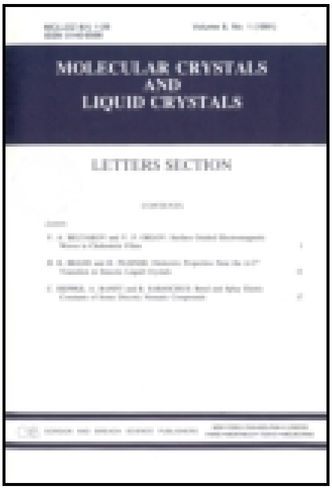

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A Stable Super-Hydrophobic and Self-Cleaning Al Surface Formed by Using Roughness Combined with Hydrophobic Coatings

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A Stable Super-Hydrophobic and Self-Cleaning Al Surface Formed by Using Roughness Combined with Hydrophobic Coatings

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A stable super-hydrophobic and self-cleaning surface with a high contact angle above 150° and the contact angle hysteresis below 3° were produced by using roughness combined with hydrophobic coatings, which were also confirmed to exhibit extreme water repellence and self-cleaning properties which facilitate removal of contaminant particles. To fabricate micro-patterened aluminium surface, the aluminium was etched with hydrochloric acid. A very thin polytetrafluoroethylene (PTFE) film was coated on the etched aluminium surface in order to achieve the super-hydrophobic surface. Roughness factors on the aluminium surfaces coated with PTFE were calculated as a function of etching time, based on the homogeneous interface (Wensel model). A critical roughness factor on the super-hydrophobic surface of the aluminium coated with PTFE was found to be 1.51 which can be formed on the surface of the aluminium etched over 10 min with hydrochloric acid of 7 wt.%.

Keywords Super-hydrophobic; Al surface; PTFE; water contact angle; coating; rf-sputtering

Introduction

The wettability of solid surface is a very important property, and is governed by both the chemical composition and the geometrical micro-structure of the surface [1]. The generation by UV illumination of a super-hydrophilic TiO2 surface with a water contact angle (WCA) below 10 degree has attracted significant attention [2]. This material has already been successfully applied as a transparent super-hydrophilic coating with anti-fogging and self-cleaning properties [3].

Currently, super-hydrophobic surfaces with WCA higher than 150° also have attracted much attention because they will being great convenience in daily life as well as in many industrial processes [4]. Various phenomena, such as snow sticking, contamination

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or oxidation, and current conduction, are expected to be inhibited on such a surface [5]. Super-hydrophobic surfaces exhibit extreme water-repellent properties [6, 7]. These surfaces with high contact angle and low contact angle hysteresis also exhibit a self-cleaning effect and low drag for fluid flow. Certain plant leaves, such as lotus leaves, are known to be super-hydrophobic and self-cleaning due to the hierarchical roughness of their leaf surfaces [7, 8]. The self-cleaning phenomenon is widely known as the lotus effect. Super-hydrophobic and self-cleaning surfaces can be produced by using roughness combined with hydrophobic coatings [9–17].

In this work, Al substrates were etched with the hydrochloric acid (HCl) to form microstructure on their surface. From the measured WCA on the etched Al surface, the roughness factor was calculated as a function of etching time, based on the homogeneous interface (Wensel) [7, 8]. To achieve a stable super hydrophobic surface, PTFE film that is so thin that does not change the roughness factor was coated on the etched Al surfaces [18–22]. The PTFE was chosen because of its hydrophobic nature with a low surface energy. Liquid may form either a homogeneous interface with a solid or a composite interface with air pockets trapped between the solid and the liquid. The mathematical models that provide relationships between roughness and contact angle and the contact angle hysteresis are discussed. In addition, their influence on adhesive force as well as efficiency of self cleaning, stability of the super-hydrophobic surface are also discussed. An optimum etching time on the Al surface and thickness of PTFE film have been determined for creating the roughness which are basic requirements for a stable super-hydrophobic surface.

Experimental Details

PTFE films were deposited by conventional rf magnetron sputtering. PTFE powder (F7 type Solvay) was well stirred for 2 hours by Ball Mill and this powder was calcined at 300°C in the air for 2 hours. The calcined powder was molded as a pellet of cylindrical type with a radius of 2.5 cm and a height of 5 mm by pressure of 11 tones. This pellet was used as a sputter target for PTFE films. Aluminum alloys (AA6061) with a size of 25 mm $\times$ 25 mm $\times$ 2 mm (thickness) were used as substrates for deposition of PTFE films. The aluminum (Al) substrates were etched with 7wt.% HCl for different times from 1 to 13 min. All the etched substrates were ultrsonically cleaned with deionized water to remove any residual dust, particles from their pores. Finally, the etched clean substrates were dried in an oven at 80°C for more than 8 hours prier to PTFE coating. The well dried Al substrates were placed parallel to the target surface at a distance of 60 mm. Sputtering depositions were carried out under a constant Ar gas pressure of 2×10^{-3}Torr. The applied rf powers was fixed by 50 W for all films. Thickness of PTFE films deposited on the etched aluminum were varied between from 5 nm and 450 nm. The thicknesses were controlled by deposition time. The surface morphologies of PTFE films were analyzed using a field emission scanning electron microscopy (FESEM : Jeol Co.). The water contact angle and contact angle hysteresis on the etched Al surface coated with PTFE were investigated by using contact angle analyzer (Kruss Co.). The contact angle measurements were made at room temperature by droplet with a volume of 5μl using a Kruss DSA100 goniometer following a very standard and commonly used experimental procedure as reported in the literature [16].

Results and Discussion

Figure 1 shows water contact angle as a function of etching time for the aluminum substrates etched with 7 wt.% HCl acid. As-received aluminum substrate shows a WCA of 116°, and

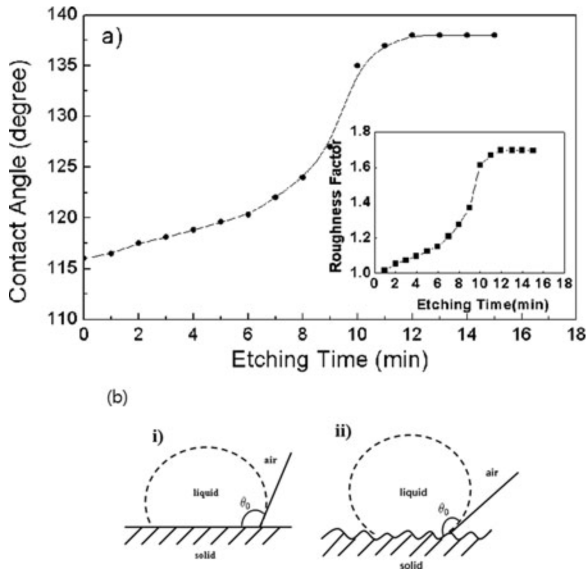

Figure 1. (a) Changes of water contact angle as a function of etching time for etched aluminum substrates with HCl solution. The inset shows roughness factors for the etched Al substrate which is calculated based on Wensel equation. (b) Schematic of a liquid droplet in contact with (i) a smooth solid surface (contact angle, θ_0) and (ii) a rough solid surface (contact angle, θ_0)

the WCA are increased with increasing etching time. The WCA is also found to increase to 122^o for the aluminum substrate etched for 7 min and 138^o on the aluminum etched for 10 min. At etching time longer than 10 min, WCA is almost saturated to 138 + 2^o. The WCA increase depends on the roughness formed on the surface of etched Al substrates. Consider a rough solid surface with a typical size of roughness details smaller than the size of the droplet as shown in Fig. 1(b). For a droplet in contact with a rough surface without air pockets, referred to as a homogeneous interface(or Wensel's model). According to Wensel, the contact angle is given as [7].

$$COS\theta = R_f COS\theta_0 \tag{1}$$

where θ is the contact angle for the rough surface; θ_0 is the contact angle for a smooth surface; and R_f is a roughness factor defined as the ratio of the solid-liquid area A_{SL} to its projection on a flat plane A_f, The dependence of the contact angle on the roughness factor is predicted for various values of θ_0, based on equation (1). The model predicts that a hydrophobic surface ($\theta_0 > 90^\circ$) becomes more hydrophobic with an increase in R_f, and that a hydrophilic surface ($\theta_0 < 90^\circ$) becomes more hydrophilic with an increase in R_f.

The roughness factors calculated based on Wensel equation (1) are plotted as a function of etching time in the inset of Fig. 1(a). It is found that the R_f values increase with increasing etching time and is almost saturated to value of 1.695 at etching time longer than 10 min. The WCA on the flat(unetched) Al surface is 116° which exhibit that Al has hydrophobic surface. Thus, the increase of WCA with etching time is because of the increase of roughness factor on the Al surface after the chemical etching, this result is good agreement to Wensel model (eq. 1). However, the saturation of roughness factor (or WCA) is closely related to etching characteristic of Al substrate.

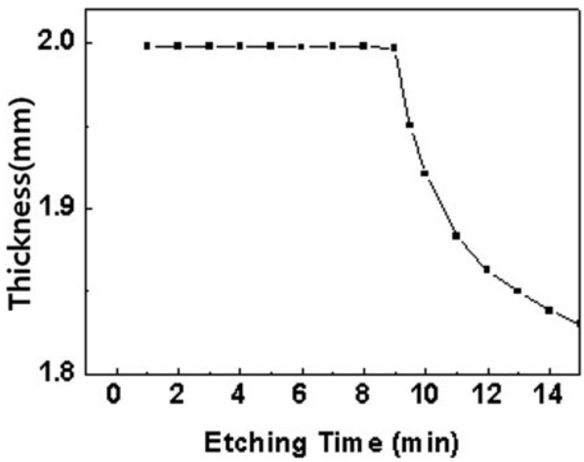

Figure 2. Thickness changes of the aluminum substrates as a function of the etching time.

In order to investigate the film property, we measured thickness change of the aluminum substrates during the aluminum substrates etched with 7 wt.% HCl for different times ranging from 1 to 13 min. The thickness of unetched aluminum substrate is exactly 1.998 mm. Very little variation in the thickness of the aluminum substrates are observed after etching up to 9 min as shown in Fig. 2. The little variations in the thickness due to etching may be attributed to the presence of a thin layer of aluminum oxide(Al2O3) on the aluminum surface. The removal of aluminum oxide layer is very slow taking nearly 9 min to be removed. However, after etching time of 10 min, the thickness reduced to 1.95 mm, which further reduced to 1.838 mm after longer etching time of 15 min. Once the aluminum oxide layer is removed, the hydrochloric acid react with aluminum vigorously as the free energy of reaction is negative [17], and the thickness of the films start reducing exponentially as depicted in Fig. 2. However, after etching time of 10 min, all Al substrates have almost a similar surface with a fractal structure (see Fig. 3).

Figure 3 shows typical SEM images on the etched Al surface with different etching time. During the etching process (a-d), the density of micro-structure on the surface of Al increases slowly with increasing etching time, in this process, the roughness factor increases very slowly with etching time. While many pits are formed in the etching process (e-f), the roughness factor rapidly increases. On the other hand, after etching time of 12 min, the micro-structures formed on the Al surface were found to be indistinguishable because they represented a similar fractal structure regardless etching time and concentration of HCl. Thus, their contact angles are saturated at near 138° at etching time longer than 12 min, as shown in Fig. 1(a).

To enhance the hydrophobic property of the etched Al surface, thin PTFE film was coated on the etched Al surface. PTFE was chosen because of its hydrophobic nature with a low surface energy. However, thick-PTFE film may change roughness factor of the etched Al surface. Thus, to obtain a high WCA on the etched Al surface, the coating on the etched aluminum surfaces must be so thin film that does not reduce roughness factor of the etched Al surface [18–22]. The PTFE was coated for 30 sec (thickness equivalent to approximately 10 nm) on the surface of the etched Al substrates with different etching time to maintain their roughness factors. The flat (unetched) Al surface coated with PTFE showed a static contact angle of 125°. this value can be used as a value of θ_0 for calculation

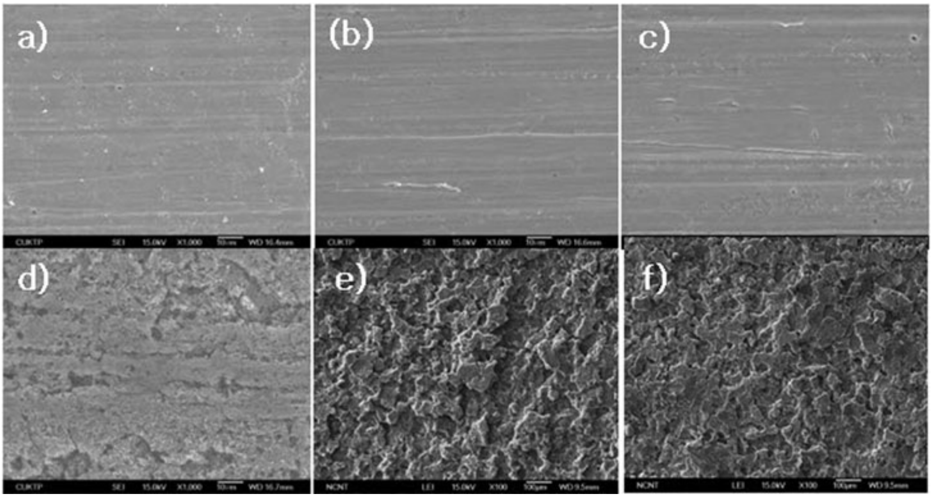

Figure 3. Typical SEM images of the etched Al subatrate for a) 0, b) 1 min, c) 3 min, d) 8 min, e) 10 min, and f) 12 min, with 7.5 wt.% HCl solution.

of theoretical WCA values for the etched Al surfaces coated with PTFE. The calculated WCA(solid line), based on the homogeneous interface (Wensel's equation), using $\theta_0 = 125^\circ$ and the roughness factors corresponding to each etching time that were obtained in the inset of Fig. 1(a) were plotted as a function of etching time in Fig. 4, which the measured values (squares) of WCA for the etched Al substrates coated with PTFE were also depicted. The measured values were good agreement to the calculated values up to etching time of 9 min. However, over 9 min, the measured values largely depart from the calculated values. For a rough surface, a wetting liquid will be completely absorbed by the rough surface cavities, while a non-wetting liquid may not penetrate into surface cavities, resulting in

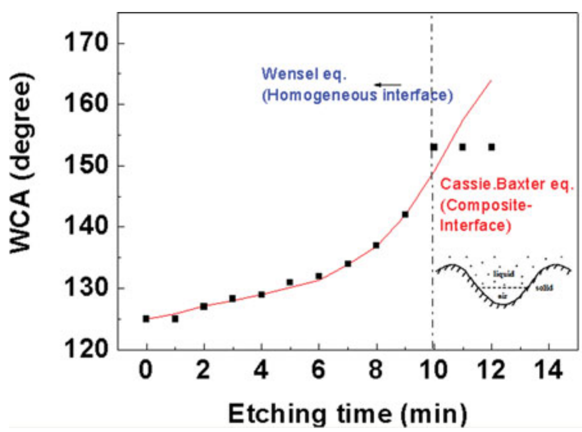

Figure 4. WCA change (squares) as a function of etching time for the etched Al surface deposited for 30 sec by PTFE. For comparison, the calculated WCA change(solid line), based on Wensel equation are also shown. The inset shows schematic of the formation of a composite solid-liquid- air interface for a rough surface.

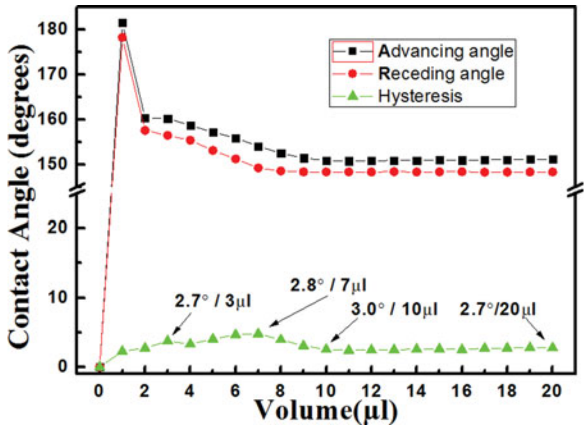

Figure 5. Water contact angle hysteresis for the etched (20 min) Al surface coated with PTFE thin-film.

the formation of air pockets, leading to a composite solid-liquid-air interface, as shown in the inset of Fig. 4. Cassie and Baxter extended the Wenzel equation, which was originally developed for a homogeneous solid-liquid interface, to the case of a composite interface. For this case, there are two sets of interfaces: a solid-liquid interface with the ambient environment surrounding the droplet, and a composite interface involving the liquid-air and solid-air interfaces. In order to calculate the contact angle for the composite interface, Wenzels equation can be modified by combining the contribution of the fractional area of wet surfaces and the fractional area with air pockets ($\theta_0 = 180^\circ$) [7,8].

$$COS\theta = R_f COS\theta_0 - f_{AL}(R_f COS\theta_0 + 1) \tag{2}$$

where f_{AL} is the fractional flat geometric area of the liquid-air interfaces under the droplet. Thus, the disagreement at etching times over 9 min is due to the transition to the composite interface (Cassie and Baxter regime) from the homogeneous interface (Wensel regim), the dotted line shown in Fig. 4 represents the transition criteria range for the transition to the composit interface (Cassie and Baxter regime) from the homogeneous interface(Wensel regime). Thus, at the etching time over 8 min, the contact angle very rapidly increases because of the transition.

The contact angle hysteresis is another important characteristic of a solid-liquid interface [7]. The measured contact angles while increasing or reducing amount of water with a constant velocity correspond to the advancing or receding contact angle, respectively. The advancing angle is greater than the receding angle, which results in contact angle hysteresis. The contact angle hysteresis (the difference between the advancing and receding contact angles) occurs due to surface roughness and heterogeneity rather than gravity [8]. Although, for surfaces with roughness controlled on the molecular scale, it is possible to achieve a contact angle hysteresis as low as 1° or less, hysteresis cannot be eliminated, since even atomically smooth surfaces have a certain roughness and heterogeneity.

The etched Al surface coated with PTFE shows a very low contact angle hysteresis between 2.7° and 3°, as shown in Fig. 5. The low contact angle hysteresis assurances that the PTFE on the etched Al surface are packed to the full, which results in a stable super-hydrophobic surface with the contact angle over 150° even for the droplet with a volume of 20 μl. A stable composite interface is essential for the successful design of super-hydrophobic surfaces. However, a composite interface is fragile and can be irreversibly transformed into a homogeneous interface, thus damaging super-hydrophobicity. In order to form a stable composite interface with air pockets between solid and liquid, destabilizing factors, such as capillary waves, nanodroplet condensation, surface inhomogeneities and liquid pressure, should be avoided. The etched Al substrates coated with PTFE, are confirmed to have a good stability and an excellnt reproducibility on their super-hydrophobic surface and self-cleaning effects. It is also confirmed that their WCAs are measured every week, the WCAs are maintained even after more 12 weeks for the etched Al surfaces coated with PTFE.

Conclusion

Aluminum substrates were etched with a hydrochloric acid of 7 wt.% to enhance their hydrophobicity. For the etched Al substrates, their water contact angles were measured as a function of etching time. The water contact angles were increased with increasing etching time. For the etched Al surface, roughness factors (R_f) were calculated as a function of etching time, based on the homogeneous interface (Wensel model) using the measured water contact angles. It was found that one way to increase the hydrophobic property of the surface was to increase surface roughness. However, the super-hydrophobic surface could not be formed only by increasing roughness due to etching. Super-hydrophobic and self-cleaning surfaces were produced by using roughness combined with hydrophobic coatings. To more enhance the hydrophoicity of the etched Al substrates, thin PTFE films with a thickness below approximately 10 nm that is so thin that does not reduce the roughness factor were coated on the surface of the etched Al substrates. For these coated Al substrates, the water contact angles were calculated based on Wensel equation. According to Wensel model, the super-hydrophobic surface due to the PTFE coating can be achieved on the surface of Al substrates with roughness factor over 1.510, this result was good agreement to the experimental result. On the other hand, the water contact angle on the super-hydrophobic surface could be explained by the composite interface due to the air porket formed in the valleys of the microstructure under the droplet. It was, therefore, also found that a critical roughness factor corresponds to the transition from the homogeneous interface to the composite interface for the etched Al substrates coated with PTFE, was 1.510 that can be formed on the surface of Al substrates etched over 10 min with a hydrochloric acid of 7 wt.%

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