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Formation of Superhydrophobic Surfaces on Fluoropolymer Films Using Ion Implantation

Yong-Woon Park, Yong-Jun Jo, Chan-Hee Jung, In-Tae Hwang and Jae-Hak Choi*

Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup 580-185, Korea

Abstract - In this study, a facile method to fabricate superhydrophobic surfaces on perfluoroalkoxy (PFA) films using ion implantation was developed. PFA films were implanted at 100 keV with a fluence ranging from 4×10^{16} to 7×10^{16} ions cm^{-2}. The surface properties of the implanted films were investigated in terms of their surface morphology, wettability, and chemical composition. As the fluence increased to 6×10^{16} ions cm^{-2}, the surface morphology and surface roughness of the PFA films were dramatically changed. The PFA surface implanted at a fluence of 6×10^{16} ions cm^{-2} showed a maximum contact angle (CA) of 157.1°, while the control CA of the smooth PFA surface was 103.6°. Thus, the superhydrophobic surface was successfully fabricated by ion implantation.

Key words : Ion implantation, PFA, Superhydrophobicity, Contact angle

INTRODUCTION

The fabrication of superhydrophobic surfaces with a water contact angle larger than 150° has received considerable interest over the past few years owing to their potential scientific and industrial applications including self-cleaning surfaces, antifouling coatings, stain resistant textiles, and ice repellent surfaces (Li *et al.* 2007; Nimittrakoolchai and Supothina 2008; Nysteöm *et al.* 2009). The design of superhydrophobic surfaces has been generally based on two different Wenzel and Cassie models that interpret the phenomenon related to a substantial reduction in the contact area between the water droplet and rough hydrophobic surface resulting from the air entrapment within the rough microstructure of polymer surfaces (Spohr *et al.* 2010; Li *et al.* 2012). Therefore, the surface topology and chemical environment are great factors to generate the superhydrophobic surfaces (Burkarter *et al.* 2007; Jafari *et al.* 2010).

Two general approaches to form superhydrophobic surfaces were approved. One is the direct fabrication of rough structures on a low surface energy material, and the other includes an additional modification process with a low surface energy compound onto a pre-formed rough surface (Jiang *et al.* 2004; Zhai *et al.* 2004; Wei *et al.* 2010). By considering these approaches, various methodologies for the formation of superhydrophobic surfaces have been developed such as mechanical stretching (Nimittrakoolchai and Supothina 2008), electrospinning (Lee *et al.* 2010), microphase separation (Kwong *et al.* 2007), etching (Wang *et al.* 2011), self-assembly (Li *et al.* 2012), and layer-by-layer deposition (Li *et al.* 2007). However, these methodologies exhibited limitations such as multi-step processes, severe processing conditions, and a low stability of the super-hydrophobic surfaces (Wang *et al.* 2011; Yilgor *et al.* 2012). Thus, a simple, low time-consuming, and eco-friendly method to form robust superhydrophobic surfaces has been required for piratical

* Corresponding author: Jae-Hak Choi, Tel. +82-63-570-3062, Fax. +82-63-570-3090, E-mail. jaehakchoi@kaeri.re.kr

applications.

In this study, a facile method is proposed to fabricate super-hydrophobic surfaces through ion implantation, which is suitable to manipulate the surface characteristics without affecting the bulk property (Chen *et al.* 2007; Chen *et al.* 2008). PFA films were implanted by accelerated heavy ions under various conditions to generate super-hydrophobic surfaces, and the surfaces of the resulting films were investigated in terms of the morphology, wettability, and chemical composition.

MATERIALS AND METHODS

Surface modification of PFA films by ion implantation

Perfluoroalkoxy (PFA) films (50 μm thickness, Ashai Glass Co. LTD.) were washed by ultrasonication in acetone for 30 min and dried in a vacuum oven at room temperature overnight prior to use. Well-cleaned PFA films, which were cut into 80 mm × 80 mm samples, were ultrasonically cleaned with acetone for 30 min, and finally dried in an oven at 60 ˚C for 1 h. The PFA films were irradiated by 100 keV Xe^+ ions at various flunences ranging from 4×10^{16} to 7×10^{16} ions cm^{-2} using a 300-keV ion implanter in the Advanced Radiation Technology Institute (ARTI) of the Korea Atomic Energy Research Institute (KAERI). The pressure in the implanter's target chamber was 10^{-5} to 10^{-6} Torr, and the current density of the ion beam was kept at about 30 μA cm^{-2}.

Surface characterization

The surface morphologies of the control and implanted PFA films were observed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7500F) and the detailed roughness of the implanted surfaces were measured based on the root mean square of surface roughness (RMS) using an atomic force microscope (AFM, Park system XE-100). The water contact angle measurement was performed using a contact angle analyzer (Phoenix 300, Surface Electro Optical Company). A deionized water droplet (4 μl) was dropped carefully onto the surface at room temperature, and the photograph of the water droplet was taken with a camera. The average contact angle from five measurement was obtained. The FTIR-ATR spectra of the control and implanted PFA surfaces were recorded using a Varian 640 Fourier transform infrared spectrometer (FTIR) equipped with an attenuated total reflection (ATR) prism. The changes in the chemical composition of the PFA surface after ion implanta-

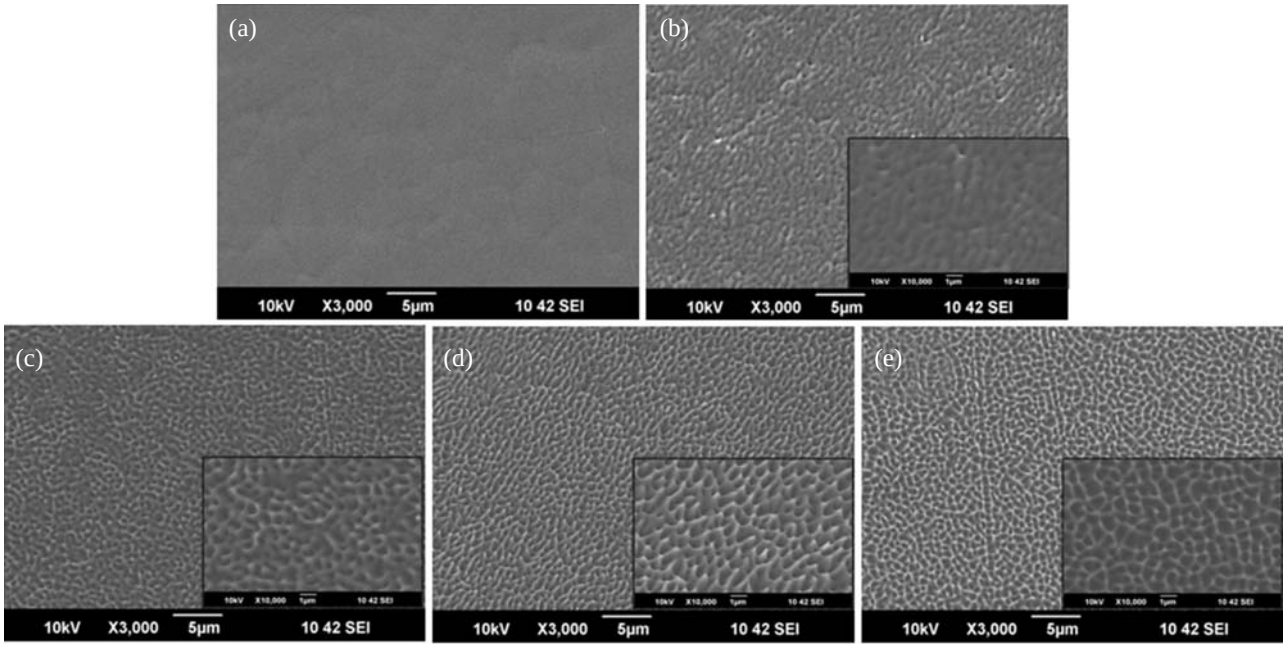

Fig. 1. SEM images of the control (a) and implanted PFA films at fluences of 4×10^{16} (b), 5×10^{16} (c), 6×10^{16} (d), and 7×10^{16} ion cm^{-2}. The insets exhibit the corresponding magnified images.

tion were investigated using an X-ray Photoelectron Spectrometer (XPS, MultiLab 2000, Thermo electron corporation, England) by employing Mg-Kα radiation.

RESULTS AND DISCUSSION

The changes in the surface morphology of PFA films after ion implantation were investigated by SEM analysis. As shown in Fig. 1(a), the control PFA film shows an even and smooth surface. After ion irradiation, the surface of the PFA films begins to change, becoming quite embossed at a fluence of 4×10^{16} ions cm^{-2}, and the surface roughness dramatically increased at a fluence higher than 7×10^{16} ions cm^{-2}, as shown in Fig. 1(b-e). This result indicates that the surface morphology of PFA films can be easily modified by ion implantation (Chen *et al.* 2007).

To confirm the change of the surface roughness after ion implantation, the root-mean-square (RMS) roughness was examined by AFM analysis. As shown in Fig. 2, in comparison to the roughness of the control PFA, the RMS values of the implanted PFA surfaces were significantly increased with an increase in the fluence, beyond which it decreased slightly (Lee *et al.* 2004). The surface morphology of the implanted PFA at a fluence of 6×10^{16} ions cm^{-2} showed the roughest surface, the RMS value of which was increased to 195 nm. This newly formed morphological structure in the PFA surface can be attributed to the sputtering of ions and atoms from the surface caused by a physical bombardment of Xe^{+} ions (Kwong *et al.* 2007).

To investigate the ion implantation effect on the wettability of the PFA surface, the changes in the water contact angles (CA) of the PFA surfaces after ion implantation were measured using a contact angle analyzer, and the results are shown in Fig. 3. The CA of the control PFA surface was about 103.6°. With an increase in the fluence, the CA of the implanted PFA films gradually increased at fluences below 6×10^{16} ions cm^{-2}, beyond which it decreased. The surface implanted at a fluence of 6×10^{16} ions cm^{-2} showed a superhydrophobic property with a maximum CA of 157.1°. Therefore, the superhydrophobic surface was successfully formed on the PFA surface. At a fluence of 7×10^{16} ions cm^{-2}, the CA was decreased slightly; however, a superhydrophobic property with a CA of over 150° was maintained. Based on the results of the surface roughness, the hydrophobicity of the implanted PFA surfaces was dependent on the RMS roughness, indicating that the surface roughness plays a crucial role in the formation of a superhydrophobic surface

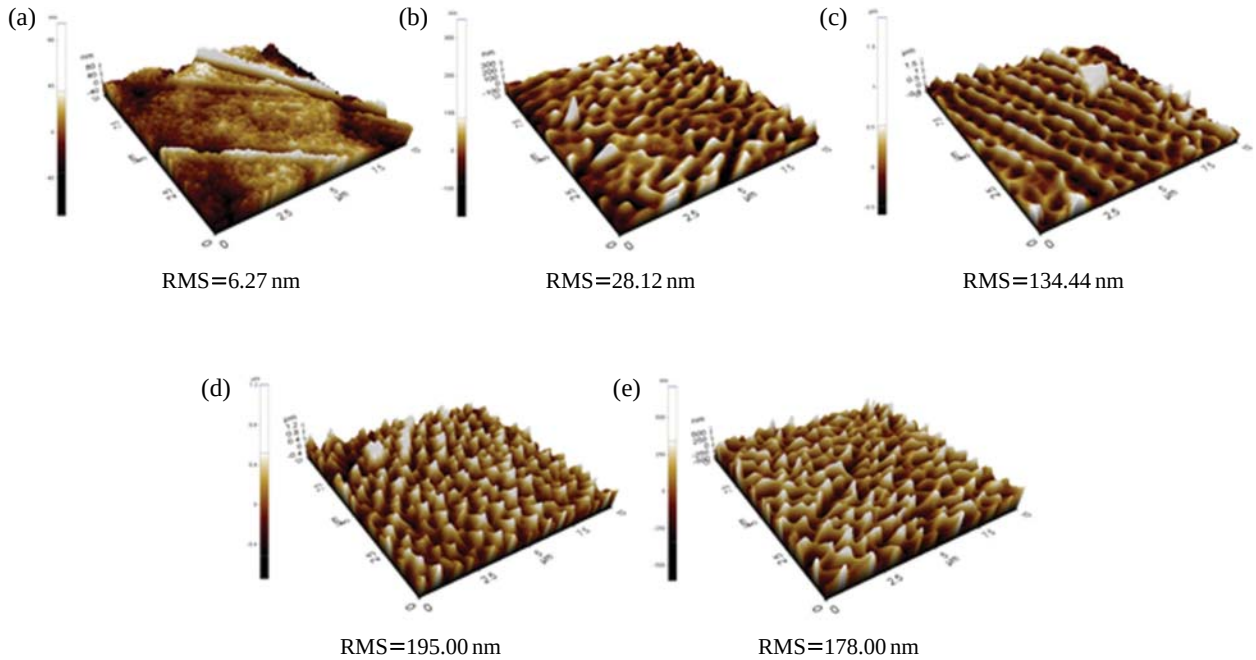

Fig. 2. AFM images and root mean square of surface roughness (RMS) of the control (a) and implanted PFA films at fluences of 4×10^{16} (b), 5×10^{16} (c), 6×10^{16} (d), and 7×10^{16} ion cm^{-2} (e).

(Zhang *et al.* 2004).

In addition to the surface morphology, the chemical changes are very important to understand the surface wettability because they can offer critical evidence about CA behavior. The changes in the chemical structure of the PFA surfaces after ion implantation were investigated by ATR-FT-IR analysis, and the results are shown in Fig. 4. In the spectrum of the control PFA, characteristic peaks corresponding to C-F asymmetric and symmetric stretching vibrations in CF_2 groups were observed at 1147, 1201, and 985 cm^{-1}, as shown in Fig. 4(a). After implantation, the FTIR spectrum of the PFA surfaces implanted at all fluences in Fig. 4(b-e) was not significantly different from that of the control PFA film (Okubo *et al.* 2008).

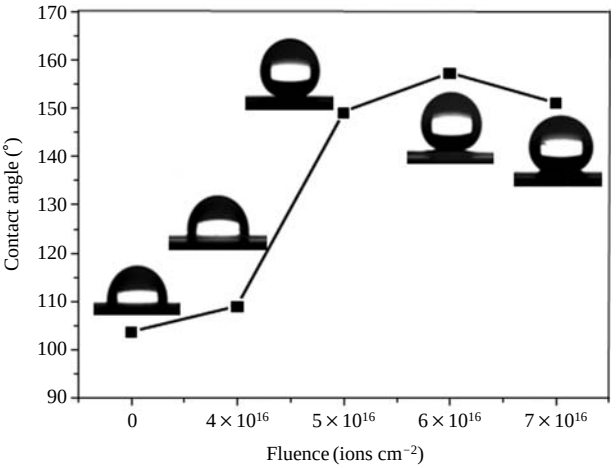

Fig. 3. The contact angles of the control and implanted PFA films as a function of the fluence.

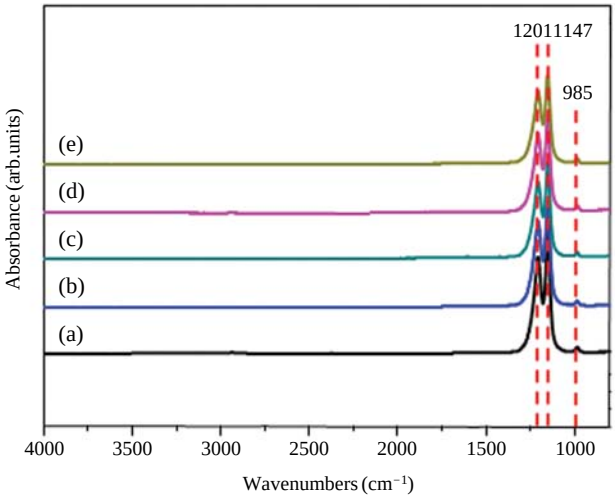

Fig. 4. FTIR spectra of the control (a) and implanted PFA films at fluences of 4×10^{16} (b), 5×10^{16} (c), 6×10^{16} (d), and 7×10^{16} ion cm^{-2} (e).

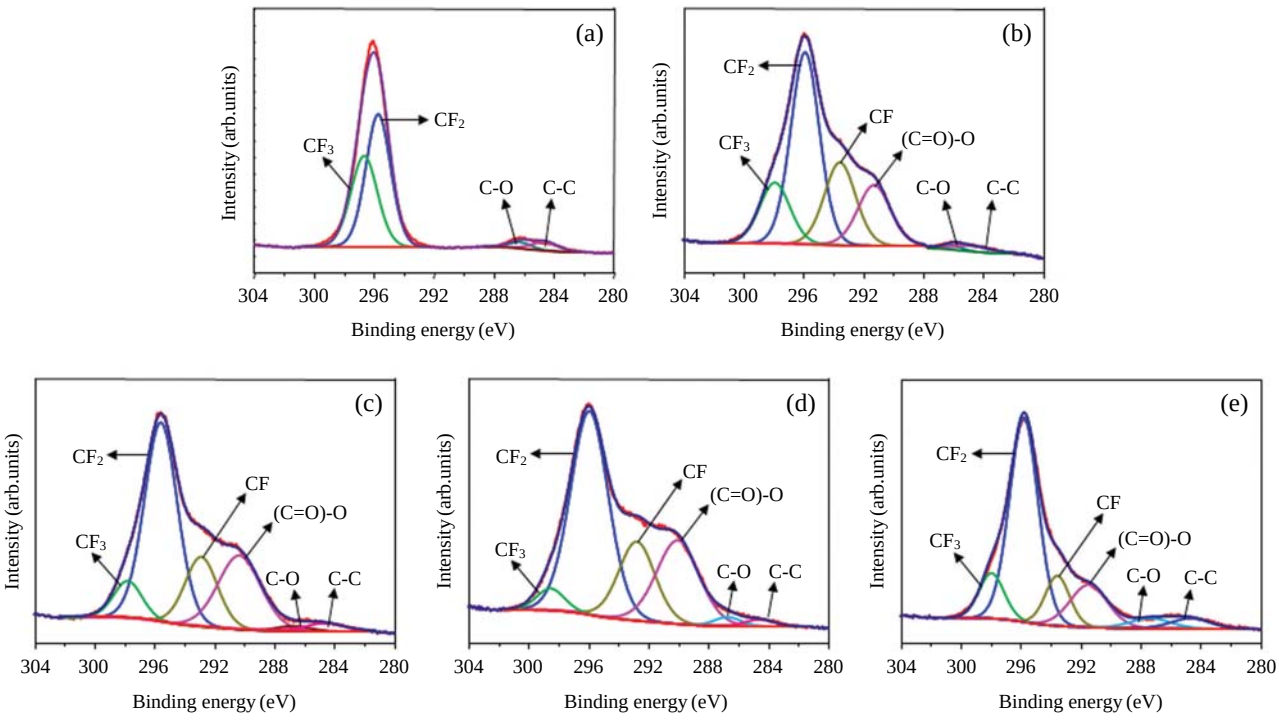

Fig. 5. C1s core-level spectra of the control (a) and implanted PFA films at fluences of 4×10^{16} (b), 5×10^{16} (c), 6×10^{16} (d), and 7×10^{16} ion cm^{-2} (e).

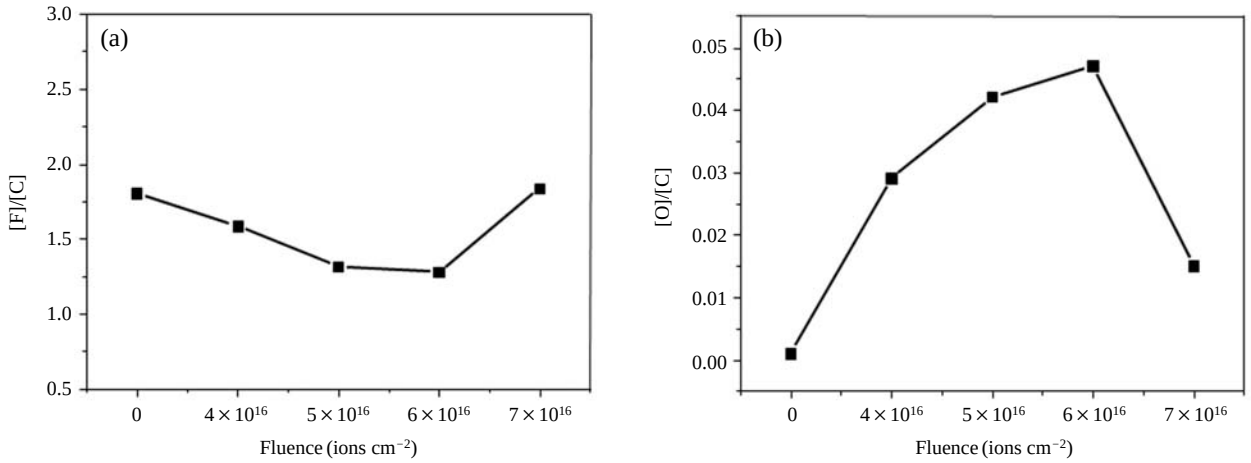

Fig. 6. [F]/[C] (a) and [O]/[C] (b) ratios of the control and implanted PFA films as a function of the fluence.

To further investigate the surface chemical composition of the PFA films after implantation, XPS analysis was carried out. Fig. 5 shows the C1s XPS spectra of control, and implanted PFA films at fluences of 4×10^{16}, 5×10^{16}, 6×10^{16}, and 7×10^{16} ions cm^{-2}. As shown in Fig. 5(a), the CF_3, CF_2, C-O, and C-C peaks of the control PFA film appeared at 296.4, 295.7, 286.3, and 284.8 eV, respectively. In the case of the implanted PFA films, the peaks of the CF were newly generated, which indicates that chain scission occurs and smaller polymer chains are created on the PFA surfaces during ion implantation. Moreover, a peak of (C=O)-O appeared noticeably, which was attributed to the oxidation resulting from the interaction of the free radicals created on the implanted PFA surface with oxygen in air, as shown in Fig. 5(b-e) (Choi *et al.* 2009).

The atomic composition ratio was also changed as a function of ion fluence. As shown in Fig. 6, in comparison to that of the control, the [F]/[C] atomic ratio of the implanted PFA films decreased to 1.274, while the [O]/[C] atomic ratio of the implanted PFA films dramatically increased to 0.047 with increasing the fluence below 6×10^{16} ions cm^{-2}. On the basis of the XPS result, it is considered that the wettability of the implanted PFA surfaces should be gradually increased owing to the increase in [F] and decrease in [O] atomic ratios to [C], respectively. Nevertheless, the surface implanted at a fluence of 6×10^{16} ions cm^{-2} showed a superhydrophobic property, indicating that the superhydrophobic property was crucially caused by the surface morphology rather than the surface chemical changes, although the changes of the chemical composition and surface morphology occurred simultaneously during the ion implantation. Additionally, by considering the results of the CA and XPS at 7×10^{16} ions cm^{-2}, although [F]/[C] and [O]/[C] atomic ratios were reversed, the superhydrophobicity with a CA of over 150° was maintained, which supports the dominant influence of the surface roughness on the superhydrophobicity (Lee *et al.* 2004).

CONCLUSION

In this study, the surface modification for the formation of superhydrophobic surfaces was successfully performed by ion implantation. The results of the SEM, AFM, and CA measurement analyses showed that the morphology of the PFA surface was remarkably changed to an extremely rough structures by ion implantation, and the superhydrophobic property was observed on the roughest PFA surface implanted at a fluence of 6×10^{16} ions cm^{-2}. The results of the XPS analysis also confirmed that the superhydrophobic property was crucially caused by the surface morphology rather than the surface chemical changes. The ion implantation-based approach suggested in this study provides a promising way to prepare superhydrophobic surfaces.

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