Fabrication of Super-Hydorphobic Surfaces via Two-Step Chemical Etching and Plasma Deposition Technique

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Abstract:

Superhydrophobic(SHP) surfaces have various types of application. They are being created by the nature to solve problems such as plant leaves and butterfly wings contacting with water drops. In such cases, they prevent water to stick on surfaces that should be kept dry and/or clean. Nowadays, human being is also trying to solve similar problems dealing with surfaces that should be free of liquids such as oil and water via fabrication of synthetic superhydrophobic or superoleophobic surfaces. Super-hydrophobic surfaces are those who are considered to have a contact angle with water more than 150°. It has experimentally approved that a smooth surface made by an intrinsically hydrophobic matter cannot have a contact angle more than 108°. However, based on cassie-baxter rule, a roughened hydrophobic surface demonstrated higher contact angles than a smooth one. In present study, Super-Hydrophobic (SHP) surfaces were fabricated using two-step chemical etching followed by Magnetron Sputtering Deposition (MSD) technique. Straight aluminum plates were treated and their surface were chemically corroded by conventional strong acids under well tailored conditions. The resulted surfaces were fully roughened. In the following step, a super thin film of Polytetrafluoroethylene (PTFE) was been deposited by MSD technique. Contact angle measurements of the resulting SHP surfaces were up to 160°.

Introduction:

Hydrophobic surfaces have several benefits. A well known hydrophobic surface that is also considered as the symbol of cleanliness is “Lotus Leaf” [1]. Its hydrophobicity is well tailored so that when a drop of rain for example falls on it, the drop not even does not stick, but also while rolling off the leaf, absorbs dust particles left on it leaving the Lotus Leave always clean (Fig. 1).

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Fig. 1, Lotus Leaf and its famos hydrophobicity[1].

Another natural example of applications of hydrophobicity is insects walking on water [2]. Their feet are covered with microscopic hair and every single hair has a nano-structured texture. These hairs make the insect always dry (Fig. 2). Not becoming wet by water means that the insect is free from surface tension of the water.

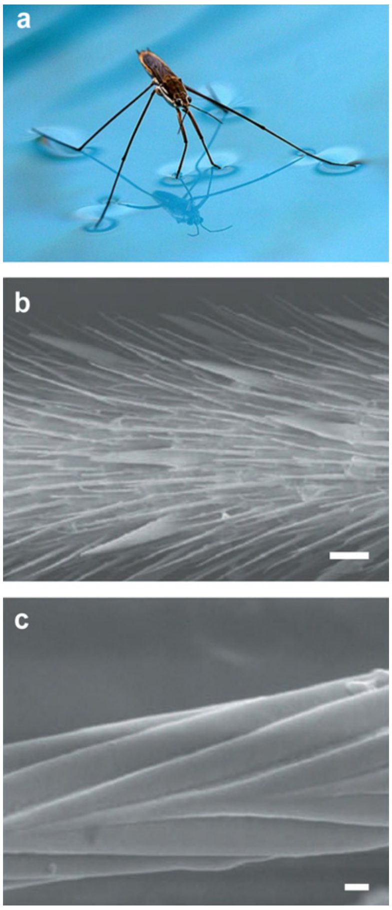

Fig. 2, a) Insect that is not being immerged in water. b) Micro-hairs that cover its whole body especially its feet. c) A single Nano-structured hair surface [2].

A newly developed application of superhydrophobic (SHP) surfaces is in corrosion science [3]. Based on well established theories of corrosion of metals, a principal step in solving a metallic object in aqueous solution is that the metallic cation enters into the water. But if the surface of the object be treated to become hydrophobic, this means that there is a gap between solution and metallic surface. This gap simply reduces the solving rate of metallic cations (Fig. 3).

Another application that has found technical interest is reduction of drag force in fluid mechanics [4]. As a bottom line, when a subject moves inside the fluid or a fluid flows inside a duct, drag forces appear in the liquid-solid interface since the fluid tends to stick to solid. Consequently, more energy or driving force should be demanded to make the fluid pass through the duct or object travel into the fluid as well. But if the wetability of solid be reduced, less force would be needed to fluid and solid move with respect to each other (Fig. 4).

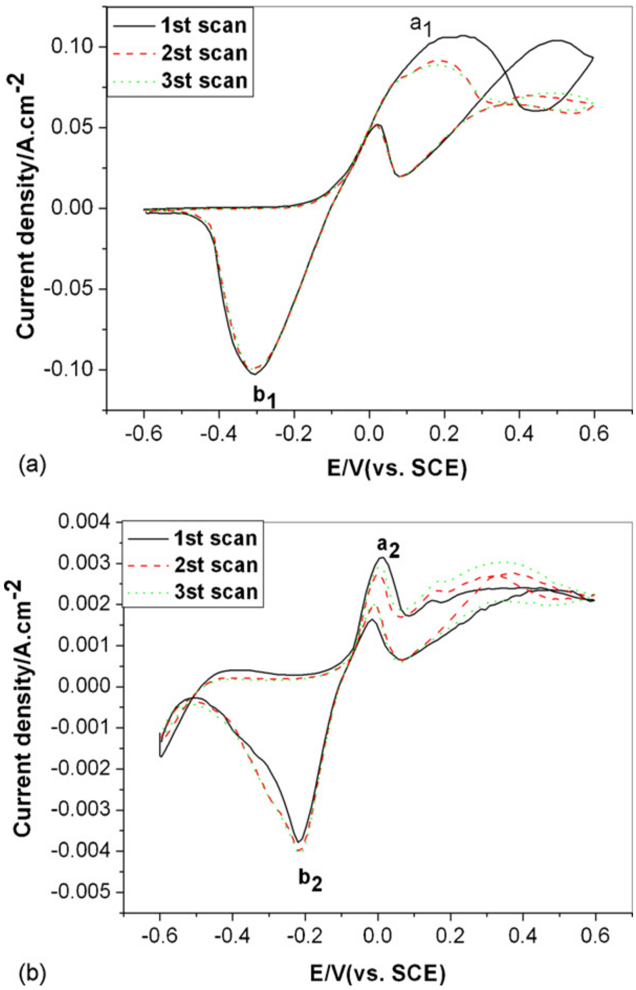

Fig. 3, Corrosion prevention by applying SHP surface on a copper plate. a) corrosion rate in normal conditions, b) corrosion rate while SHP treatment was applied. The results show reduction of corrosion rate up to ten times[3].

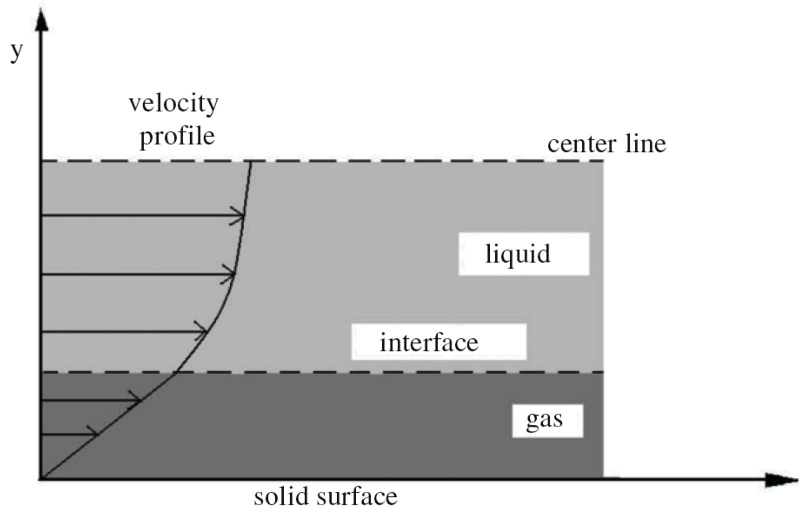

Fig. 4, Velocity profile in an ideal super-hydrophobic surface in a duct[4].

Another desirable property of a super-hydrophobic surface is its potentially ice-phobic behavior[5]. Ice accretion on external surfaces of aircrafts as well as their sensors can make them malfunction and cause several performance problems. A recently approach to combat ice accretion in aviation is application of super-hydrophobic surfaces. A recent study featured that covering wing edges of aircrafts with super-hydrophobic coating can remarkably reduce the quantity of ice formed[6] (Fig. 5).

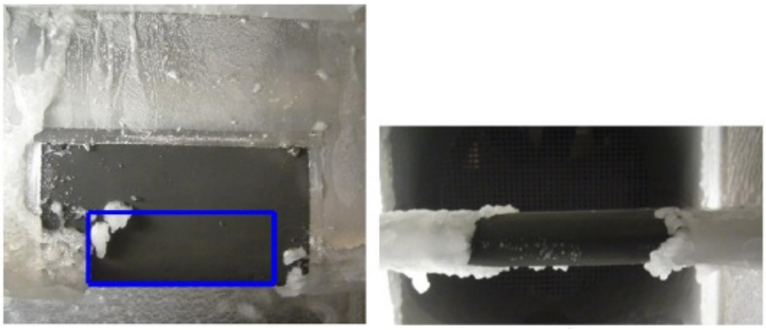

Fig. 5, resistance of a super-hydrophobic surface in cryogenic conditions against ice build-up on aircraft wing [6].

There are two measurement methods in order to analyze wetting behavior of surfaces [7]. The first called “wetting” angle is more common. The second is more used in dynamic application where fluid tends to move upon the surface. It is called “hysteresis” angle which is obtained by subtraction of receding and advanced angle of a moving drop (Fig. 5).The objective is to get a surface with maximum contact or wetting angle and minimum hysteresis angle. It is interesting to note that, hydrophobic surfaces made of low surface energy (e.g. fluorinated) materials may have water contact angles as high as 120°. But it is kind of impossible to enhance this number just by changing the surface material itself. The reason might be the presence of Wander Walls forces that always are present.

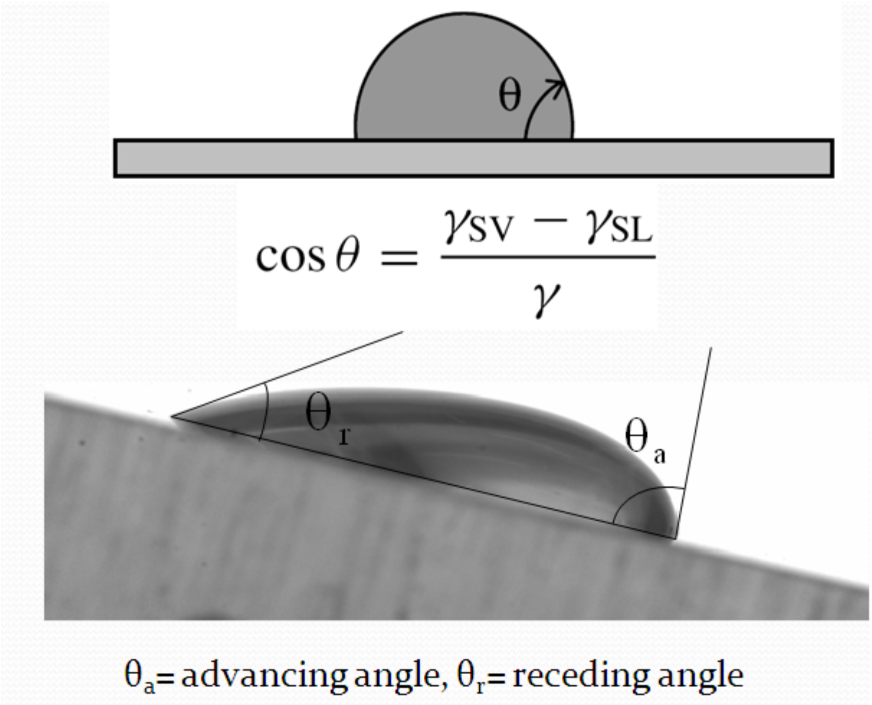

Fig. 6, Different types of analyzing the wettability of surfaces[7].

During study of natural super-hydrophobic surfaces it has been observed that they do not have an even surface [8]. Lots of them have an uneven surface with micro structured roughness. This technique makes the surface enable to hold air pockets between this rough structure and liquid drop. As the most hydrophobic material would be air, these captured pockets of air are like a bed for water drop resulting in lesser wettability of the whole surface. However the uppermost points of surface are still in contact with the water drop which can limit the wetting angle. To overcome this challenge, there are nano-structured roughness which covers the whole microstructured surface so that even upper point would not have direct contact angle with drop [9]. This is the ultimate concept that is been seen in the nature as the structure of a super-hydrophobic surface: "a naturally hydrophobic surface with micro-roughness and nano-structured covering of the whole structure as a hierarchical structure" (Fig. 8).

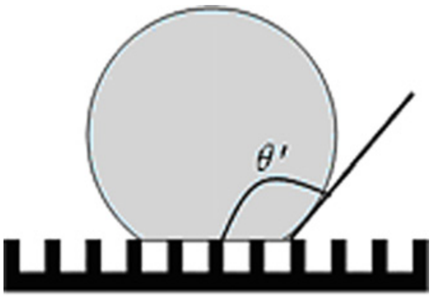

Fig. 7, roughened surface and its effect on contact angle [8].

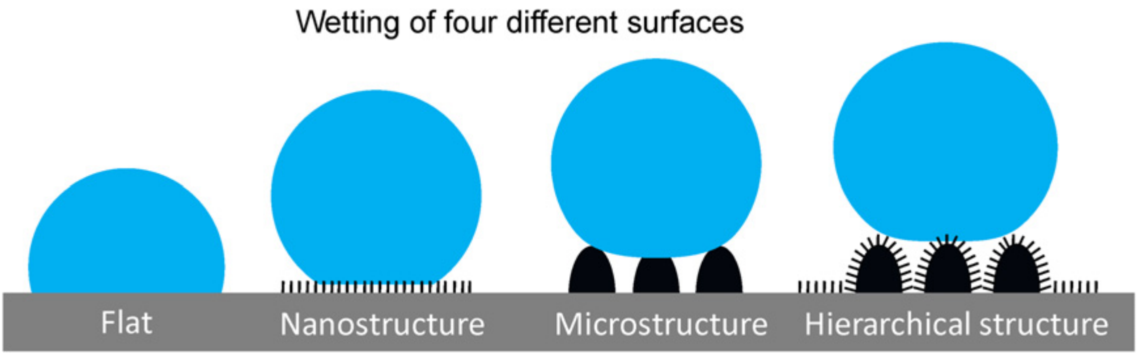

Fig. 8, Ordering of wetting angle from lesser to more, changed by structure of surface being studied [9].

In order to estimate contact angle of roughened surfaces Wenzel and Cassie offered two different models [10]. In Wenzel state, it is considered that water tends to enter into porosities of the surface while in the Cassie state, it remains on top of the roughness and inside the porosities will be kept dry (Fig. 8). Base on these two models, it is required to measure the roughness factors of surface and put them in each one of the equations. Whatever that fits with experimental angle measurements is considered as predominate state.

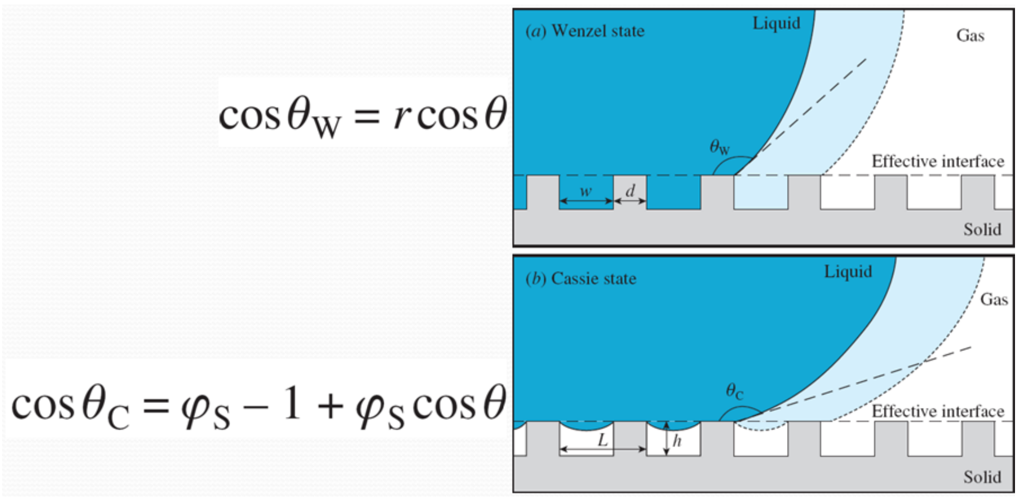

Fig. 9, a) Wenzel and b) Cassie states for uneven surface[10].

Radio Frequency Plasma Sputtering (RFPS) is a physical deposition process that is used to fabricate thin films of electrically insulating materials such as polymers. Principles of Plasma sputtering are based on the fact that ions of an inert gas can accelerate in an oriented electric field and bombardment a target material. Then, kinetic energy of ions can be transferred to the target’s atoms and force them to fly to the substrate where they become absorbed and form a thin film (Fig. 10).

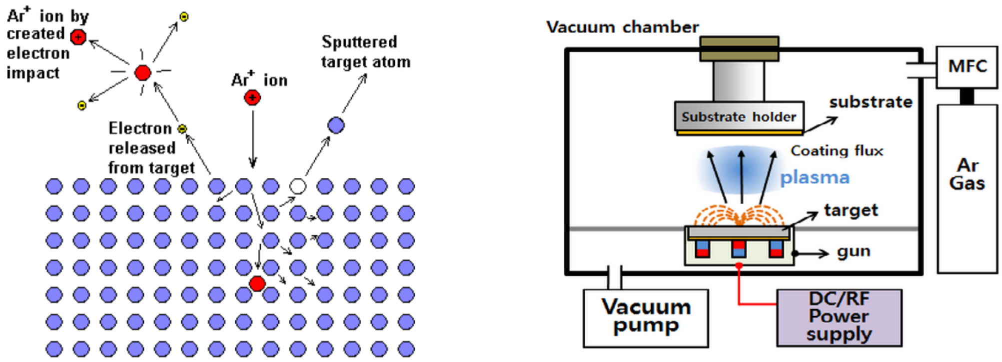

Fig. 10, schematics of RFPS; Left) principal steps of sputtering. The ionized Argon atom accelerates in an alternative electrical filed in radio frequency above 50Hz. Right) installation of RFPS chamber. Note that either DC or AC current can be used depending on electrical conductivity of target.

Polytetrafluoroethylene (PTFE) is a naturally hydrophobic material. A totally smooth surface made by PTFE represents a high contact angle with water up to 110° [11]. It is possible to deposit e thin film of PTFE via Radio Frequency Plasma Sputtering (RFPS) techniques [12]. Corrosion of metals in highly reactive solutions such as strong chloridric acid leaves a completely roughened and attacked surface which degree of roughness depends on metal which is being corroded, solution type, concentration, time and temperature [13]. In present work, these two aspects are brought together. In other words, a highly roughened surface was fabricated by chemical etching and a thin film of PTFE was deposited on it so that results in higher water contact angle than smooth one.

Materials and Methods:

Commercially pure aluminum plates were cut in 2×2cm^2 dimensions and cleaned with alcohol. A an aquatic solution of hydrochloric acid (19 wt%) was prepared. As prepared plates were immersed in acidic solution for one minute at room temperature. An intensive corrosion reaction took part and left the surface of the plates fully roughened. A Scanning Electron Microscope (SEM model: ZEISS NEON 40) was used to take micrographs of roughened substrates.

As etched substrates were rinsed with distilled water and left to be in ultra-sonic bath for 10 minuts to remove all residual particles. Afterwards, they were dried by air blow. LEYBOLD Z550 radio frequency sputtering equipment was used to deposit a thin film of Polytetrafluoroethylene (PTFE) on both roughened substrates and standard silicon chips. The power was set to 100W. The distance between target and substrates was 30cm. A constant argon gas flow was set to be 60ml/min. vacuum was set to be 10^{-4} mbarr. The sputtering deposition was done for 15 to 120 minuts. Wettability with water was studied using Ramé-Hart 200 Standard contact angle goniometer.

Results and discussions:

Fig. 11 features SEM micrographs of chemically attacked substrates. It is observed that the resulted surfaces have a topology similar to those of naturally super-hydrophobic surfaces. After measuring of contact angle (CA) of as PTFE coated substrates it has been observed that CA increases with the deposition duration (Fig. 12). wetting angle with time is demonstrated

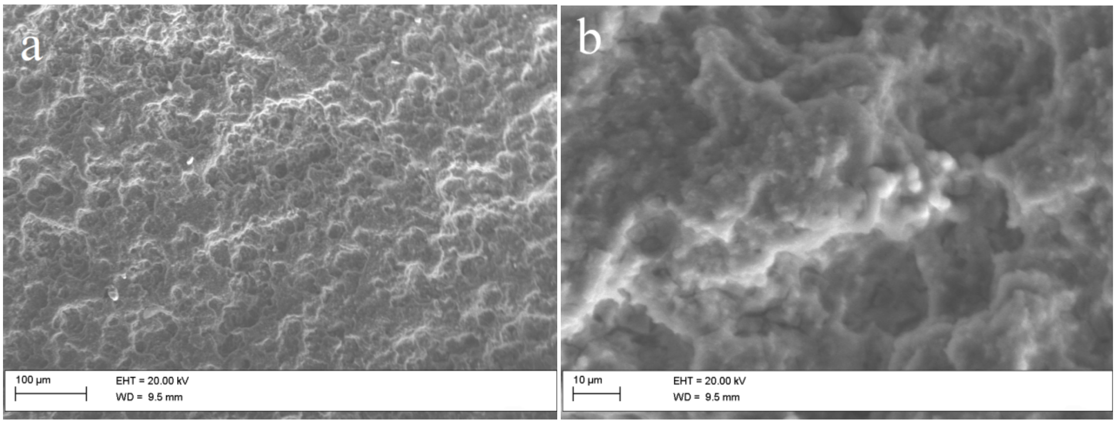

Fig. 11, SEM micrographs of chemically etched substrate with different magnifications; a) 150 and b) 1000. The chemical attack made micro-hills and each single one of them has been covered by nano-scale spheres.

Since deposition time is a determining factor in coating properties, four samples with different deposition run duration were prepared and afterwards, wettability of each sample was investigated (Fig. 12). It has been shown that deposition time has a direct relation with contact angle of resulted samples. It is due to the fact that the more deposition duration, the more fraction of substrates outer surface becomes covered with PTFE. Consequently, it demonstrate less affinity to water adhesion.

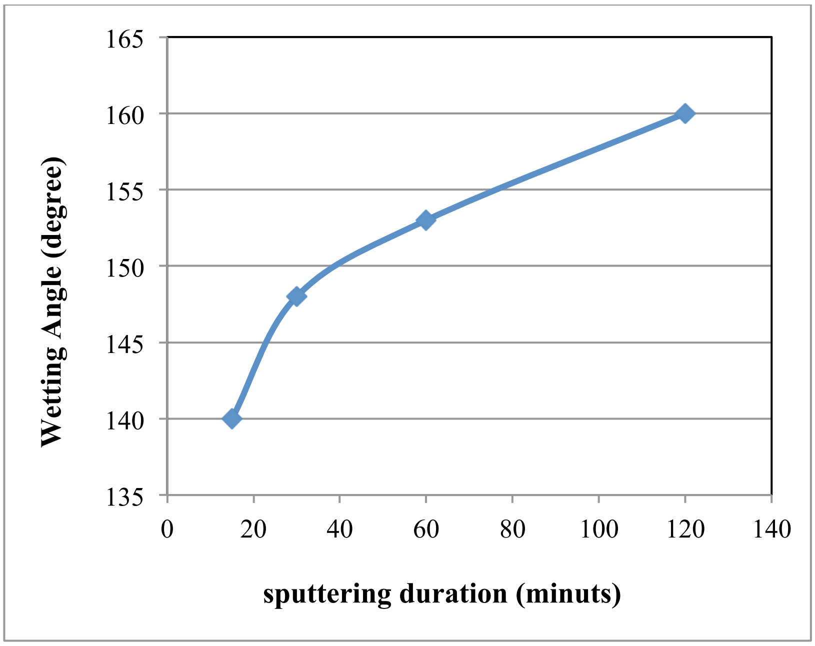

Fig. 12, wettability vs. sputtering time of prepared samples. All other deposition factors such as power, target-substrate distance, inert gas flow rate were kept the same as reported earlier.

As samples roughness has a critical effect on their wettability a test was carried out investigate its direct effect on contact angle of ultimate substrate after PTFE deposition; a totally smooth standard silicon substrate was cut in $2\times2\ cm^2$ dimensions and was used as substrate. Deposition was done in the same regime of roughened plates. It is observed that for all PTFE deposited samples, substrates with roughness demonstrate contact angle up to 45 degrees more than smooth ones (Fig. 13).

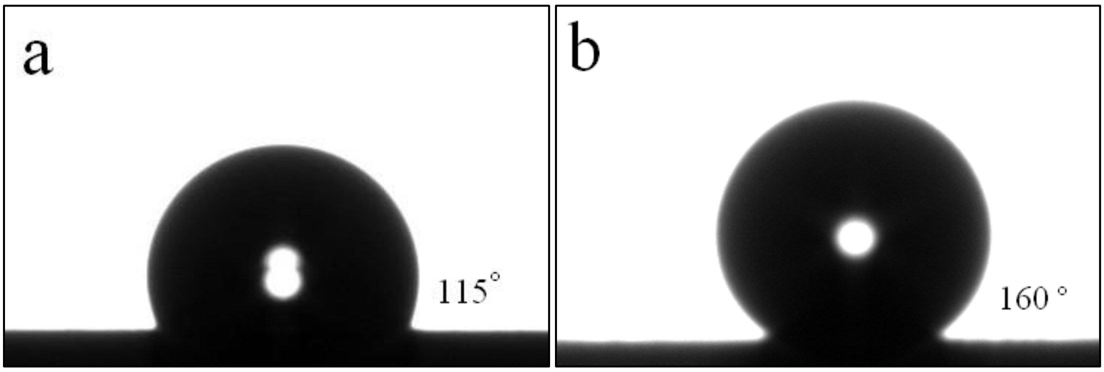

Fig. 13, Images taken by CCD camera from droplets on PTFE deposited substrates; a) smooth silicon substrate and b) fully roughened aluminum plate.

Conclusions:

- Thin films of PTFE were deposited successfully on both roughened and smooth metallic substrates. Some factors such as deposition duration can have a critical effect on wettability of resulted samples.
- The roughness effect on wettability was investigated and approved that it can dramatically increase contact angle of as fabricated samples covered with the same deposition run. The surface roughening can approximately increase C.A up to 30%.
- As fabricated samples showed complete super-hydrophbicity. However, some characteristics such as durability of specific propeorties and ice-phobicity of them should be studied in more details.
- There are other roughening techniques such as anodizing, also other hydrophobic materials than PTFE. Much more studies should be carried on in order to find the best combination of roughness texture and selected hydrophobic material.

Akhnowlegment:

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