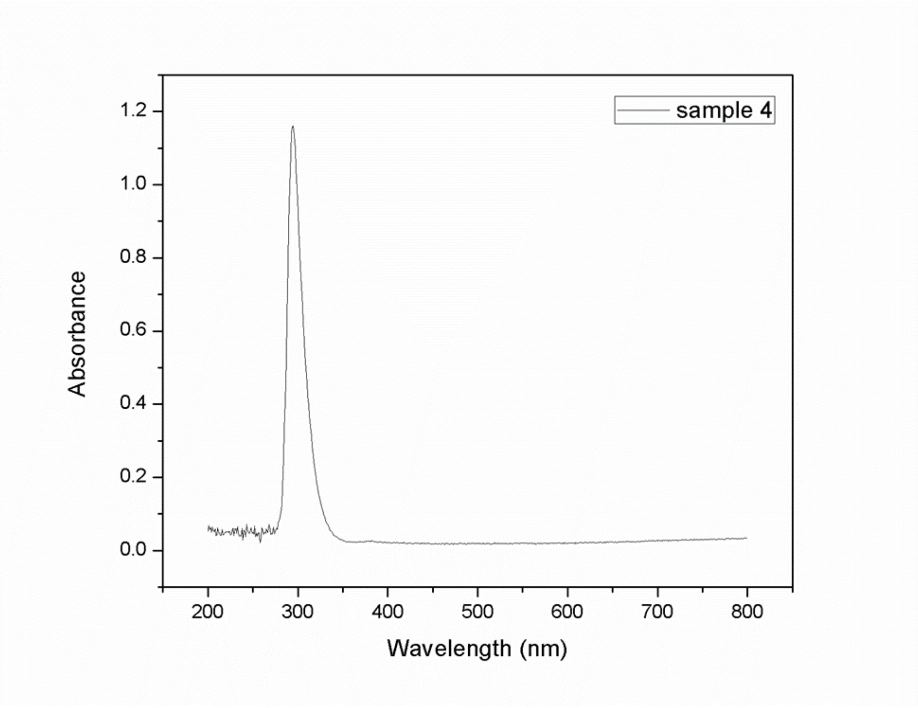

Fig 4.5.1 (b) Absorbance vs Wavelength plot of TMES/TEOS based Silica thin films

4.5.2 Optical bandgap

Optical band gap can be computed by plotting tauc plots using data obtained by UV- Vis Spectrophotometric analysis. Tauc plots of silica thin films have been depicted below.

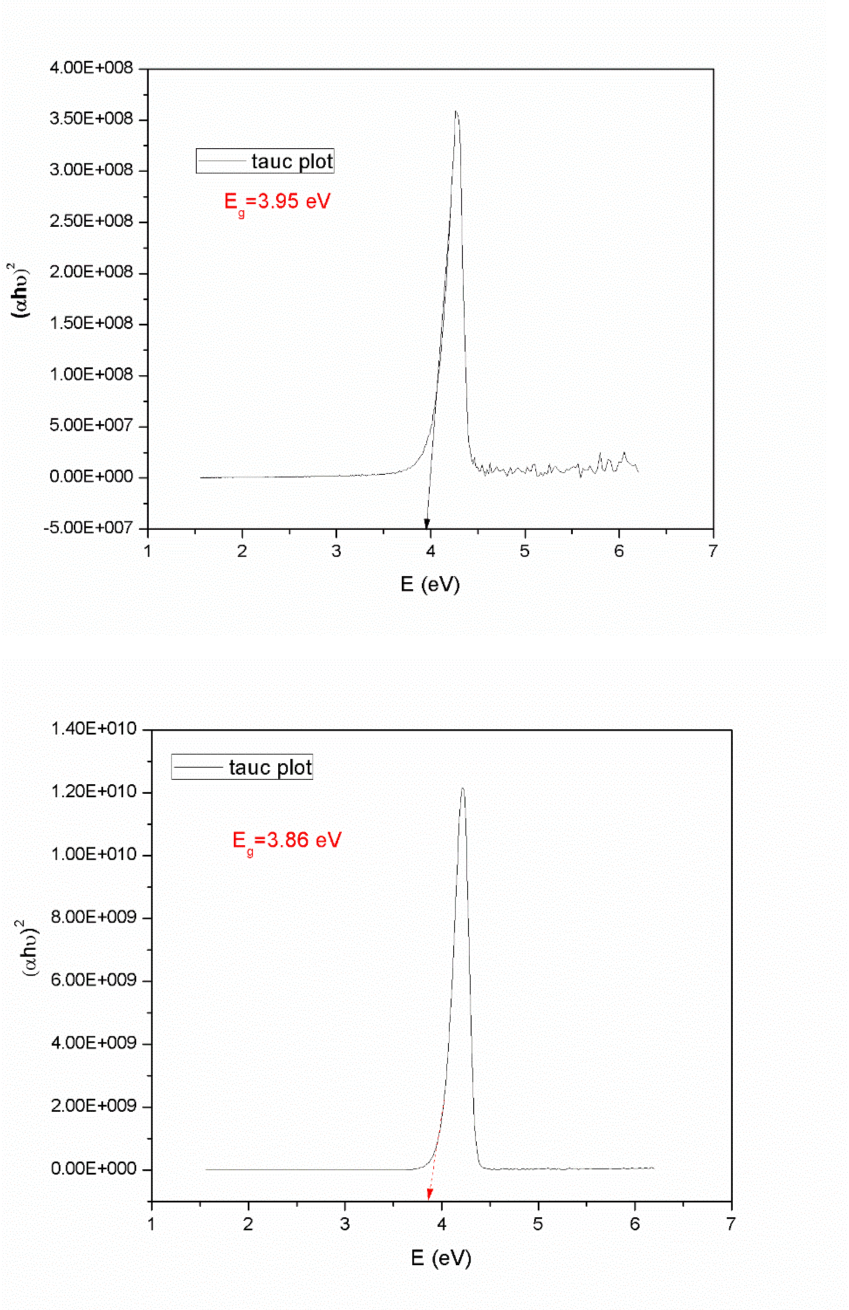

Fig 4.5.2 (a), (b) Tauc plots of silica thin films showing average optical band gap value of 3.9 eV

CHAPTER 5

CONCLUSION

5.1 Conclusion

Multilayer thin film coating was deposited on soda lime glass substrates in order to make it hydrophobic and ice-phobic. Self-cleaning for the purpose of anti-contamination was achieved through hydrophobicity using silica thin films and nanocomposite films. Silica films along with films modified with cnts grafted with silica were deposited at room temperature onto the substrates. The effects of varying ratios of TMES/TEOS in sol preparation on the hydrophobicity of silica films were observed. Films are highly transparent (>90%) in visible spectrum (400nm-700nm), almost unaffected by exposure to UV radiation. The maximum contact angle obtained was around 95^0, with 1.1 TMES/TEOS ratio in sol. The roughness of the films is also observed to slightly increase with the TMES/TEOS ratio and hydrophobicity. In conclusion, transparent silica coatings for the prevention of contamination, water wetting, and ice formation were deposited onto glass substrate using cost-efficient solution-based methods.

5.2 Future Recommendations

5.2.1 Deposition via Dip Coating

Large samples can be coated using dip coating technique, which is relatively simple as compared to the already employed spray pyrolysis technique in which pre-heating and heating during deposition is required as well.

5.2.2 Durable super hydrophobic silica/epoxy resin coatings:

A frequently experienced issue regarding superhydrophobic films is the lack of durability of the surface coating. Regardless of the use of high quality superhydrophobic particles, it is still quite tricky to adhere such particles to the substrate surface while retaining the superhydrophobic behavior. Hence, there exists a typical trade-off condition between durability and superhydrophobic behavior [33]. Several efforts have been done to retain the optical transparency, as well as super hydrophobicity of the films. [34, 35]

The method that is intended to be included in this work is the preparation of durable superhydrophobic silica/epoxy resin coatings with compatible transparency and stability. This method would utilize the colourless epoxy grade (Bisphenol- A type epoxy resin) to bind silica onto the substrate surface[34].

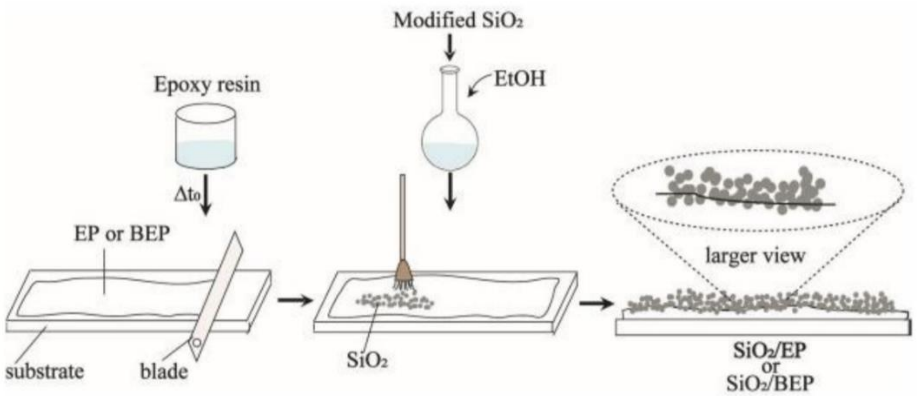

Fig 5.2.3 Schematic of general Silica/Epoxy thin film development over substrate material

5.2.3 Mechanical Testing of Thin Films

The thin films need to be tested for their durability and mechanical strength against abrasiveness. This can be done by the following tests:

1. Scotch tape peel-off test
2. Weather resistance tests
3. Nano-indentation hardness test

5.2.4 Synthesis Using Other Co-precursors

Other silanes as co precursors can be used to increase the silica content of the films, to enhance the self-cleaning property.

BIBLIOGRAPHY

[1] J. Laforte, M. Allaire, and J. Laflamme, "State-of-the-art on power line de-icing," *Atmospheric Research,* vol. 46, pp. 143-158, 1998.

[2] J. Lv, Y. Song, L. Jiang, and J. Wang, "Bio-inspired strategies for anti-icing," *ACS nano,* vol. 8, pp. 3152-3169, 2014.

[3] W. Barthlott and C. Neinhuis, "Purity of the sacred lotus, or escape from contamination in biological surfaces," *Planta,* vol. 202, pp. 1-8, 1997.

[4] M. Song, J. Ju, S. Luo, Y. Han, Z. Dong, Y. Wang, *et al.*, "Controlling liquid splash on superhydrophobic surfaces by a vesicle surfactant," *Science advances,* vol. 3, p. e1602188, 2017.

[5] Y. Lei, Q. Wang, and J. Huo, "Fabrication of durable superhydrophobic coatings with hierarchical structure on inorganic radome materials," *Ceramics International,* vol. 40, pp. 10907-10914, 2014.

[6] T. Wang, L. Chang, S. Yang, Y. Jia, and C. Wong, "Hydrophobic properties of biomorphic carbon surfaces prepared by sintering lotus leaves," *Ceramics International,* vol. 39, pp. 8165-8172, 2013.

[7] S. Liu, S. S. Latthe, H. Yang, B. Liu, and R. Xing, "Raspberry-like superhydrophobic silica coatings with self-cleaning properties," *Ceramics International,* vol. 41, pp. 11719-11725, 2015.

[8] Z. Chu and S. Seeger, "Superamphiphobic surfaces," *Chemical Society Reviews,* vol. 43, pp. 2784-2798, 2014.

[9] X. Deng, L. Mammen, H.-J. Butt, and D. Vollmer, "Candle soot as a template for a transparent robust superamphiphobic coating," *Science,* vol. 335, pp. 67-70, 2012.

[10] H. Yabu and M. Shimomura, "Single-step fabrication of transparent superhydrophobic porous polymer films," *Chemistry of materials,* vol. 17, pp. 5231-5234, 2005.

[11] V. Skroznikova, N. Popovich, and T. Dimitrov, "Transparent hydrophobic sol–gel silica coatings on glass," *Sci. Works Russ. Univ.*, vol. 52, pp. 61-64, 2013.

[12] T. Yoneda and T. Morimoto, "Mechanical durability of water repellent glass," *Thin solid films,* vol. 351, pp. 279-283, 1999.

[13] L. Nikolic and L. Radonjic, "Effect of the silica sol–Gel coatings on the properties of glass substrate," *Ceramics International,* vol. 24, pp. 547-552, 1998/09/01/ 1998.

[14] Y. Huang, H. Zheng, I. Ball, and Z. Luo, *Advances in Sol-Gel Technology Advances in Sol-Gel Technology,* 2019.

[15] J. D. Mackenzie and E. P. Bescher, "Physical Properties of Sol-Gel Coatings," *Journal of Sol-Gel Science and Technology,* vol. 19, pp. 23-29, 2000/12/01 2000.

[16] M. Guglielmi, "Sol-gel coatings on metals," *Journal of Sol-Gel Science and Technology,* vol. 8, pp. 443-449, 1997/02/01 1997.

[17] L. Xu, R. G. Karunakaran, J. Guo, and S. Yang, "Transparent, Superhydrophobic Surfaces from One-Step Spin Coating of Hydrophobic Nanoparticles," *ACS Applied Materials & Interfaces,* vol. 4, pp. 1118-1125, 2012/02/22 2012.

[18] M. Im, H. Im, J. H. Lee, J.-B. Yoon, and Y. K. Choi, *A robust superhydrophobic and superoleophobic surface with inverse-trapezoidal microstructures on a large transparent flexible substrate* vol. 6, 2010.

[19] H. F. Bohn and W. Federle, "Insect aquaplaning: Nepenthes pitcher plants capture prey with the peristome, a fully wettable water-lubricated anisotropic surface," *Proceedings of the National Academy of Sciences of the United States of America,* vol. 101, p. 14138, 2004.

[20] U. Bauer, T. U. Grafe, and W. Federle, "Evidence for alternative trapping strategies in two forms of the pitcher plant, Nepenthes rafflesiana," *Journal of experimental botany,* vol. 62, pp. 3683-3692, 2011.

[21] R. J. Good, "A thermodynamic derivation of Wenzel's modification of young's equation for contact angles; together with a theory of hysteresis1," *Journal of the American Chemical Society,* vol. 74, pp. 5041-5042, 1952.

[22] A. Cassie, "Contact angles," *Discussions of the Faraday society,* vol. 3, pp. 11-16, 1948.

[23] R. N. Wenzel, "Surface roughness and contact angle," *The Journal of Physical Chemistry,* vol. 53, pp. 1466-1467, 1949.

[24] C. Dorrer and J. Rühe, "Advancing and receding motion of droplets on ultrahydrophobic post surfaces," *Langmuir,* vol. 22, pp. 7652-7657, 2006.

[25] J.-O. Carlsson and P. M. Martin, "Chemical vapor deposition," in *Handbook of deposition technologies for films and coatings*, ed: Elsevier, 2010, pp. 314-363.

[26] S. S. Latthe, H. Hirashima, and A. V. Rao, "TEOS based water repellent silica films obtained by a co-precursor sol–gel method," *Smart Materials and Structures,* vol. 18, p. 095017, 2009/07/17 2009.

[27] D. A. H. Hanaor, I. Chironi, I. Karatchevtseva, G. Triani, and C. C. Sorrell, "Single and mixed phase TiO2 powders prepared by excess hydrolysis of titanium alkoxide," *Advances in Applied Ceramics,* vol. 111, pp. 149-158, 2012/04/01 2012.

[28] D. Perednis and L. J. Gauckler, "Thin Film Deposition Using Spray Pyrolysis," *Journal of Electroceramics,* vol. 14, pp. 103-111, 2005/03/01 2005.

[29] J.-D. Brassard, D. Sarkar, and J. Perron, *Fluorine Based Superhydrophobic Coatings* vol. 2, 2012.

[30] E. Velayi and R. Norouzbeigi, *Synthesis of hierarchical superhydrophobic zinc oxide nano-structures for oil/water separation* vol. 44, 2018.

[31] J. T. Simpson, S. R. Hunter, and T. Aytug, "Superhydrophobic materials and coatings: a review," *Reports on Progress in Physics,* vol. 78, p. 086501, 2015.

[32] M. J. Nine, M. A. Cole, L. Johnson, D. N. H. Tran, and D. Losic, "Robust Superhydrophobic Graphene-Based Composite Coatings with Self-Cleaning and Corrosion Barrier Properties," *ACS Applied Materials & Interfaces,* vol. 7, pp. 28482-28493, 2015/12/30 2015.

[33] M. Aegerter, R. Almeida, A. Soutar, K. Tadanaga, H. Yang, and T. Watanabe, *Coatings made by sol gel and chemical nanotechnology* vol. 47, 2008.

[34] M. Zhong, Y. Zhang, X. Li, and X. Wu, *Facile fabrication of durable superhydrophobic silica/epoxy resin coatings with compatible transparency and stability* vol. 347, 2018.

[35] C.-H. Xue, X. Bai, and S.-T. Jia, "Robust, Self-Healing Superhydrophobic Fabrics Prepared by One-Step Coating of PDMS and Octadecylamine," *Scientific Reports*, vol. 6, p. 27262, 06/06/online 2016.