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Super hydrophobicity of sputtered PTFE films on nanotextured aluminum surface

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Abstract

In this research, the superhydrophobic surface was prepared by using the polytetrafluoroethylene (PTFE) thin films which deposited on aluminum (Al) nanotextures. The Al nanotextures have been prepared under different alkaline-treatment concentrations, and deposited with the PTFE thin films by the RF magnetron sputtering technique. During the alkaline treatments, the Al surface was immersed in the potassium hydroxide (KOH) solution with the concentrations of 1 mM to 0.10 mM. Then, the samples of PTFE films were deposited on Al nanotextures were characterized; the crystal structures, chemical compositions, physical morphologies, and surface roughness by photoelectron spectroscopy (PES), field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM), respectively. The results show that, after the KOH treatment, the nano flask-like structures were observed on the Al surface. The surface roughness of the prepared samples was also increased with the highly concentrated KOH treatments. In addition, the wettability of the prepared samples was contributed from the presence of the functional groups and surface morphologies, as observed by the X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM) analyses. Finally, the results clearly demonstrated that the super-hydrophobic surface could be developed by the PTFE films deposited on the Al nanotextures according to the combination of the small surface-energy material and the surface nanostructures. The influence of the surface nanotextures on the super-hydrophobicity was investigated and discussed, based on the Wenzel and Cassie-Baxter models of the water contact angles on the solid surface.

1. Introduction

Polytetrafluoroethylene (PTFE) was an interested material due to its properties: low surface energy, lubricant, good dielectric, and chemical inert [1]. At present, it was applied on a flat surface for Anti-biofouling [2] and anti-freezing applications [3] because of its low surface energy. Therefore, there are many researcher groups try to develop PTFE structure to fabricate the superhydrophobicity, but the PTFE thin films have the $–CF_3–$ bonding, so, it has the limitation of contact angle (WCA) at 120° [4]. For enhancement this properties, the surface roughness is one interesting way to fabricate the superhydrophobicity [5]. This way was successful reported by Jafari and Farzaneh [6] in 2011. The Jafari and Farzaneh group explained that surface roughness of aluminium (Al) was effected on the lower surface energy of PTFE films and affected on their superhydrophobic properties. Therefore, the surface roughness of the substrate before deposited PTFE was interested in this research. The surface roughness of the substrate could prepare by various method, such as mechanical stretching, sol–gel processing [4], layer-by-layer assembly [7], etching, lithography [8], chemical and electrochemical depositions [9] and chemical vapor deposition [10]. As mentioned, the chemical treatment is the simplest and the lowest cost method for Al surface roughening. The strong acid [11] or base [12] could be used to treat the Al surface. In the other way, the boiling Al in water was improved surface roughness very well [6].

In this work, we study the effect of alkaline treatment on Al surface before coating with PTFE.

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The prepared samples were analyzed for physical morphology and surface wettability.

2. Experimental

The 1.5 × 1.5 cm Al thin film samples were fabricated by DC-pulsed magnetron sputtering on the Si-wafer (100) substrate. The Al with purity of 99.95% and diameter of 2 in was used as a sputtering target. The sputtering chamber was pumped as vacuum via rotary pump and turbo molecular pump to the base pressure of 5×10^{-6} mbar. The 99.9995% purity of Ar was flow into the chamber as the sputtering gas with the flow rate of 20 sccm; the operating pressure was fixed at 5 mTorr by control valve. The power of 240 W was supplied to DC magnetron sputtering gun for preparation of Al thin films. The Al thickness of 500 nm was prepared with deposition time of 1 h. After that, the samples were modified surface by alkali treatment. The as-deposited Al thin film was dipped into the 200 cm^3 KOH solution with a concentration varying of 1 mM and 100 mM for 1 min. Then the sample was immersed into boiling deionized water at 80°C with different time as 1, 5, 10 and 15 min. Then, drying them by N_2 gas. Finally, the Al after treatment was used as the substrate and the PTFE was deposited onto its. The RF-magnetron sputtering with constant Ar flow rate of 20 sccm, operating pressure of 10 mTorr, power of 50 W and deposition time of 15 min were used as the PTFE thin films deposition condition. The 2 in diameter of PTFE was applied as a target. Then, the samples were characterized morphology, surface roughness, wettability and chemical composition by field-emission scanning electron microscope (FE-SEM, Hitachi), atomic force microscope (AFM, JPK instrument), contact angle measurement and X-ray photoelectron spectroscopic (XPS), respectively.

3. Results and discussion

The microstructure of the Al and its surface were characterized by FE-SEM as shown in Figure 1. The Figure 1(a) shows the cross-section image of as-deposited Al thin film. The thickness of 420 nm and low surface roughness were shown. It confirms that the Al film is dense enough for using as the substrate. After alkali surface modification, the thin film sample became the bilayer structure of Al and $Al(OH)_3$ as seen in Figure 1(b). The Al layer was etched and the $Al(OH)_3$ layer with thickness of 760 nm was formed above its. The results show two interesting regions as seen in inset Figures 1(c) – 1(d). Region I in Figure 1(c) show the nano sheet-like structure was formed uniformly with indirection growth of $Al(OH)_3$. Region II in Figure 1(d) show the micro-sheet of $Al(OH)_3$. These results indicate that the etching rate of Al substrate and $Al(OH)_3$ growth rate are different. The two types structure made the surface to be both micro- and nano-roughness which hierarchical structure imitation. In addition, the total thickness of treated samples were higher than 420 nm because the growth rate of $Al(OH)_3$ was higher than the etching rate of Al.

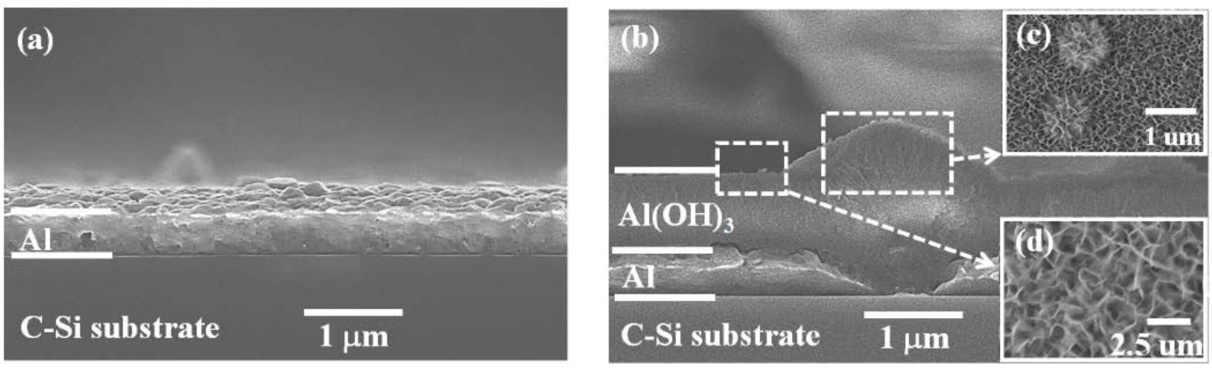

Figure 1. Top-viewed and cross-section FE-SEM micrographs: (a) the cross-section of as-deposited Al thin film before the alkaline treatment, (b) the cross-section of Al thin film after the alkali treatment, (c) the top-viewed of $Al(OH)_3$ after the alkali treatment and (d) the top-viewed of Al surface after the alkali treatment.

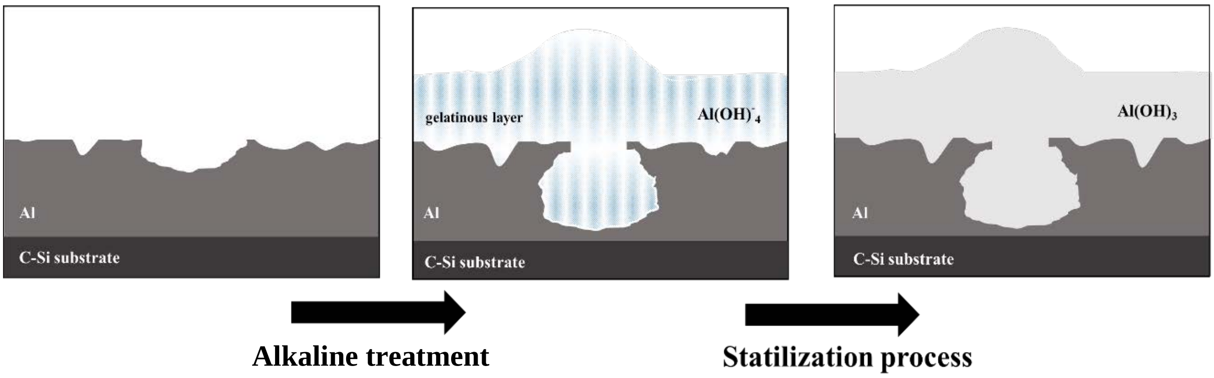

Figure 2. Mechanism forming Al(OH)$_3$ layer above the Al thin film by alkaline treatment process.

This mechanism could be explained by model illustrated in Figure 2. The modelling shows two step of Al(OH)$_3$ formation. Firstly, the Al-thin film was dipped into KOH solution; then Aluminium oxide can react with OH$^-$ and formed oxides on the top of the Al surface, as shown by equations 1 and 2:

$$Al_2O_3 + 2KOH + 3H_2O \rightarrow 2Al(OH)_4^- + 2K^+ \quad (1)$$

$$2Al + 2KOH + 6H_2O \rightarrow 2Al(OH)_4^- + 2K^+ + 3H_2 \quad (2)$$

From equation 1, the main product from chemical reactin that was produced by aluminate ion (Al(OH)$_4^-$) was gelatin, which is formed on the sample surface due to its highly-hydrophobicity property [6]. After that, as the sample were immerged into boiling water, the Al(OH)$_3$ were formed as shown by equation 3:

$$Al(OH)_4^- \rightarrow Al(OH)_3 + 2OH^- \quad (3)$$

Then, the concentration of KOH and boiling time were varied and so were used as a basis to study their effect on surface roughness of Al surface. The surface roughness of all sample was characterized by atomic force microscopy (AFM). The Figures 3(a) and 3(b) show AFM images of Al surface with various boiling time and different concentration of 1 mM and 100 mM, respectively. The results show that the surface roughness of Al was increased as boiling time is increased. Moreover, the maximum surface roughness is not higher than 50 nm. The Al which was immerged into KOH 100 mM for boiling time of 15 min has the highest surface roughness of 47 nm, while that of another sample conditions were not higher than 20 nm. These results showed that the KOH concentration has a small effect on the surface roughness of the samples.

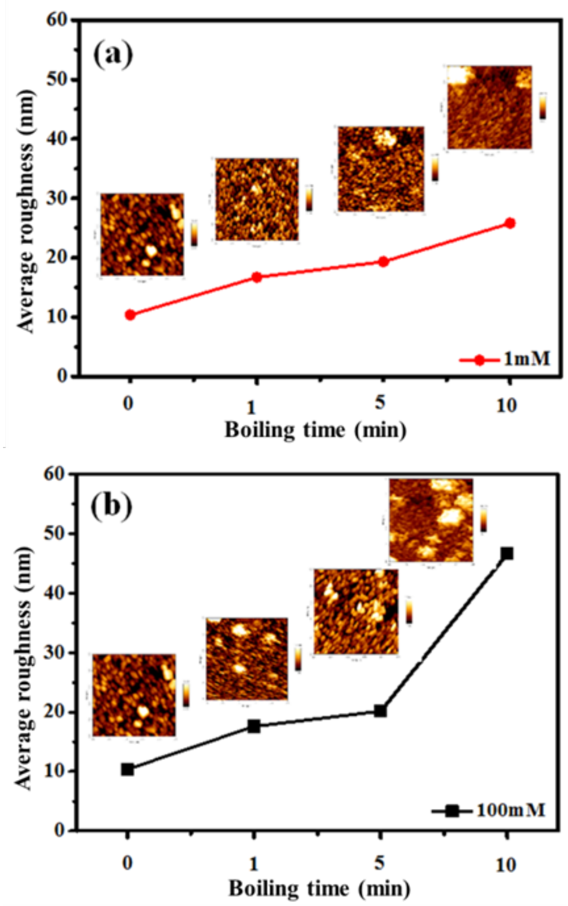

Figure 3. Two dimentional AFM image of Al surface after alikaline treatment with various boiling times at different KOH concentrations (a) 1 mM (b) 100 mM.

Moreover, the wettability of all sample were characterized by contact angle measurement. Figure 4(a) shows that the Al surface exhibited a hydrophilicity with contact angle of 87°. We also found that the contact angle decreased to 20° as boiling time increased. These phenomena confirm that the Al oxide was formed on Al surface, so that the hydrophobicity property was shown. In addition, Figure 4(b) shows wettabilities of PTFE deposited on the top of $Al(OH)_3$ layer. The contact angles of PTFE film which deposited on untreatment Al surface is 110°. However, when the PTFE was deposited onto Al surface treated by KOH, the superhydrophobic was shown as suggesting by the contact angle of 140°. This results indicate that the surface roughness of nanostructure of Al substrate affects on superhydrophobicity property of PTFE film.

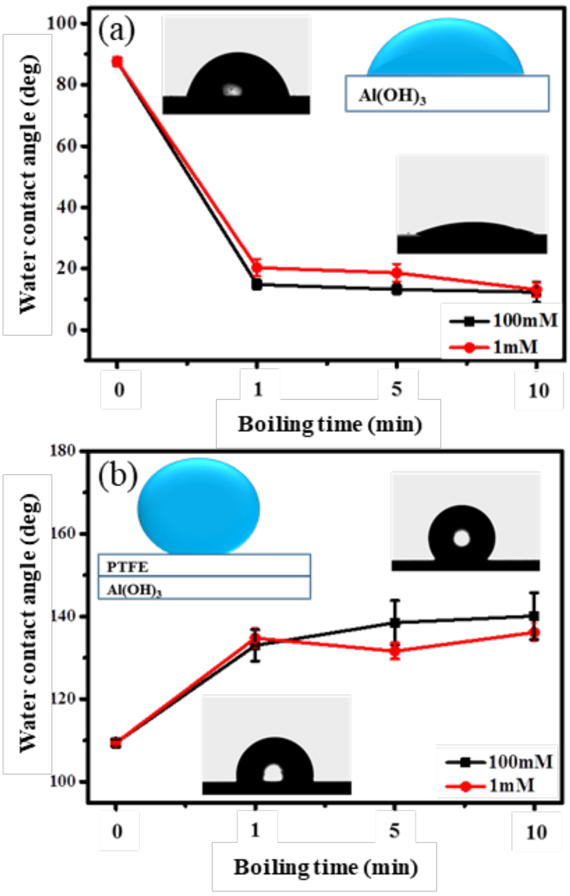

Figure 4. The contact angle measurement of (a) $Al(OH)_3$ surface and (b) PTFE deposited on Al surface with various boiling time.

Finally, we characterize the chemical bonding of PTFE film by XPS. The result was shown in Figures 5(a) - 5(b). The Figure 5(a) shows the binding energy of Al and Al_2O_3 of the substrate. Figure 5(b) shows the spectral bonding of -C-C (BE = 285.0 eV) and -CF (BE = 290.0 eV), indicate that there is –CF bonding in the chemical bonding of PTFE which deposit by sputtering. This structural is very important, as it can be used to indicate the super hydrophobicity property due to the lowest surface energy of the PTFE film.

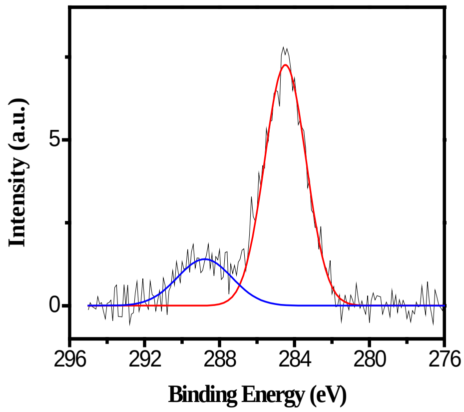

Figure 5. The XPS spectra of PTFE film deposited on Al treatment in KOH solution: C-C bonding in red line and –CF bonding in blue line.

4. Conclusions

In this work, we study the effect of alkaline treatment on Al surface before coating with PTFE. The prepared samples were analyzed the physical morphology and surface wettability by FE-SEM, AFM, XPS and contact angle measurement. It was found that the alkali treatment can help to create the hierarchical structure on the Al thin film surface. The result of AFM images show that the surface roughness affected the hydrophobicity property while the concentration of alkaline treatment did not. Therefore, the nanotextures of $Al(OH)_3$ affected on superhydrophobicity of PTFE. Moreover, the XPS spectra indicates that the hydrophobicity property of PTFE with CF bonding could develop by creating the high degree of the surface roughness of the substrate. This research is sucessful to improve that the surface roughness of $Al(OH)_3$ surface could develope the hydrophobicity of PTFE film.

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