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Surface Modification of Polytetrafluoroethylene by Ion Implantation

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Abstract − The surface property of polytetrafluoroethylene (PTFE) films implanted with Ar^+ ions has been investigated. After ion implantation, various chemical bonds and damaged surface structures were observed. The hydrophilicity of the implanted PTFE increased with increasing fluence up to 5×10^{16} ions · cm^{-2}.

Key words : Ion implantation, Polytetrafluoroethylene, Surface property

INTRODUCTION

Polytetrafluoroethylene (PTFE) is widely used for a variety of applications due to an outstanding combination of chemical and physical properties such as high-temperature stability, excellent chemical resistance, low dielectric constant, and low frictional coefficient (Zhang *et al*. 2002). However, its poor adhesion property and poor wettability restrict its application in some fields (Kim 2000). Thus, to improve those defects, it is necessary to modify surface characteristics by means of surface modification techniques.

There are a number of surface modification techniques including plasma treatment, chemical or electrical treatment, and particle beam (electron, neutron, ion and proton) irradiation treatment. Among them, ion irradiation (or, ion implantation) technique is particularly attractive because of its flexibility, effectiveness, and environmentally friendly nature compared with other techniques (Guzman *et al*. 2002). Moreover, it is more fascinating tool to modify the properties of near-surface regions of materials while conserving bulk properties due to its shallow penetration depth ranging from several nano-meters to several micrometers.

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With this merit, ion implantation technique has been applied to modify surface characteristics of numerous materials such as polymers, metals, ceramics and so on (Ikeyama *et al*. 1996; Bai *et al*. 2001; Dworecki *et al*. 2001; Yoshinari *et al*. 2001; Suzuki 2003; Guenther *et al*. 2004; Kane *et al*. 2005; Jagielski *et al*. 2006; Park *et al*. 2006; Budzynski *et al*. 2007; Liu *et al*. 2007). With regard to the application in polymers, this technique has been utilized to control optical (Ikeyama *et al*. 1996), chemical (Colwell *et al*. 2003), physical (Guenther *et al*. 2004), mechanical (Park *et al*. 2006), and electrical (Dworecki *et al*. 2002) properties as well as bio-compatibility (Suzuki *et al*. 2002; Jagielski *et al*. 2006).

In this article, we implanted Ar^+ ions onto the surface of PTFE films with an energy level of 150 keV. The surface property of PTFE samples were observed by means of scanning electron microscopy (SEM) analysis, X-ray photoelectron spectroscopy (XPS) analysis, and contact angle measurement.

MATERIALS AND METHODS

Ion implantation

Commercial PTFE films (Hanmi rubber and Plastics co., thickness 0.2 mm) were cut into small pieces of 40×40 mm^2. They were cleaned ultrasonically for 30 minutes with

acetone and extensively rinsed with ethanol. All samples were finally dried in an oven at 100°C in atmospheric pressure for 1.5 h. The implantation was carried out with Ar ion at an energy of 150 keV with fluence ranging from 1×10^{14} to 1×10^{17} ions · cm^{-2} at room temperature. The pressure in the implanter target chamber was 1×10^{-5} to 1×10^{-6} Torr, and the ion beam current density was about 1 μA · cm^{-2} to prevent the increase of the specimen temperature.

Measurements

The surface morphology was investigated by using scanning electron microscopy (SEM, Jeol, JSM-6390). Gold was deposited on the specimen preventing charge-up by electron-beam. The chemical state environment of ion implanted PTFE surface was investigated using X-ray photoelectron spectrometer (MultiLab 2000, Thermo Electron Corporation, England) employing Mg-K_α radiation. The applied power was 14.5 keV and 20 mA and the base pressure of the analysis chamber was less than $\sim 10^{-9}$. The wettability of the samples was determined by measuring the water contact angle. The contact angle was measured with a sessile drop method using a Contact Angle Analyser (Pheonix 300, Surface Electro Optics Company). Redistilled water (10 μl) was gently placed on the ion implanted surface. Each value of the contact angles was taken as an average value measured from five different samples fabricated under the same experimental conditions.

RESULTS AND DISCUSSION

Surface morphology

We observed the surface morphological changes of the PTFE by varying fluence ranging from 1×10^{14} to 1×10^{17} ions · cm^{-2} at an energy level of 150 keV. Fig. 1. shows the SEM images of pristine and Ar^+ implanted samples. For pristine sample and implanted sample with fluence of 1×10^{14} ions · cm^{-2}, there was no significant change in the surface morphology. Both samples exhibited plain surface. Above the fluence of 5×10^{14} ions · cm^{-2}, the surface begun to show modified topography. At 5×10^{14} ions · cm^{-2}, the surface exhibited moderately flat appearances with very irregularly placed small-sized pores or dots. As the fluence increased to the value of 5×10^{16} ions · cm^{-2}, the roughness was also increased and pore size became more larger. In case of the sample at 5×10^{16} ions · cm^{-2}, the surface exhibited relatively dark color and showed more distorted or damaged morphology. The surface morphology has been changed with increasing fluence due to chain scission, carbonization, and/or ion erosion phenomena (Zhang *et al*. 2002). At 1×10^{17} ions · cm^{-2}, the topography of implanted PTFE sample showed similar surface compared with the sample of the fluence of 5×10^{16} ions · cm^{-2}.

Surface chemical composition

XPS analysis was performed to investigate the chemical

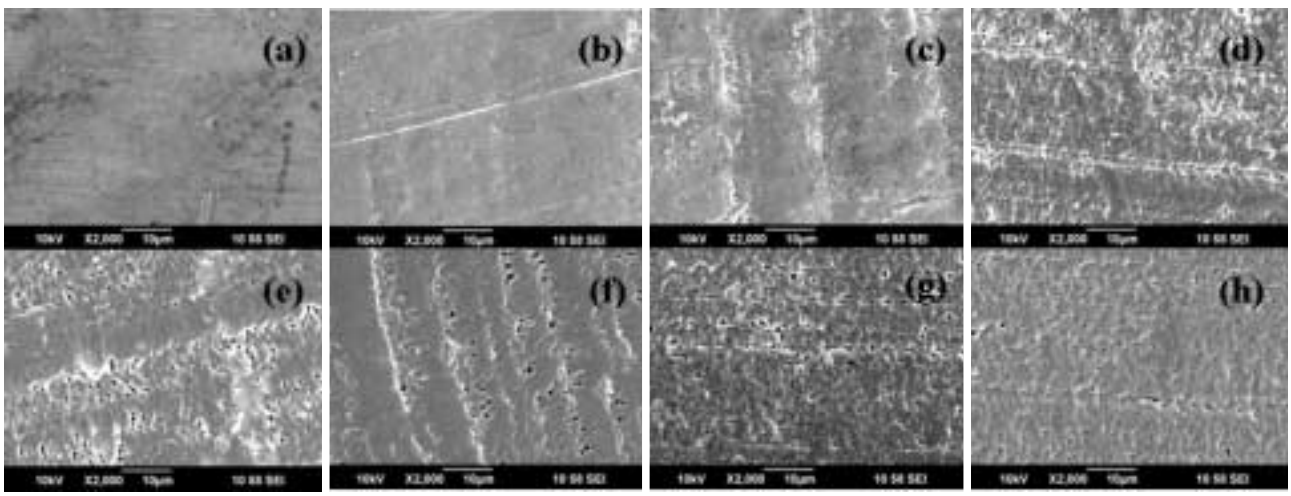

Fig. 1. SEM images of pristine PTFE (a) and Ar^+ implanted PTFE with 1×10^{14} ions cm^{-2} (b), 5×10^{14} ions cm^{-2} (c), 1×10^{15} ions cm^{-2} (d), 5×10^{15} ions cm^{-2} (e), 1×10^{16} ions cm^{-2} (f), 5×10^{16} ions cm^{-2} (g), and 1×10^{17} ions cm^{-2} (h).

composition of the PTFE samples. Table 1 shows the relative intensity of C1s, F1s, and O1s peaks (%) and the F/C and O/C atomic ratios of pristine and implanted samples. The observed data exhibited the increased C1s peak ratio and decreased F1s peak ratio with increasing fluence, which resulted in the decreased F/C ratio. The value of O/C ratio was, on the whole, increased with increasing fluence. The increased O/C ratio and decreased F/C ratio denote the oxidation and de-fluorination of the surface of implanted PTFE, respectively.

Table 1. The relative intensity of C1s, F1s, and O1s peaks (%) and the F/C and O/C atomic ratios of pristine and ion implanted samples.

Ion fluence (ions · cm^{-2})	0	1×10^{14}	5×10^{14}	1×10^{15}	5×10^{15}	1×10^{16}	5×10^{16}	1×10^{17}
C1s	36.69	35.98	44.86	50.33	71.61	79.84	81.11	84.48
CF3 bond		1.67	5.51	3.20				
CF2 bond	22.41	20.31	15.49	15.37	2.24			
CF bond					2.16		2.59	
C-C	14.28	8.33	5.73	17.86	46.24	63.73	60.62	69.29
C=C		1.72	2.05	1.92		1.84		
C=O		1.30	7.50	5.39	6.38	3.95	4.14	5.25
C-O		2.65	8.58	6.59	14.39	10.32	13.76	9.94
F1s	63.30	61.98	53.04	45.42	15.41	6.27	5.84	2.15
O1s		2.04	2.1	4.24	12.98	13.89	13.07	13.37
[F] / [C] ratio	1.72	1.72	1.18	0.90	0.21	0.08	0.07	0.03
[O] / [C] ratio		0.05	0.05	0.08	0.18	0.17	0.16	0.15

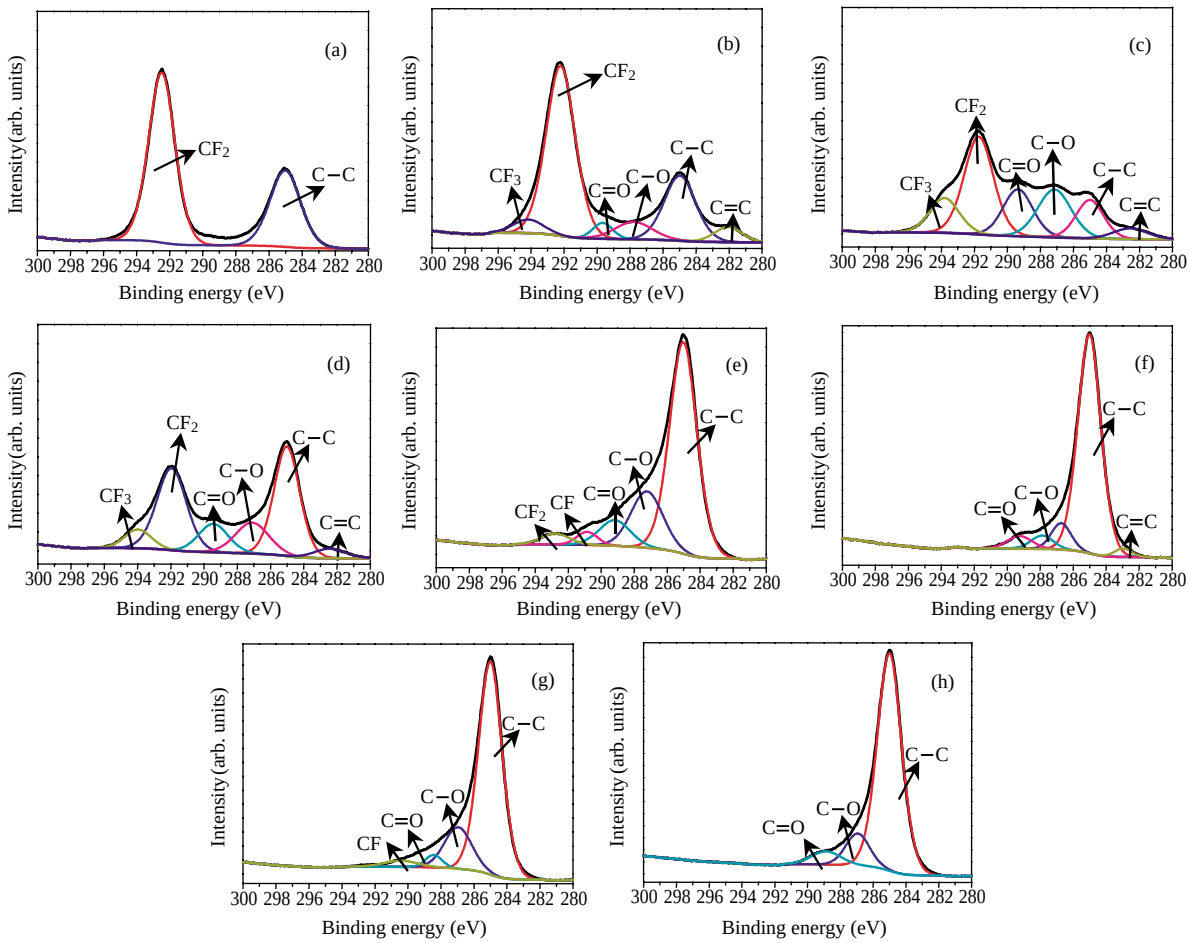

Fig. 2. XPS spectra of C1s for pristine PTFE (a) and Ar^+ implanted PTFE with 1×10^{14} ions cm^{-2} (b), 5×10^{14} ions cm^{-2} (c), 1×10^{15} ions cm^{-2} (d), 5×10^{15} ions cm^{-2} (e), 1×10^{16} ions cm^{-2} (f), 5×10^{16} ions cm^{-2} (g), and 1×10^{17} ions cm^{-2} (h).

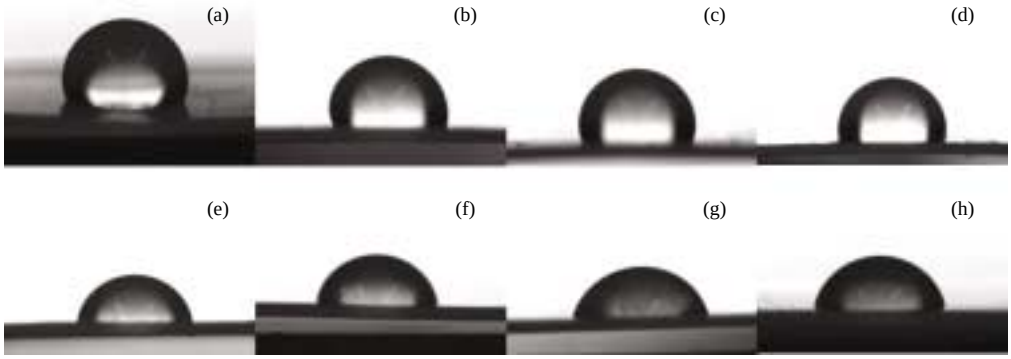

Fig. 3. Water droplet images of pristine PTFE (a) and Ar^+ implanted PTFE with 1×10^{14} ions cm^{-2} (b), 5×10^{14} ions cm^{-2} (c), 1×10^{15} ions cm^{-2} (d), 5×10^{15} ions cm^{-2} (e), 1×10^{16} ions cm^{-2} (f), 5×10^{16} ions cm^{-2} (g), and 1×10^{17} ions cm^{-2} (h).

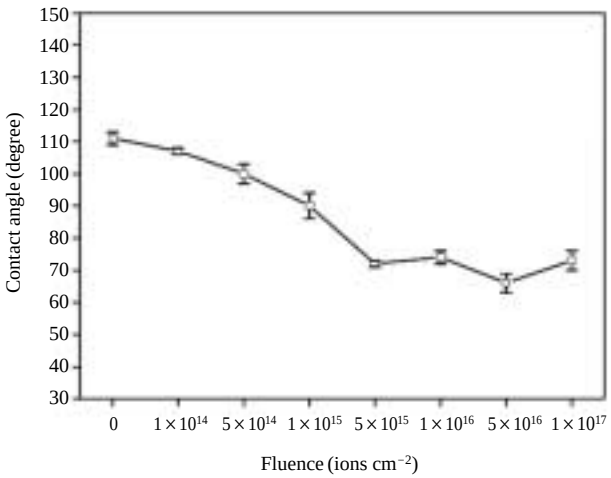

Fig. 4. Water contact angle as a function of fluence.

Fig. 2 shows the XPS spectra of C1s for pristine PTFE and Ar^+ implanted PTFE samples with fluence ranging from 1×10^{14} ions · cm^{-2} to 1×10^{17} ions · cm^{-2}. The C1s peaks at 292.5 eV for the CF2 bond and at 285 eV for the C-C bond were observed on pristine sample as shown in Fig. 2, and the binding energy difference between two was about 7.5 eV. The arbitrary change in C1s peaks was found due to the variation in intensity of CF_3, CF_2, CF, C-C, C=C, C-O, and C=O bonds with increasing fluence. De-fluorination, chain-scission, cross-linking, carbonization, and chemical reaction seem to be the main reason for the change of chemical bonds (Koh *et al*. 1997; Zhang *et al*. 2002). One can see the formation of C-O bond and the intensified C-C bond with increasing fluence. The formation of C-O bond resulted from the generation of free radicals due to the electronic excitation (Zhang *et al*. 2002), which react with oxygen in air when extracting the implanted samples from Target Chamber. And, chain-scission and carbonization seem to be the dominant reason for the increased C-C bond.

Wettability

Fig. 3 and 4 show the water droplet images and contact angle values (degree) between the water droplet and the surface of pristine and Ar^+ implanted PTFE samples. The water contact angle of pristine PTFE sample was about 111°, and this high contact angle is very special among polymeric materials. It implies that PTFE has a very low surface energy (Kim 2000). With increasing fluence, the water contact angle was decreased to 66° at 5×10^{16} ions · cm^{-2}, and it slightly increased to 73° at 1×10^{17} ions · cm^{-2}. The decrement of contact angle means the surface of implanted PTFE sample becomes more hydrophilic, and the increment of that value denotes that surface of the implanted PTFE sample exhibits more hydrophobicity due to the carbonization at the higher fluence.

CONCLUSIONS

Ion implantation technique was applied to PTFE sheets by means of Ar^+ ions at an energy level of 150 keV with fluence range from 1×10^{14} to 1×10^{17} ions · cm^{-2}. The SEM images exhibited the discolored and deformed morphologies with randomly situated irregular-sized pores, as the fluence increased. For XPS analysis, it appears that due to de-fluorination, chain-scission, cross-linking, carbonization, and chemical reaction, a variety of phenomena, such as increased O/C ratio, decreased F/C ratio, formation and

change of C-O bond, and variation of C-C bond, were occurred. With increasing fluence, the water contact angle of PTFE sample was decreased to about 66° at 5×10^{16} ions · cm^{-2}, which denotes the hydrophobicity of PTFE has changed to the hydrophilicity by means of ion implantation. Additional work is underway to investigate bio-compatibility of Ar ion implanted PTFE film for artificial blood vessels, cell patterning, cell chips, etc.

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