Materials Letters
Volume 62, Issues 8–9, 31 March 2008, Pages 1226–1229

Superhydrophobic properties of ultrathin rf-sputtered Teflon films coated etched aluminum surfaces

D.K. Sarkar[a], M. Farzaneh[a], R.W. Paynter[b]
[a] Industrial Chair on Atmospheric Icing of Power Network Equipment (CIGELE) and Canada Research Chair on Atmospheric Icing Engineering of Power Networks (INGIVRE) at Université du Québec à Chicoutimi, 555, Boulevard de l'Université, Chicoutimi, Québec, Canada G7H 2B1
[b] INRS-ÉMT, 1650 boul. Lionel-Boulet, Varennes, Québec, Canada J3X 1S2

Received 2 April 2007, Accepted 7 August 2007, Available online 23 August 2007

Abstract

Superhydrophobicity has been demonstrated on ultrathin rf-sputtered Teflon coated etched aluminum surfaces. The etching of aluminum surfaces has been performed using dilute hydrochloric acid. An optimized etching time of 2.5 min is found to be essential, before Teflon coating, to obtain a highest water contact angle of 164 ± 3° with a lowest contact angle hysteresis of 2.5 ± 1.5°, with the water drops simply rolling off these surfaces with even the slightest inclination of the sample. The presence of − CF3 radicals along with − CF2 radicals in the ultrathin rf-sputtered Teflon films, as investigated by X-ray photoelectron spectroscopy (XPS), contributes to the lowering of the surface energy on the aluminum surfaces. The presence of patterned microstructure as revealed by field emission scanning electron microscope (FESEM) together with the low surface energy ultrathin rf-sputtered Teflon films renders the aluminum surfaces highly superhydrophobic.

Keywords : Superhydrophobicity; Etch-patterns; Ultrathin rf-sputtered Teflon; Chemical etching; Contact angle

1. Introduction

Researchers have created several superhydrophobic surfaces where water drops roll off, removing surface contamination, an effect observed on the lotus leaf and several other life forms in nature [1], [2] and [3]. In general, the contact angle of water on smooth flat hydrophobic surfaces, such as Teflon, does not exceed 120° [4]. However, the addition of roughness to the surface can increase the contact angle of water without altering the surface chemistry. The resulting superhydrophobicity is attributed to the combined effects of surface morphology and surface chemistry. These superhydrophobic surfaces exhibit a very high contact angle (CA) of water and a very low contact angle hysteresis (CAH). As a result, water drops roll off such surfaces with even the slightest tilt, giving them great potential in various technological areas, for example, microfluidic devices, textile industries and possibly anti-icing applications. Recently many methods have been developed to fabricate such superhydrophobic surfaces [5], [6], [7], [8], [9] and [10]. Erbil et al. [5] described a simple and inexpensive method for forming a superhydrophobic coating using polypropylene and a suitable selection of solvents and temperatures to control the surface roughness. Recently, lithography has been used to create ordered structures on surfaces to demonstrate superhydrophobicity [6]. Onda et al. [7] achieved a contact angle of 174° on the surface of the fractal structure of alkylketene. Other methods include the sol–gel process to generate a porous rough surface [8], the anodic oxidation of aluminum surfaces [9] and plasma polymerization [10]. In many of these cases, a rough surface was initially created, which was then coated with a low surface energy thin film to enhance superhydrophobicity.

Chemical etching is one of the methods very frequently used in applied [11], [12] and [13] and basic research [14]. These literatures show that chemical etching changes surface morphology with the existence of microstructure patterns. In this study we have demonstrated superhydrophobicity on micropatterned aluminum surfaces obtained by chemically etching with hydrochloric acid and coated with ultrathin rf-sputtered Teflon film. An optimum etching time has been determined for creating such micropattern which is a basic requirement for the surfaces to exhibit superhydrophobicity.

2. Experimental

Rolled sheets of aluminum alloy (AA6061) (Al 97.9 wt.%, Mg 1.0 wt.%, Si 0.60 wt.%, Cu 0.28 wt.%, Cr 0.20 wt.%) of dimension 25 mm × 25 mm × 1.58 mm were used as substrates. The substrates were etched with 14.8 wt.% hydrochloric acid (HCl) for different times ranging from 1 to 5 min. All the etched samples were ultrasonically cleaned with deionized water to remove any residual dust particles from their pores. The etched clean samples were dried in an oven at 70 °C for more than 10 h prior to Teflon coating. Ultrathin Teflon films were coated by rf-sputtering of a Teflon target using Ar plasma in an inductively coupled plasma reactor by applying power of 50 W. The distance between the target and the substrates (aluminum and silicon) was fixed to 30 cm and the time of sputtering was ∼ 15 min. The Ar pressure of 20 mTorr was maintained in the chamber during plasma coating of Teflon. The base pressure of the chamber, however, was 2×10^{-6} Torr. The XPS spectra were collected by using the ESCALAB 220iXL spectrophotometer, equipped with a monochromatic Al Kα (1486.6 eV) source. The surface morphology of the samples was investigated using an LEO field emission scanning electron microscope (FESEM). The contact angle measurements were made at room temperature using a Krüss DSA100 goniometer following a very standard and commonly used experimental procedure as reported in the literature [15]. In this method, a water drop of volume ∼ 5 μL was suspended with the needle and brought in contact with the superhydrophobic surfaces using a computer controlled device as provided by Krüss GmbH. The contact angle hysteresis was measured by holding the water drop with a stationary needle in contact with the surface and moving the goniometer stage in one direction.

3. Results and discussion

Fig. 1(a) shows the change of thickness of the aluminum substrates with the etching time. The thickness of the as-received aluminum substrates is 1.58 ± 0.006 mm. Variation in the thickness of the aluminum substrates is not observed up to after etching for even a duration of 2 min as shown in Fig. 1(a). The presence of a thin layer of aluminum oxide (Al_2O_3) on the aluminum surfaces may be the cause for the unchanged thickness up to 2 min of etching. Hydrochloric acid (HCl) when reacting with Al_2O_3, produces aluminum chloride ($AlCl_3$) and water (H_2O). Aluminum also produces aluminum chloride ($AlCl_3$) and hydrogen (H_2) when reacting with HCl. The free energies of reactions are calculated for both the reactions. By definition, the free energy of reaction is equal to the free energy of products minus the free energy of reactants [16].

According to our calculations, the free energies of reactions are + 183.1 kJ/mol when HCl reacts with Al2O3 and − 688 kJ/mol when HCl reacts with aluminum (Al). As the free energy of reaction of Al2O3 with HCl is positive, the removal of aluminum oxides is very slow taking nearly 2 min to be removed. However, after 2.5 min of etching period, the thickness reduced to 1.46 ± 0.014 mm, which further reduced to 1.25 ± 0.012 mm after a prolongation of etching period to 5 min. The change of thickness of the aluminum substrates etched between 2 and 5 min of duration follows a first order exponential decay law with time as presented in Eq. (1):

Equation (1)
$d=1.22+1.74\exp(-t/1.28)$$d=1.22+1.74\exp(-t/1.28)$

where d is the thickness of the aluminum substrates and t is the time of etching.

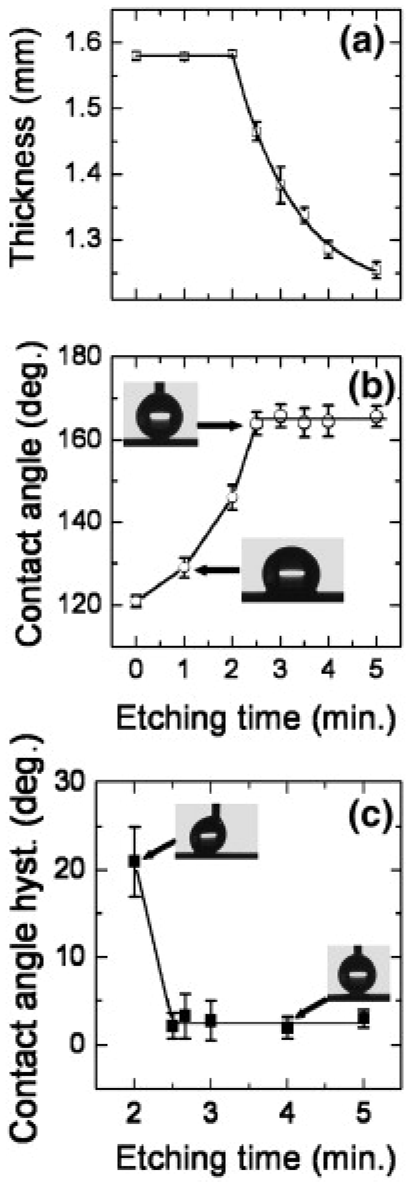

Fig. 1.

(a) Change of thickness of aluminum substrates with etching time, (b) Contact angle of water on ultrathin rf-sputtered Teflon coated aluminum substrates with etching time, inset shows the shape of water drop on 1 min and 2.5 min etch surfaces and (c) contact angle hysteresis of water on ultrathin rf-sputtered Teflon coated aluminum substrates with etching time, inset shows the shape of water drop on 2 min and 4 min etch surfaces while hysteresis measurement.

Once the aluminum oxide layer is removed, the hydrochloric acid reacts with aluminum vigorously as the free energy of reaction is negative, and the thickness of the films start reducing exponentially as presented by Eq. (1) and depicted in Fig. 1(a).

Fig. 1(b) shows the contact angle data of water on ultrathin rf-sputtered Teflon thin film coated etched aluminum substrates. According to the literatures, the term “ultrathin” films mean that the thickness of the films is less than 5 nm [17], [18], [19], [20] and [21]. Moreover, our XPS analysis also shows a very faint signal from the substrates (figure is not included); indicating that the thickness of the Teflon films is less than 5 nm. Such a low thickness of the ultrathin Teflon coating on the etched aluminum surface does not change the morphology of the etched aluminum surfaces. The ultrathin rf-sputtered Teflon coated as-received aluminum substrate showed a contact angle of $\sim 121 \pm 1.3°$. The contact angle is found to increase to $129 \pm 2.4°$ for the ultrathin rf-sputtered Teflon coated aluminum substrates that were etched for 1 min and $146 \pm 3°$ on those that were etched for 2 min. The contact angle further increases to $164 \pm 3°$ on the ultrathin rf-sputtered Teflon coated aluminum substrates that were etched for 2.5 min. It is interesting to notice that the contact angle remains constant on the ultrathin rf-sputtered Teflon coated aluminum surfaces that were further etched for longer than 2.5 min as shown in Fig. 1(b). While the ultrathin rf-sputtered Teflon coated etched aluminum surfaces demonstrated the property of rolling off of water drops, it is observed that the water drops are completely absorbed by the surfaces of etched aluminum which had no Teflon coating. It is observed from Fig. 1(a) that the thickness of the aluminum substrates reduces exponentially with etching time however; Fig. 1(b) shows that the contact angle remains constant after etching for longer than 2.5 min. The thickness of the aluminum substrates reduces by 7.6% for those etched for a period of 2.5 min. However, after 5 min of etching period, the contact angle still remains the same but with a loss of $\sim$ 21% of the thickness. Therefore, the highest contact angle of $164 \pm 3°$ has been obtained on ultrathin rf-sputtered Teflon coated aluminum substrates with the loss of only 7.6% thickness. The contact angle values similar to our observation or even higher have been reported in the recent literatures [22], [23] and [24]. The insets of Fig. 1(b) show the shapes of water drop on 1 min and 2.5 min etch surfaces for visualizing the values of contact angles.

Fig. 1(c) shows the change of contact angle hysteresis of ultrathin rf-sputtered Teflon coated aluminum substrates. The contact angle hysteresis on the ultrathin rf-sputtered Teflon coated as-received and 1 min etched samples were impossible to measure, as the water drops just stuck to the surfaces. The contact angle hysteresis, which is the difference between advancing and receding contact angle, on the ultrathin rf-sputtered Teflon coated aluminum substrates etched for 2 min is found to be ∼ 21 ± 4°. However, the contact angle hysteresis drastically reduces to 2.17 ± 1.42° for the samples that were etched for 2.5 min. An average contact angle hysteresis of 2.5 ± 1.5° (a straight line has been drawn between the experimental points) remains nearly constant for the rest of the aluminum surfaces that were etched up to 5 min. The lowest contact angle hysteresis of 2.5 ± 1.5° has been obtained on the samples that have been etched for a minimum of 2.5 min. The contact angle together with contact angle hysteresis data suggests that the optimum etching time of 2.5 min is adequate to obtain superhydrophobicity. Such a very low hysteresis of 1.4 ± 0.5° is comparable with very low hystereses of ∼ 2° as reported by Ming et al. [22] on poly(dimethylsiloxane) modified rough raspberry-like silica particles and < 1° as reported by Zhu et al. [24] on fluorocarbon films coated carbon nanotube arrays. The insets of Fig. 1(c) also show the shapes of water drop on 2 min and 4 min etch surfaces for visualizing the values of advancing and receding contact angles.

Fig. 2(a) and (b) show FESEM micrographs of ultrathin rf-sputtered Teflon coated as received aluminum surface and ultrathin rf-sputtered Teflon coated aluminum surface etched with 14.8 wt.% HCl acid for 2.5 min, respectively. It is clear from Fig. 2(b) that etch pits are formed on the aluminum surface after etching with HCl acid. In a crystalline metal, there exist a large number of dislocation defects. Due to their high energy, these defect sites are easily attacked by the chemical etchant and are as attacked preferentially compared to defect-free parts of a crystal [25]. The etch patterns are formed due to this preferential etching which effectively change the surface morphology [12] and [13] and shows superhydrophobicity after Teflon coating.

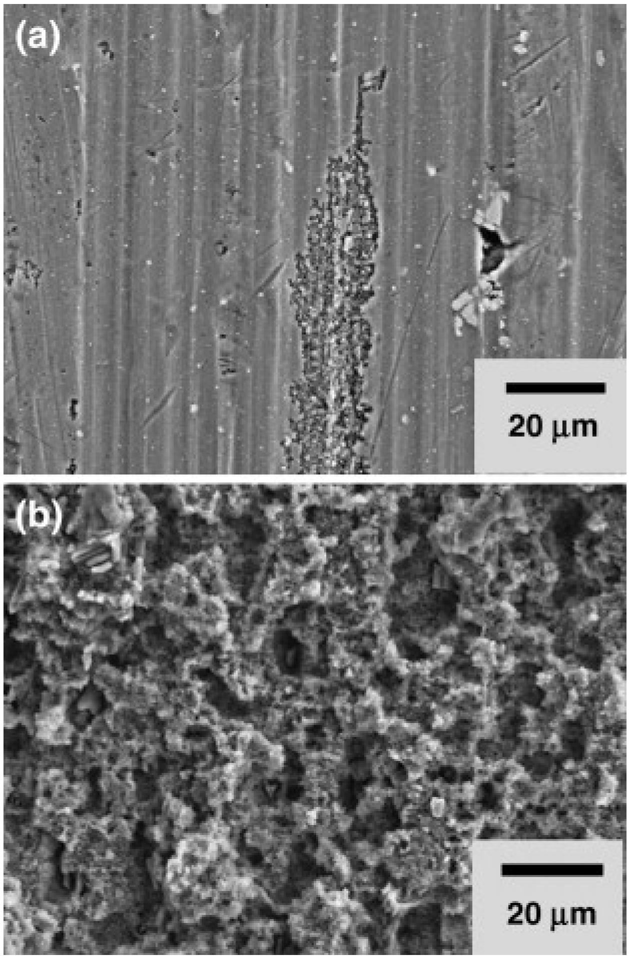

Fig. 2.

FESEM images of ultrathin rf-sputtered Teflon coated (a) as-received aluminum substrate (b) aluminum substrates etched with 14.8 wt.% HCl for 2.5 min.

X-ray photoelectron spectroscopy (XPS) analysis has been carried out to confirm the presence and the chemical composition of the ultrathin rf-sputtered Teflon films. Fig. 3 shows the C 1s peak of an ultrathin rf-sputtered Teflon film. The XPS spectrum of C 1s peak has been fitted with six components having equal width corresponding to CF3 at 293.3 eV, CF2 at 291.3 eV, CF–CFn at 289.3 eV, CF at 287.8 eV, C–CFn at 286.5 eV and C–C at 285 eV. The XPS quantification in atomic concentration has been carried out taking into account the individual peak areas and the corresponding sensitivity factors. The atomic ratio of F/C is found to be $\sim$ 1.7 which is higher than any reported result for ultrathin rf-sputtered Teflon films deposited by means of an Ar plasma [26] and [27]. Moreover, the CF3 and CF2 peaks are very distinct and separated from each other by 2 eV. In contrast to the C 1s spectra reported recently [28], [29] and [30] and which showed hardly any CF3 peak, we observed a very distinct CF3 peak in our ultrathin rf-sputtered Teflon films (Fig. 3). In general, a surface terminated with-CF3 radical has lower surface energy than a surface terminating with-CF2 radical [31]. Although, Teflon is a polymer of [− CF2]n functional group, several-CF3 radicals are also formed in a rf-sputtered Teflon film as shown by the XPS spectra in Fig. 3. These excess-CF3 groups along with-CF2 groups in the ultrathin rf-sputtered Teflon films lower the surface energy of the etched aluminum surfaces rendering them highly superhydrophobic, making a water contact angle of ~ 164 ± 3° with a very low contact angle hysteresis of lower than 2.5 ± 1.5°. Water drops simply roll of from such surfaces. This simple, low cost and efficient way of preparing substrates with superhydrophobic properties will have tremendous industrial application.

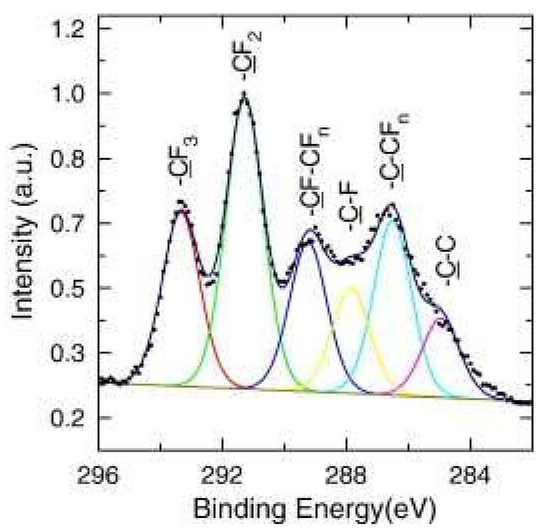

Fig. 3.

X-ray photoelectron spectroscopy (XPS) spectrum of C 1s of ultrathin rf-sputtered Teflon films.

4. Conclusion

Superhydrophobic properties have been achieved on ultrathin rf-sputtered Teflon coated etched aluminum surfaces. The microstructural evolution of the etch-patterns created before and after etching using hydrochloric acid has been investigated by FESEM. A water contact angle as high as 164 ± 3° with a contact angle hysteresis as low as 2.5 ± 1.5° have been achieved on ultrathin rf-sputtered Teflon coated aluminum substrates etched for an optimum time of 2.5 min. XPS investigations have revealed the presence of a large quantity of − CF3 and − CF2 groups in the ultrathin rf-sputtered

Teflon films that effectively reduces the surface energy of etched aluminum. The presence of patterned morphology along with the low surface energy ultrathin rf-sputtered Teflon coating makes the aluminum surfaces highly superhydrophobic.

Acknowledgments

This work was carried out within the framework of the NSERC/Hydro-Quebec/UQAC Industrial Chair on Atmospheric Icing of Power Network Equipment (CIGELE) and the Canada Research Chair on Engineering of Power Network Atmospheric Icing (INGIVRE) at the Université du Québec à Chicoutimi. The authors would like to thank the CIGELE partners (Hydro-Québec, Hydro One, Électricité de France, Alcan Cable, K-Line Insulators, CQRDA and FUQAC) whose financial support made this research possible. They also extend their thanks to Ms H. Grégoire of NRC-CTA NSERC for FESEM measurements, and to R. Subasri, visiting fellow of Max-Planck-Institut für Metallforschung, Stuttgart, Germany for providing thermodynamics data for the chemical reactions.

References

[1] W. Barthlott, C. Neinhuis
Planta, 202 (1997), p. 1
[2] W. Lee, M.K. Jin, W.C. Yoo, J.K. Lee
Langmuir, 20 (2004), p. 7665
[3] X.F. Gao, L. Jiang
Nature, 432 (2004), p. 36
[4] G.S. Tzeng, H.J. Chen, Y.Y. Wang, C.C. Wan
Surf. Coat. Technol., 89 (1997), p. 108
[5] H.Y. Erbil, A.L. Demirel, Y. Avci, O. Mert
Science, 299 (2003), p. 1377
[6] J. Bico, C. Marzolin, D. Quéré
Europhys. Lett., 47 (1999), p. 220
[7] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii
Langmuir, 12 (1996), p. 2125
[8] K. Tadanaga, J. Morinaga, T.J. Minami
J. Sol-Gel Sci. Technol., 19 (2000), p. 211

[9] S. Shibuichi, T. Yamamoto, T. Onda, K. Tsujii
J. Phys. Chem., 100 (1996), p. 19512
[10] S. Coulson, I. Woodward, J. Badyal, S.A. Brewer, C. Willis
J. Phys. Chem., B, 104 (2000), p. 8836
[11] S. Siau, A. Vervaet, A.V. Calster, I. Swennen, E. Schacht
Appl. Surf. Sci., 237 (2004), p. 456
[12] J.M. Montero-Moreno, M. Sarret, C. Müller
Surf. Coat. Technol., 201 (2007), p. 6352
[13] V. Kapaklis, A. Georgiopoulos, P. Poulopoulos, C. Politis
Physica, E, Low-Dimens. Syst. Nanostruct., 38 (2007), p. 44
[14] D. Aurongzeb
J. Phys., Condens. Matter, 17 (2005), p. 2655
[15] M. Callies, Y. Chen, F. Marty, A. Pépin, D. Quéré
Microelectron. Eng., 100 (2005), p. 77
[16] O. Knacke, O. Kubaschewski, K. Hesselmann
Thermochemical properties of Inorganic Substances (second edition), vol. ISpringer Verlag (1991)
[17] D.K. Sarkar, M. Falke, H. Giesler, S. Teichert, G. Beddies, H.-J. Hinneberg
J. Appl. Phys., 89 (2001), p. 6506
[18] D.K. Sarkar, M. Falke, H. Giesler, S. Teichert, G. Beddies, H.-J. Hinneberg
Appl. Phys., A, 70 (2000), p. 681
[19] J. Kim, K. Yong
J. Vac. Sci. Technol., B, 22 (2004), p. 2105
[20] M. Ishii, B. Hamilton, N.R.J. Poolton, N. Rigopoulos, S. De Gendt, K. Sakurai
Appl. Phys. Lett., 90 (2007), p. 063101
[21] A. Opitz, M. Scherge, S.I.-U. Ahmed, J.A. Schaefer
J. Appl. Phys., 101 (2007), p. 064310
[22] W. Ming, D. Wu, R. van Benthem, G. de With
Nano Lett., 5 (2005), p. 2298
[23] E. Hosono, S. Fujihara, I. Honma, H. Zhou
J. Am. Chem. Soc., 127 (2005), p. 13458
[24] L. Zhu, Y. Xiu, J. Xu, P.A. Tamirisa, D.W. Hess, C.-P. Wong
Langmuir, 21 (2005), p. 11208
[25] G.F. Vander Voort

Metallography: Principles and Practice McGraw-Hill, New York (1984)
[26] Y. Zhang, G.H. Yang, E.T. Kang, K.G. Neoh, W. Huang, A.C.H. Huan, S.Y. Wu
Langmuir, 18 (2002), p. 6373
[27] M.E. Ryan, J.L.C. Fonseca, S. Tasker, J.P.S. Badyal
J. Phys. Chem., 99 (1995), p. 7060
[28] V. Stelmashuk, H. Biederman, D. Slavínská, J. Zemek, M. Trchová
Vacuum, 77 (2005), p. 131
[29] D.S. Bodas, A.B. Mandale, S.A. Gangal
Appl. Surf. Sci., 245 (2005), p. 202
[30] Y. Pihosh, H. Biederman, D. Slavinska, J. Kousal, A. Choukourov, M. Trchova, A. Mackova, A. Boldyryeva Vacuum, 81 (2006), p. 38
[31] E.F. Hare, E.G. Shafrin, W.A. Zisman
J. Phys. Chem., 58 (1954), p. 236