

Applications of Plasma Technology in Development of Superhydrophobic Surfaces: A Review

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Abstract

Superhydrophobic surfaces, originally inspired by nature, have gained a lot of interest in the past few decades. Superhydrophobicity is a term attributed to the low adhesion of water droplets on a surface, leading to water contact angles higher than 150° . Due to their vast variety of possible applications, ranging from biotechnology and textile industry to power network management and anti-fouling surfaces, many methods have been utilized to develop superhydrophobic surfaces. Among these methods, plasma technology has proved to be a very promising approach. Plasma technology takes advantage of highly reactive plasma species to modify the functionality of various substrates. It is one of the most common surface treatment technologies which is widely being used for surface activation, cleaning, adhesion improvement, anti-corrosion coatings and biomedical coatings. In this paper, recent advances in the applications of plasma technology in the development of superhydrophobic surfaces are discussed. At first, a brief introduction to the concept of superhydrophobicity and plasma is presented, then plasma-based techniques are divided into three main categories and studied as to their applications in development of superhydrophobic surfaces.

Keywords: Plasma polymerization, etching, sputtering, superhydrophobic surfaces, thin films, nano-structured surfaces

1 Introduction

Wettability of a surface depends on its chemical composition and surface micro/nano roughness. These two parameters determine the extent

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of adhesive forces between a liquid droplet and the surface. Superhydrophobicity is where surface roughness meets low surface energy, so the adhesion force between water droplet and solid surface significantly decreases [1]. The concept of superhydrophobicity initially emerged from the investigation of natural surfaces with high contact angle and low contact angle hysteresis, notably the lotus leaf (Nelumbo) surface (Figure 1) [2–4].

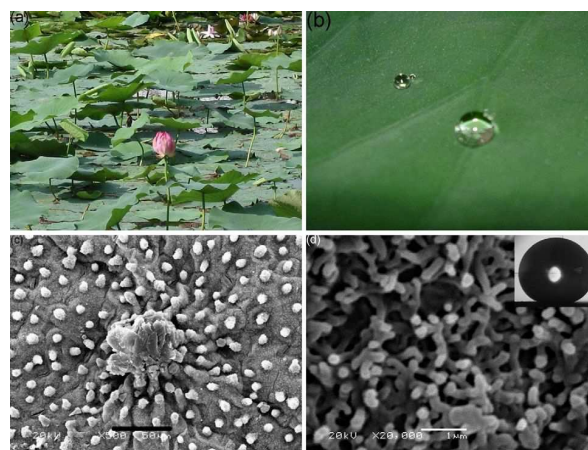


Figure 1: The photos of some lotus leaves (a) and of a water droplet on a lotus leaf (b) and the SEM images of lotus leaves with different magnifications (c and d). The inset of (d) is a water contact angle on a lotus leaf, with a value of $161^\circ \pm 2^\circ$ [5].

Lotus is usually considered as a symbol of purity due to its self-cleaning effect [2, 6]. The superhydrophobic characteristics of the micro-nanostructured and wax-coated surface of the lotus leaf was first studied by Dettre and Johnson in 1963 [7]. Since then, several other examples of natural superhydrophobic surfaces have been dis-

covered. The wax nano-crystals on the leaves of *Colocasia esculenta* (taro leaf) are capable of trapping air between a water droplet and the leaf surface [8]. *Euphorbia myrsinites*, another plant native to South-eastern Europe and Asia Minor, has superhydrophobic leaves due to its hierarchically nano-structured leaf surface. Rice leaf, Chinese watermelon and India canna leaf are also known to be superhydrophobic [9]. Barthlott et al. studied 350 plant leaves by SEM imaging and showed that the hierarchical roughness on a leaf surface plays an important role in the self-cleaning effect [2]. For more information on natural superhydrophobic surfaces, see [2, 3, 5, 9].

On a self-cleaning surface, water droplets roll-off easily carrying away any contamination, which is why superhydrophobic surfaces are usually considered self-cleaning [3]. During the past few decades, many studies have tried to mimic the natural structures to develop artificial superhydrophobic surfaces, which can be useful in numerous applications. These applications range from textile industry to power network design and maintenance [10]. Several superhydrophobic textiles have been designed to produce water-repellent self-cleaning fabrics [11–13]. In biomedical applications, superhydrophobic surfaces can be used in vessel replacements or wound management [14]. Since icephobicity (i.e. low adhesion force between ice and the substrate) shows a correlation with superhydrophobicity [15], superhydrophobic coatings can be used to reduce the ice accumulation on various structures, notably power network equipment [1, 4, 16–19]. Construction industry can also benefit from the development of superhydrophobic surfaces for manufacturing self-cleaning windshields and windows [4, 20–22]. In marine industry, superhydrophobic coatings can be used to develop anti-fouling surfaces for vessel bodies [23]. Finally, due to the minimized liquid/surface contact area, hydrophobic and superhydrophobic surfaces are able to be utilized as anti-corrosion surfaces [9, 24–26].

Many approaches and techniques can be utilized in order to generate superhydrophobic characteristics on various metallic and polymeric substrates. However, all these methods have their own advantages and disadvantages. Sol-gel reactions [27–29], electrochemical deposition [30–32], layer-by-layer deposition [33–36] and spin coating [37] have been used to fabricate superhydrophobic surfaces. One

of the most promising approaches to the development of superhydrophobic surfaces is plasma related techniques. Plasma surface treatment is gaining popularity in many applications and therefore, many studies have been done on the applications of various plasma-based techniques in generating superhydrophobic surfaces. In plasma processing, plasma parameters have a significant effect on the film properties and characteristics. Hence, to better design and fabricate a low surface energy coating with a micro/nano structured pattern, which is the defining characteristic of superhydrophobic surfaces, the effects of plasma parameters on the chemistry and morphology of the surface should be fully understood. Each category of plasma processing, which will be discussed shortly, contributes to the surface roughness and/or surface chemical composition. By modifying these properties by plasma processing, it is possible to design fast, economical and practical approaches to develop superhydrophobic coatings.

In this paper, at first a brief introduction of wetting behaviour, superhydrophobicity, plasma and plasma surface treatment will be presented. Then the development of superhydrophobic surfaces by means of plasma surface treatment methods are divided into three categories and each category is discussed independently. Finally, a brief conclusion will be presented.

2 Superhydrophobicity

The physical interaction between liquid droplets and solid surfaces has been a point of interest for many decades. According to Young, the contact angle of a liquid droplet on an ideally flat, rigid and homogeneous surface depends only on the surface energy in solid/liquid, solid/air and liquid/air interfaces (Equation 1) (Figure 2) [38]:

$$\cos\theta_c = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad (1)$$

In this equation, θ_c is the liquid contact angle and γ is the surface energy for which the subscript denotes the relative interface. As mentioned before, the above equation is only valid for ideally flat surfaces. It has been proven that by modifying the surface chemical composition of a flat surface, and thus reducing the surface energy, the maximum contact angle achievable is 120° [39]. However, the wettability behaviour of a surface depends on two

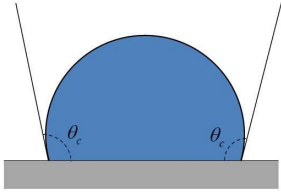


Figure 2: A liquid droplet on an ideal surface. The contact angles on both sides are equal (Young model)

factors: (i) surface energy and (ii) surface roughness [40]. To precisely predict the contact angle on a roughened surface, the effect of roughness on the solid/liquid interface should be taken into account. Many studies have tried to formulate a relationship between surface chemical energy, roughness and contact angle. However, two main models exist which are generally accepted throughout different studies: (a) Wenzel model and (b) Cassie-Baxter model. The *Wenzel model* predicts that the water penetrates the holes on the surface and therefore the contact area between water and solid surface increases with roughness. The surface condition for which the penetration occurs is called the *Wenzel regime* (Figure 3a). Wenzel predicts that the contact angle on a rough surface can be calculated through the Wenzel equation (Equation 2) [41]:

$$\cos\theta_W = r_s \cos\theta_c \quad (2)$$

In the above equation, θ_c is the equilibrium contact angle, θ_W is the Wenzel contact angle and r_s is the surface roughness. It is clear that according to Wenzel, roughness will cause the contact angle to increase only if the contact angle is higher than 90° . In other words, roughness in Wenzel regime increases the hydrophobicity in an already hydrophobic surface and increases the hydrophilicity in an already hydrophilic surface [9, 42].

However in many cases, due to an increased height-to-area aspect ratio in the roughness, liquid phase cannot penetrate the roughness cavities. In this state, air is trapped between the liquid and the solid and therefore a mixed-phase interface is formed [43]. The second model deals with the latter state and is called the *Cassie-Baxter model*. A mixed phase interface will increase the contact angle, regardless of the surface energy [9]. The Cassie-

Baxter model predicts the relationship between the surface roughness and contact angle through the Cassie-Baxter equation (Equation 3) [44]:

$$\cos\theta_{CB} = f_s \cos\theta_c - (1 - f_s) \quad (3)$$

In the above equation, θ_c is the equilibrium contact angle, θ_{CB} is the Cassie-Baxter contact angle and f_s is the fraction of the solid in contact with the liquid (Figure 3b).

Several studies were performed in order to identify the transition point between Wenzel and Cassie-Baxter regimes regarding the roughness dimensions. Theoretically, it has been shown that the dominant regime is always the one with the smaller contact angle [22, 45]. In other words, contact angle can be completely translated to Gibbs free energy. Patankar et al. showed that for some roughness geometries, an energy barrier has to be overcome for the transition to occur [46]. They further argued that the decrease in the gravitational potential energy, resulted from the gradual penetration of water into the surface gaps, can help to overcome this barrier. Xia et al. showed that the spacing between the roughness features (b) can determine the dominant wetting regime [45]. They used plasma etching with a photoresistive mask to fabricate 12 samples with different spacings, ranging from 5 to $60 \mu m$.

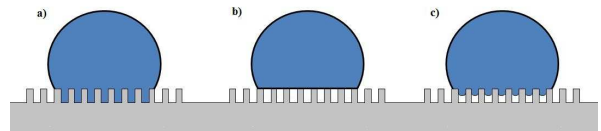


Figure 3: (a) Wenzel regime, liquid penetration in the roughness cavities is visible, (b) Cassie-Baxter regime, air is trapped between the liquid and the surface, forming a composite interface and thus reducing the adhesion forces and (c) Mixed regime, where the partial penetration of water occurs.

On the other hand, it has been showed that the dominant wetting regime is also depended on the size of the droplet used in contact angle measurement [45, 47]. Brown et al. studied the droplet behaviour upon impact on fluorinated superhydrophobic surfaces with different roughness scales from nano to micro structure [47]. They argued that for a droplet in microlitre size, the liq-

uid/substrate contact area is extremely larger than the surface features, and therefore the droplet impact behaviour is less affected by surface characteristics. When the size of the droplet decreases to the range of picolitres, contact area is only one order of magnitude larger than surface asperities, and therefore picolitre droplets exhibit completely different behavior on nano-roughness than on micro-roughness structures.

Finally, it should be noted that the Cassie-Baxter regime is a quasi-stable state and tends to gradually transform into Wenzel regime. However, the mechanism responsible for the penetration of liquid into the surface texture and therefore transition between two regimes is not yet fully understood [48, 49].

Complete Wenzel or Cassie-Baxter regime is rare in occurrence, and usually a mixed state is observed where water partially penetrates the holes in the roughness (Figure 3c) [50].

As mentioned before, the above equations can generally be utilized in various applications. However, some studies have cast doubts on the generality of Wenzel and Cassie-Baxter equations. It is proven that these models are only true when the drop size is infinitely bigger than the roughness sizes. Very small drops will become axisymmetric, even if the surface shows no sign of symmetry whatsoever [51]. Marmur et al. added an extra criterion for transition to the Cassie-Baxter regime in relation to Gibbs free energy. They indicated that even if the Cassie-Baxter equation is satisfied without this extra criterion, Wenzel regime will be dominant [22]. Brandon et al. also demonstrated that two dimensional models, like Wenzel and Cassie-Baxter, are not truly accurate. They proposed a simulation-based method, which is claimed to be more accurate than the current models [52]. However, most studies on hydrophobic surfaces assume that these models are accurate enough to estimate the surface wettability behaviour.

Besides static contact angle considerations, contact angle hysteresis (CAH) is another important criterion in studying the surface behaviour of various materials. Contact angle hysteresis is defined with regards to dynamic contact angles, i.e. contact angles related to moving liquid fronts (interfaces). For instance, when a droplet is moving on a surface, the contact angle in the movement direction is called the advancing contact angle and the con-

tact angle on the other side of the droplet is called the receding contact angle.

It is notable that some studies suggest that the concept of *static contact angle* should be reconsidered [53–57]. It is argued that every so-called static contact angle is in fact an advancing contact angle, and it should be treated as such. Others have claimed that although measurement of static contact angle is not easy, but by giving the droplet enough time to reach the state of global minimum energy, in some cases it is possible to observe the ‘equilibrium’ droplet [58]. Either way, most studies reviewed in this paper refer to the contact angle measured for a drop at rest on a surface as static, stationary or equilibrium contact angle.

Contact angle hysteresis is defined as the difference between two dynamic contact angles [43]. It is known that the droplets in Cassie-Baxter regime tend to have smaller contact angle hysteresis compared to droplets in Wenzel regime [43].

Contact angle hysteresis is an important factor in roll-off behaviour. Lower contact angle hysteresis usually means lower adhesion force between the droplet and the surface and easier sliding of the droplet on the surface [1]. Easy sliding of a liquid droplet on the surface has been proven to be an essential factor in many applications, notably self-cleaning surfaces and anti-icing applications [3]. In the roll-off phenomena, droplets will roll off the surface easily, absorbing dirt and external particles [59]. It has been even suggested that in order to accurately demonstrate the wettability behaviour, measuring the dynamic contact angles is essential. It has been argued that contact angle hysteresis is a significant tool to fully realize the surface topography and that instead of maximum contact angle achievable, CAH should be taken into account [60].

Generally, superhydrophobic surfaces are defined as any surface for which the water contact angle (WCA) is more than 150° [39, 61–63]. However, some studies add the criteria of low sliding angle or contact angle hysteresis to the definition [10, 14].

As mentioned before, two factors contribute to the superhydrophobicity of a surface: (i) surface roughness and (ii) surface chemical composition. Thus there are two approaches to generate the surface structures leading to superhydrophobic surfaces: (i) roughening an already low surface energy material or (ii) roughening a surface and then treating it with low surface energy coatings [14]. Poten-

tially, plasma processing is an ideal technique for both approaches. It can be relatively fast, economical and easily controlled, which makes it a suitable choice for industrial processes. One notable advantage is the fact that it can be used to change the surface chemistry while increasing the roughness, which makes it possible to fabricate superhydrophobic surfaces in a one-step processes. Therefore, it can be indicated that superhydrophobic surfaces can be developed by carefully controlling the plasma process and studying the effects of plasma parameters on surface characteristics. During the past few decades, many studies have been done involving both approaches which use plasma processing techniques for inducing roughness on a surface and/or deposition of low surface energy coatings.

3 Plasma Technology and Plasma Treatment

Generally, plasma is an ionized gas which can be considered as the fourth state of matter. It constitutes more than 99% of the universe. Macroscopically, plasma is electrically neutral. However it contains free charge carriers and is electrically conductive. To generate plasma, enough energy must be applied to a gas. This energy is usually provided by an electric source, which can be direct current (DC), radio frequency (RF), low frequency (LF) or microwave frequency (MW) [64, 65].

Plasma technology is an emerging field with astonishing potential applications. Thousands of research papers are published every year on plasma technology, revealing the vast possibilities offered by this relatively new field. In medicine, plasma treatment can be used for wound management, tumour treatment, tissue engineering, equipment sterilization and surgery equipment [66, 67]. By means of functionalization (i.e. grafting of the new functional groups on the treated surface, see 4.2), plasma technology also is being utilized to improve polymer surface properties by applying reactive gases plasmas (like O_2 , N_2 , NH_3 and H_2O) to the polymer surface [68]. It is also being used in electronics industry in a wide range of applications, from adhesion promotion and cleaning to fabrication of semiconductors [69]. Plasma reactions can also be used for plastic and nuclear waste disposal [70] and nitriding or carburizing of steels [71].

Plasma can exist at various gas pressures. The

gas pressure defines the LTEs (local thermodynamic equilibriums at the plasma) [65], and therefore can significantly affect the nature of the plasma. Low pressure plasma technology is widely industrialized and it is used in many applications, such as neon lamps and plasma screen TVs [64]. Other applications include deposition of metallic coatings with minimum impurity and metal matrix composite coatings [72]. However, low-pressure plasma imposes several technical difficulties, mainly related to the vacuum equipment [64]. To address these issues, another category of plasma has been introduced, which operates at atmospheric pressure. Atmospheric pressure plasma can be used for several applications, like surface modification, without the adversities induced by low pressures. Atmospheric pressure plasma reactors requires less energy and offers shorter process times compared to low-pressure plasma [64]. However, atmospheric pressure plasmas are usually harder to control because an unknown amount of air mixed with carrier and reactive gases. Furthermore, complex interactions can affect the efficiency of the treatment and hence the quality of the deposited layer [73].

As mentioned before, for the development of superhydrophobic surfaces, induction of the two characteristics, low-surface energy chemistry and morphological roughness, is essential. Plasma technology for enhancement of superhydrophobic characteristics is of great interest, because plasma processing can be used in generation of both characteristics. This technology can be used to deposit coatings (by means of plasma polymerization or plasma sputtering), increase the roughness (by means of plasma etching) and increase the amount of hydrophobic functions on the surface (by means of functionalization). In this paper, plasma surface modification is divided into three categories: (1) plasma etching, (2) plasma polymerization and (3) plasma sputtering. Plasma etching is mainly used to generate roughness on the surface, though it may change surface chemistry to some extent. On the other hand, plasma polymerization and plasma sputtering are generally used to develop thin films from low surface energy materials, but they may also increase surface roughness.

4 Plasma Etching

As mentioned before, roughness is an essential characteristic of superhydrophobic surfaces. Plasma etching is the process of selective removal of materials from a surface by reactive plasma radicals. Certain plasma particles react with certain atoms [74] or certain phases [61] on the surface and reaction products are ejected off the surface as gaseous compounds. For example, oxygen plasma is mainly used in etching of organic materials, where oxygen reacts with carbon and hydrogen and produces gaseous carbon dioxide, carbon monoxide and water [74].

Generally, in etching processes, a photo-resistant mask can be used to protect parts of the surface from exposure to the etching medium [74]. In conventional or wet etching methods, various chemical reactions are utilized to selectively remove the materials exposed to the solvent. However, wet etching has many disadvantages compared to the plasma etching approaches. Unlike plasma etching, wet etching techniques can be problematic for small film thickness, and they can also pose some environmental threats [65, 74]. Plasma etching on the other hand, is a dry and precise technique without the serious limitations of conventional etching methods [74].

Plasma etching is based on selective erosion, rather than homogeneous erosion which leads to significantly lower roughness. Usually one phase or compound reacts more readily with plasma gas and therefore, etching rate is different at various locations on the surface [74]. It has been suggested that other nano structures can be used as an equivalent to the photo-resist mask in order to further enhance the roughness. For example, polystyrene (PS) beads have been deposited by different chemical techniques on glass substrates [75, 76]. Oxygen erodes one phase more readily, in this case the glass layer on the bottom, therefore an increase in roughness can be observed compared to the case without the PS layer.

A wide variety of gases can be used in plasma etching technique. However, some gases, like O_2 , Ar and CF_4 have proven to be more suitable in development of micro-nano structured roughness on various substrates. In development of superhydrophobic surfaces, CF_4 is of specific interest, since it has been shown that plasma etching with

CF_4 can simultaneously fluoridate and roughen the surface. [77–79].

Generally, etching is used to induce nano/micro sized roughness on various substrates to generate superhydrophobicity. However, there are two approaches available for different materials. Etching can be used as pretreatment before coating the surface with low surface energy material [21, 61, 62, 80] or it can be used to generate roughness on a low surface energy material [59, 81].

4.1 Etching as a Pretreatment Process

The most common application of plasma etching in development of superhydrophobic surfaces is to generate a micro/nano scale roughness on the surface. As mentioned before, this roughness along with a chemical modification can enhance the surface's hydrophobic characteristics. In other words, two subsequent stages are performed (etching and coating) to induce two general characteristics of a superhydrophobic surface (roughness and low surface energy, respectively). Several studies utilized plasma etching to induce roughness on a substrate prior to subsequent coating with low surface energy materials, e.g. fluorocarbons and organosilicons. It can be expected that plasma etching as a pretreatment can result in significantly higher contact angles. The most common gas used in plasma pretreatment of organic materials is oxygen. Substrates such as polycarbonate, poly(ethylene terephthalate), cellulose paper, polyurethane and poly(propylene) have been used with oxygen plasma pretreatment. Other studies have investigated the effects of fluorocarbonic gases (e.g. CF_4 and SF_6) in plasma pretreatment on a different class of substrates, such as polished silicon and glass, but the deposition of fluorocarbon groups along with etching cannot be overlooked and therefore the process is a mixture of etching and functionalization. This phenomena will be further discussed in section 4.2. In order to better control the process, the effect of plasma parameters on the morphology, chemical composition and wetting behaviour of the surface must be fully understood. Many studies have investigated such correlations, about which a review is presented in this section.

Effect of Plasma Power and Treatment Time
It has been shown that increasing the plasma power and treatment time in plasma etching can improve

the hydrophobic behaviour up to a point, but a critical power [21, 82] and a critical treatment time [21, 80, 82, 83] exists beyond which superhydrophobicity diminishes. This threshold denotes the point where roughness units (the units consisting the roughened structure, which are named variously, such as nano fibrils, nano columns, etc.) become unstable and tend to collapse and/or agglomerate to form larger units. Larger roughness units may decrease the overall roughness (Figure 4), hence decrease the superhydrophobic characteristics. On the other hand, based on drop impact experiments, it has been suggested that larger units can also increase the mechanical stability of the coatings [83]. However, performing more mechanical tests seems to be necessary in order to reach a final conclusion.

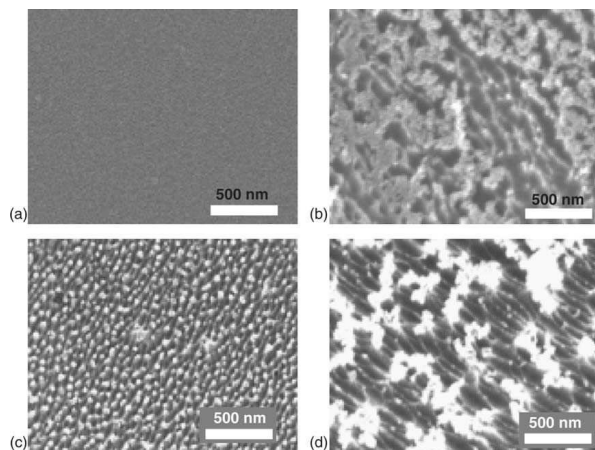


Figure 4: SEM images of the PET surfaces treated with oxygen plasma at various powers: (a) untreated, (b) 50 W, (c) 100 W and (d) 200 W. Treatment time is 10 minutes for all samples [84].

Effect of Gas Pressure Gas pressure also has a significant effect on oxygen plasma etching. It has been argued that by increasing the pressure, the collisions between plasma particles increases, so that less particles with enough energy will be able to reach the surface, resulting in reduced roughness [82].

4.2 Etching as a Treatment Process

Etching can be used as a stand-alone treatment to develop roughness on low-surface-energy materials and therefore to generate superhydrophobic coatings. Several studies have investigated

the effect of plasma etching on the generation of micro/nano structured roughness on various hydrophobic materials, specifically PTFE [77, 85–87]. In the case of PTFE, oxygen has proven to be significantly useful to enhance the hydrophobicity of PTFE substrates. It has been shown that oxygen uptake on the PTFE surface is almost non-existent even after 3 hours of plasma treatment, and thus the amount of polar oxide hydrophilic groups deposited by oxygen plasma etching is negligible [77, 86, 87].

Many parameters can affect the roughness and morphology on the surface. In this section, a review of such studies is presented.

Effect of Plasma Gas Plasma gas used in a plasma etching process can significantly affect the wetting behaviour [77]. One of the most efficient gases is oxygen. Other common plasma gases, like argon or nitrogen, have proved to be ineffective at best in etching of PTFE [85, 87]. In case of nitrogen gas, the deposition of nitrogen groups on the surface will even increase the surface energy [87]. However, adding oxygen to the mixture was shown to increase roughness, and thus increase hydrophobicity (Figure 5) [85]. The amount of oxygen grafting also appears to be minimal in the case of oxygen plasma etching [87], so that no undesired oxygen grafting is observed.

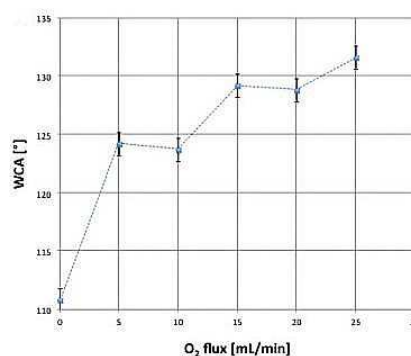


Figure 5: The effect of O_2 flux in Ar/O_2 mixture on contact angle of PTFE. Increasing the O_2 flux will enhance the hydrophobic behaviour of PTFE [85].

Effect of Plasma Power Plasma power is another parameter to be considered. Low plasma powers results in the sole activation of the surface, and therefore have proved to be ineffective

in plasma etching [86]. Increasing the power usually leads to higher amounts of erosion, which will subsequently increase the roughness (Figure 6) [81, 86, 88, 89]. However some results are inconsistent as concerns coating chemical composition. Some studies suggest that coating chemical composition only depends on the composition of the etching gas, and that both treatment time and plasma power are irrelevant as to the coating composition [81].

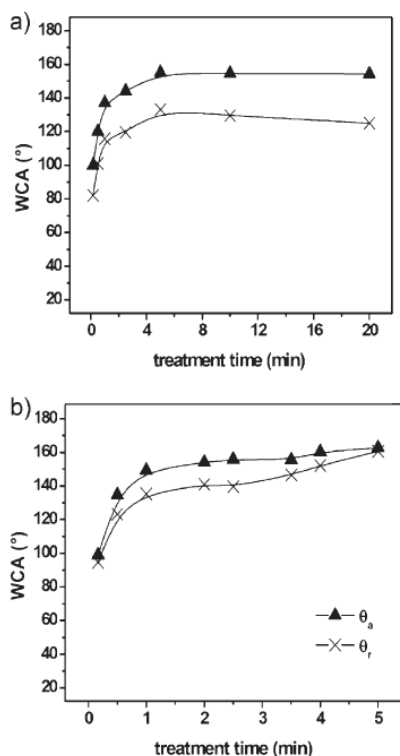


Figure 6: Advancing (θ_a) and receding (θ_r) WCA values of the PS samples treated with a CF_4/O_2 fed discharge with 17% O_2 as a function of treatment time at (a) 150W and (b) 300W [81].

Functionalization Besides the plasma etching technique on low surface energy materials, some plasma gases, mainly CF_4 can be used for simultaneous etching and fluorination of the surface. In this case, fluorinated groups deposited on the surface can further decrease the surface energy. Chemically modifying the surface by some functions with a specific application is called function-

alization [90, 91]. Technically, it is different from polymerization in the fact that it involves covalently binding plasma species to the surface, rather than coating a surface [92]. CF_4 is considered an etching gas and it does not readily polymerize on the surface [76, 80, 81]. However, samples etched with CF_4 exhibit a significant amount of fluorocarbonic groups along with high roughness [77, 89, 93]. It was also shown that fluorinated samples can be cross-linked by UV exposure or annealing [93, 94]. Cross-linked samples exhibit improved mechanical durability without any significant change in surface morphology. In the case of UV exposure, it was shown that by using a photolithographic mask, the exposed areas will be of lower height and therefore form a micro-pattern which in turn can further increase the water contact angle [94].

Due to the simultaneous roughening and functionalizing effect of CF_4 , it has proved to be more efficient in developing superhydrophobic surfaces than SF_6 , Ar , N_2 and O_2 [77–79]. Its advantage is not always due to the higher extent of roughness, but rather to the resulting lower surface energies. In fact, it has been shown that O_2 will generate slightly higher roughness on the PTFE samples in the same time (Figure 7), but lower contact angles will be achieved due to the lack of fluorine functionalization [77]. Many studies have also investigated the effect of adding CF_4 to oxygen or other common plasma gases [12, 79, 81]. For example, it has been shown that for polystyrene samples, 17% of oxygen will result in the highest extent of fluorination and texturing [81]. Although this paper, like several other studies, consider CF_4 as an etching agent, it should be noted that it can cause more effects than just erosion.

5 Plasma Polymerization

Plasma treatment can be utilized to deposit thin films on various substrates. The process, which is usually called plasma polymerization, is referred to the deposition of polymer films through dissociation and excitation of a monomer gas in plasma and subsequent deposition and polymerization of the excited species on the surface of a substrate [65]. In comparison to conventional surface treatment methods, plasma polymerization can be a very advantageous approach. Indeed, it is capable of forming ultra-thin films with suitable mechanical properties [95, 96], it requires lower tempera-

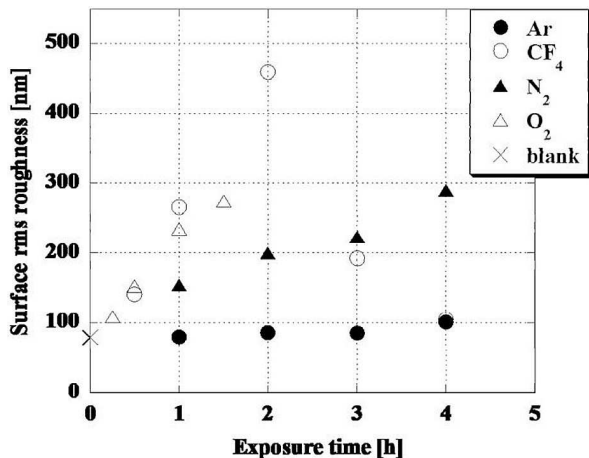


Figure 7: Effect of etching gas on contact angle. Note that etching time for oxygen is 1.5 hours and for other gases is 4 hours [77]. The highest contact angle is achieved for CF_4 after 2 hours of exposure, which can be explained by simultaneous etching and fluorination of PTFE substrate. The roughness measurement is performed by atomic force microscopy.

tures [65], can be used for monomers that do not polymerize under normal conditions [97, 98] and is environmentally friendly [12, 95].

As mentioned before in Section 3, plasma polymerization can be divided into two general categories: (1) low pressure (pressures less than atmospheric pressure) and (2) atmospheric pressure. Low pressure plasma polymerization tends to generate more homogeneous films with less impurities. It is also considered to be a green process due to significantly less amount of process gases involved [99]. On the other hand, atmospheric pressure plasma polymerization can be advantageous due to its lower energy consumption, shorter processing times, lack of need for vacuum equipment and considerably higher growth rates [100–102].

Pulsed plasmas or modulated glow discharges are used frequently in plasma polymerization applications. In a modulated glow discharge, plasma is turned on for a small fraction of the total cycle t_{total} . In the t_{off} period, enough time is given for the polymerization process. The ratio between t_{on}/t_{total} is called duty cycle, and is often abbreviated as DC. It has been shown that a pulsed plasma can lead to unique morphologies or enhance the su-

perhydrophobic behaviour [62, 103, 104]. For example, in plasma polymerization of 1H,1H,2H,2H-perfluorooctyl acrylate (PFAC), deposited layers in pulsed and continuous deposition are very similar in chemical composition. However, morphology is significantly different, leading to much higher WCA and much lower CAH values in the case of pulsed plasma polymerization (Table 1). Moreover, in pulsed plasma polymerization, duty cycle should be considered as an extra control parameter which can significantly affect the surface characteristics [62, 104].

Several materials can be used in plasma polymerization, such as oxides, nitrides, and oxynitrides of silicon, crystalline materials such as polycrystalline silicon, epitaxial silicon, and refractory metals and their silicides. These materials play a crucial role in development of microelectronics [105]. However, in superhydrophobic applications, it is essential to consider materials with low surface energy. For improvement of hydrophobic behaviour, some specific materials are suitable due to their low surface energy, such as fluorocarbons and organosilicons [14]. But it should be noted that not all the materials in the mentioned categories can be utilized in plasma polymerization. Several studies have been carried out on the development of superhydrophobic fluorocarbon surfaces which are discussed in Section 5.1. Organosilicon-based superhydrophobic surfaces are also discussed in Section 5.2. Furthermore, a few studies have investigated the development of plasma polymerized superhydrophobic surfaces with other precursors, such as $TiCl_4$, CH_4 or acetylene. These studies are reviewed in Section 5.3.

5.1 Fluorocarbonic Monomers

Fluorocarbon polymers are well known for their low surface energy attributed to CF_2 and CF_3 groups. Hare et al. showed that the surface energy of hydro/fluoro carbon groups decreases in the following manner [106]:

$$-CH_2 > -CH_3 > -CF_2 > -CF_3$$

It has also been shown that increased fluorine content in a plasma polymerized coating leads to higher contact angles [107]. Thus, fluorocarbons are among the most common choices for development of superhydrophobic surfaces [108].

Generally a fluorocarbon-based coating consists of CF_x groups. For depositing CF_x groups on a

Table 1: Comparison between pulsed plasma polymerization and continuous plasma polymerization 1H,1H,2H,2H-perfluorooctyl acrylate as precursor. Significant improvement in contact angle and contact angle hysteresis is observed [103].

deposition mode	off time	advancing	receding
Pulsed (5×1 min)	2 min	$168^\circ \pm 0.8^\circ$	$165^\circ \pm 1.2^\circ$
Continuous (1×5 min)	-	$145^\circ \pm 1.2^\circ$	$47^\circ \pm 1.5^\circ$

surface, C_2F_4 or C_4F_8 gases are usually used as the plasma gas. CF_4 is another fluorocarbon gas which is usually used along with O_2 for etching purposes. However it can lead to simultaneous functionalization with CF_x groups which in turn can enhance superhydrophobicity (see section 4.2).

PTFE (polytetrafluoroethylene) is a fluoropolymer which is also known commercially as TeflonTM. It has been widely used as a hydrophobic and low friction surface. However, due to its solid state in room temperature, PTFE is not generally considered as an appropriate choice for plasma polymerization. Therefore, PTFE coatings are often generated by sputtering or other suitable techniques. However, some efforts have been made by application of high evaporation temperatures [109] or using tetrafluoroethylene (TFE) as a precursor [62] to achieve plasma polymerized coatings close to PTFE. In fact, thin films achieved by these methods usually show a great resemblance to PTFE as to chemical composition.

Effect of Plasma Power As mentioned before, plasma polymerization is based on disintegration of plasma species and polymerization on the surface. It is clear that in higher plasma powers, the extent of energy applied on the plasma gas is increased, and therefore higher amounts of molecular fragmentation can be expected. Therefore, in studies reviewed in this paper, the amount of CF_x species decreases as the power increases [80,110,111]. However, since plasma power can also affect the surface roughness to some extent, this does not necessarily mean that by increasing the power, hydrophobicity diminishes. In fact, some studies report an increase in contact angle due to increasing roughness with increasing the plasma power, although the amount of hydrophobic organic groups on the surface decreases [110].

Effect of Monomer Partial Pressure Monomer pressure can have a significant ef-

fect on the film composition too. This correlation is mainly due to the lower monomer fragmentation at higher pressures [112].

Effect of Deposition Time Treatment time is another effective parameter which has to be considered. It has been suggested that treatment time will only increase the film thickness. Thus after a point where complete coverage occurs, treatment time should not have any effect on wetting behaviour [113]. However, another study shows that film composition is also dependent on the treatment time. It was shown that for longer treatment times, the amount of fluorocarbon groups increases on the surface [114].

5.2 Organosilicon Monomers

Besides the significantly low surface energy in fluoropolymers, some disadvantages, mainly of environmental nature, can limit the potential applications of such precursors [115,116]. Due to these issues, other precursors have been considered for superhydrophobic applications. Although the surface energy of CH_3 and CH_2 groups, to which the hydrophobicity of organosilicons is attributed, is not as low as that of fluorine-based groups [117], organosilicon based polymers are considered as an environmentally friendly alternative to fluorine-based polymers for hydrophobicity applications [118]. Organosilicon monomers can be a generally suitable choice for further studies due to their usual liquid state, volatility, safe handling, availability and low cost [119]. As a polymerized coating, they also show good optical and mechanical properties [97]. Some studies have even reported an increase in roughness after polymerization with organosilicons (Figure 8) [84]. Various precursors can be used as monomer in plasma polymerization of silicon-based coatings [14, 40, 100, 102, 118–122]. However, the most promising results have emerged from an organosilicon called Hexamethyldisiloxane ($O[Si(CH_3)_3]_2$, abbreviated as HMDSO).

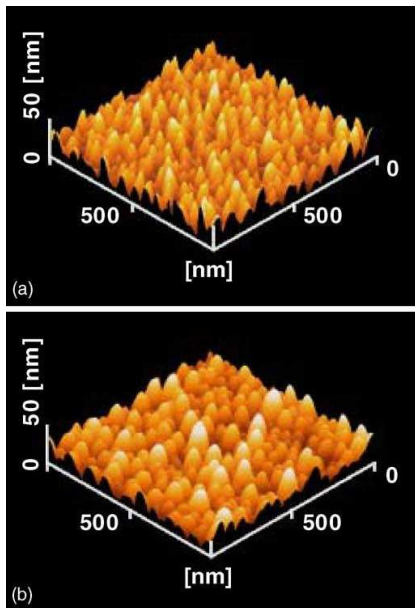


Figure 8: AFM images of PET samples (a) before plasma polymerization (after oxygen plasma etching) and (b) after the deposition of TMS [84].

Effect of Oxygen Presence The chemical composition of plasma polymerized organosilicon based thin films is greatly affected by the percentage of oxygen in the feed gas. Several studies have shown that to preserve the amount of hydrophobic organic groups (i.e. $Si-C$ bonds) on the surface, oxygen percentage should be as low as possible [21, 123, 124]. The presence of oxygen in the feed gas results in abundance of polar and hydrophilic SiO_x groups on the surface, which can render the surface more hydrophilic. Furthermore, oxygen in the plasma can react with the deposited carbon and decrease the amount of organic groups [123]. In other words, organosilicon based monomers and specifically HMDSO are suitable choices for the deposition of superhydrophobic coatings only if the percentage of oxygen in the plasma is carefully controlled.

Effect of Monomer Ratio to Overall Feed Gas The amount of organosilicon-based monomer is of great importance in plasma polymerization. It has been suggested that up to a critical amount, a higher percentage of monomer in the feed gas will lead to higher contact angles [125]. This can be due to an increase of organic groups

in the plasma with increasing monomer percentage [126]. In this case however, plasma power plays an important role. It was argued that a critical monomer percentage exists, below which the influence of concentration is dominant on the surface morphology and chemical composition [126]. If the concentration is increased above this amount, plasma power will become the controlling parameter.

Effect of Plasma Power The effect of plasma power in the plasma polymerization of organosilicons is rather similar to that of fluorocarbons. Higher plasma power will increase the degree of fragmentation in the plasma gas and therefore less organic groups will be deposited on the surface [126, 127].

Effect of Deposition Time Treatment time can have a significant influence on the chemical composition of plasma polymerized film. It was shown that the amount of $Si-(CH_3)_2$ on the surface increases with longer treatment times, thus the surface energy is reduced and superhydrophobic behaviour is enhanced [118].

5.3 Other Precursors

Although studies on plasma polymerization for superhydrophobic surfaces are mainly focused on the fluorocarbons or organosilicons, some works have considered the use of other precursors to generate water repellent surfaces. These precursors can be used with more conventional precursors as improving agents, or they can be used as the sole precursor.

HMDSO is an ideal precursor for superhydrophobic applications for several reasons. However, compared to more conventional fluorocarbons, higher surface energy of HMDSO results in weaker wetting properties. Several studies have been done to address such issues. Toluene was investigated as an improving agent for organosilicon based coatings [122, 128]. Different Toluene/HMDSO ratios have been studied and in one study, the optimized percentage of Toluene in HMDSO was determined to be 25% [128].

Hydrocarbon groups, and specially methyl groups, are responsible for the superhydrophobic behaviour of some coatings. Hence, one might expect that hydrocarbon gases themselves can be used in plasma polymerization processes to develop hydrophobic and superhydrophobic surfaces.

Indeed, several hydrocarbon gases, like methane [129–131], acetylene [132, 133] and propane [133], have been used to develop hydrophobic thin films. Some studies have investigated the addition of fluorocarbons [130, 133], and as it can be expected fluorine-based groups deposited on the surface can enhance the hydrophobic behaviour even further.

The effect of plasma parameters on the properties of polymerized films is similar to the case of organosilicons and fluorocarbons [132]. Except in the case of hydrocarbons, saturation is easily reached, which means that increasing the pressure improves the superhydrophobic characteristics up to a point [132]. Beyond that threshold, no significant change can be observed as to hydrophobicity.

At this stage, an exceptional point should be made for the case of TiO_2 . The development of superhydrophobic TiO_2 surfaces with atmospheric pressure plasma jet has been reported [134]. A mixture of oxygen, $TiCl_4$ and argon as carrier gas was used to generate a unique structure of titanium dioxide on the surface (Figure 9).

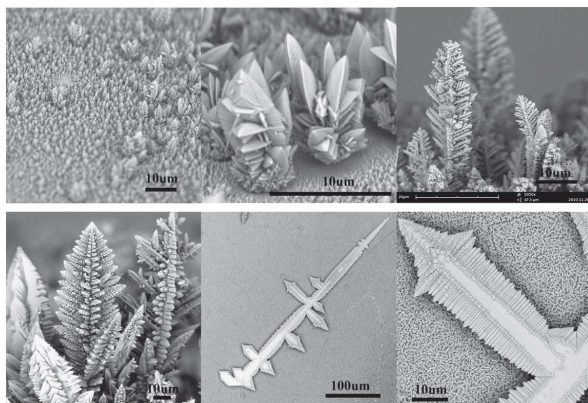


Figure 9: SEM image of TiO_2 nano-crystals developed by atmospheric pressure plasma jet. SEM images are shown in various magnifications [134]

Generally metallic oxides are considered to be of high surface energy and thus hydrophilic. Several studies have reported the generation of superhydrophobic surfaces based on titanium dioxide [29, 135–137]. This phenomena is usually attributed to the physical structure of titanium dioxide, which can be altered by changing the manufacturing process and/or UV light exposure [136, 137]. Similar studies have been done on ZnO based su-

perhydrophobic surfaces and it was shown that the high degree of roughness generated by the deposition of metallic nano-structures on the surface can lead to a superhydrophobic surface, regardless of the surface chemistry [138–140].

6 Sputtering

Sputtering is another method for plasma surface treatment. In plasma sputtering, the coating material (target) and substrate are placed as cathode and anode in a plasma reactor, respectively. A feed gas (e.g. argon) is injected between the electrodes and a voltage in the range of 100 V to several kV is applied [71]. Positively charged ions from the plasma strike negatively charged particles with high energy, thus disintegrating atoms or molecules from the cathode surface. Ejected atoms then settle on the surface of the substrate, forming a thin film from the target material [71]. Compared to conventional coating techniques, sputtering is a simple, environmentally friendly and time saving process which results in more adhesive films [141]. It is also not limited by the melting point of the coating materials [71] and is capable of forming multicomponent thin films (e.g. alloys) on various substrate [74].

Few studies have been done on the development of one-step methods for fabricating superhydrophobic surfaces. However, it should be noted that some studies have investigated the effect of pre-roughening of samples in plasma sputtering process. For example, *bohemitage* or *anodization* of aluminium samples results in micro-nano roughness on the surface [18, 39]. Just like polymerization, pre-roughening of the samples have been proven to be an efficient approach in the development of superhydrophobic surfaces.

6.1 Sputtering of PTFE and other fluorocarbon-based materials

Polytetrafluoroethylene (PTFE) is one of the most common materials in sputtering technology. Many studies have been done on the deposition of PTFE on various substrates by plasma sputtering. In the case of PTFE, plasma sputtering is of significant interest because tetrafluoroethylene does not exhibit some essential properties required in other deposition methods. It does not dissolve readily in any solvent and its vaporization temperature is more than 400°C [39]. Therefore sputtering is one of the few methods available for the develop-

ment of PTFE thin films. Furthermore, it has been proved that compared to plasma functionalization by CF_4 and H_2 , sputtering of PTFE will cause an increased deposition of some hydrophobic groups, like CF_3 and CF (Figure 10) [142]. It should be noted that this study [142] refers to the deposition of CF_2 groups by means of CF_4/H_2 glow discharge as 'polymerization', but the film thickness is reported to be about 5 nm, which indicates that the process occurring is rather functionalization than plasma polymerization.

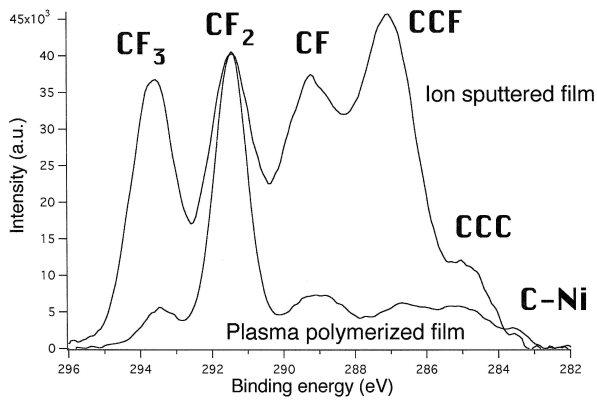


Figure 10: A comparison of the two as-deposited XPS results for functionalization and sputtering of PTFE-like thin films. The XPS spectra are normalized to the CF_2 peak. The higher CF_2 content of the plasma polymerized film indicates the presence of long linear chains, similar to that of pure PTFE. Sputtering tends to deposit a more chemically heterogeneous film [142].

Effect of Sputtering Gas Several studies have investigated the effect of different sputtering gases on surface composition and morphology. Argon is the most common gas used in plasma sputtering [143–146]. Other inert gases like neon and helium can be utilized to minimize the deposition of undesired groups on the surface [143, 145]. It was shown that in the case of inert gases, the content of fluorine increases as the atomic mass of the inert gas increases [145]. Using nitrogen was shown to lead to the deposition of nitrogen-based groups, like $C-N-F$ and $C-N$ [144]. Interestingly, using hydrogen in plasma sputtering does not result in any deposition whatsoever [145].

Effect of Pressure It has been discussed that increasing the pressure of plasma gas will lead to higher roughness and an increased deposition of $-CF_2$ groups [146–148]. The significant effect of pressure on sample roughness can be used to design unique processes to improve the superhydrophobic behaviour of various surfaces. For example, using two different pressures subsequently, two different levels of roughness were achieved [28], resulting in a hierarchical structure which is a well-known reason for superhydrophobicity in many natural examples (see Section 1). However, increasing pressure can decrease the mean energy of ions, and subsequently reduce the growth rate [148].

Effect of Target-Substrate Distance It was shown that the influence of target-substrate distance on superhydrophobic behaviour is dependent on gas pressure. At higher pressures, increasing the target-substrate distance can increase the surface roughness, while at lower pressures, target-substrate distance does not have a significant effect on wetting characteristics [146].

6.2 Other Sputtering Targets

Although conventionally PTFE was used in many sputtering studies, few studies have been done on other materials as sputtering target [42, 149].

In this case, the basics of plasma sputtering are generally similar to the processes mentioned before. However some details may be changed according to specific cases. For example, in case of copper, plasma power was shown to alter the film purity and roughness size (Figure 11). Therefore it was suggested that higher plasma powers should be utilized to decrease the extent of Cu_2O and obtain a purer copper coating, as well as to achieve a suitable roughness scale [149].

Finally, a point should be made on one specific study with a two-step method to generate hybrid superhydrophobic surfaces. A structure of cadmium/cadmium oxide was generated by plasma sputtering of cadmium and subsequent thermal oxidation [42]. Significantly high roughness observed in these samples ($R_{rms} = 50$ nm) is thought to be responsible for their highly superhydrophobic behaviour.

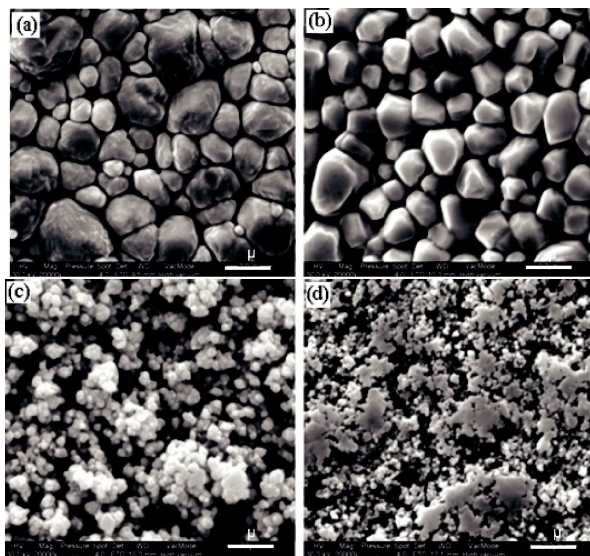


Figure 11: SEM images of films deposited by copper sputtering for (a) 400 W, (b) 300 W, (c) 200 W and (d) 100 W. The reduction in copper nano crystals dimensions is observed [149].

7 Conclusion

Superhydrophobic surfaces, once inspired by nature, are gaining a lot of interest due to their extensive range of possible applications. These potential applications, ranging from biotechnology to construction, and from power network maintenance to textile industry, motivate many researchers to investigate various approaches and techniques to develop superhydrophobic surfaces. Among these, plasma based techniques seem to be very promising. By carefully optimizing and adjusting the process parameters, plasma surface treatment can be an environmentally friendly, cheap, easy and fast method to develop cross-linked and mechanically stable superhydrophobic surfaces. During the past few years, many studies have been carried out on the development of superhydrophobic surfaces using plasma etching, plasma polymerization and plasma sputtering. Understanding the effective parameters involved with plasma treatment can lead to a better control on the surface morphology and chemistry. Many studies have aimed at optimizing these parameters in order to develop easier and cheaper methods to produce superhydrophobic surfaces with better quality and stability. These re-

cent rapid progresses in both plasma technology and surface engineering offer a promising future for this new and advancing field of science.

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