

# Surface Treatment of Polymer Film by Atmospheric Pulsed Microplasma: Study on Gas Humidity Effect for Improving the Hydrophilic Property

著者	Shimizu Kazuo, Umeda Akira, Blajan Marius
journal or publication title	Japanese Journal of Applied Physics
volume	50
number	8
page range	08KA03
year	2011-08-22
出版者	Japan Society of Applied Physics
権利	(C) 2011 The Japan Society of Applied Physics
URL	<a href="http://hdl.handle.net/10297/6173">http://hdl.handle.net/10297/6173</a>

doi: 10.1143/JJAP.50.08KA03

Surface Treatment of Polymer Film by Atmospheric Pulsed Microplasma :  
Study on Gas Humidity Effect for Improving the Hydrophilic Property

Kazuo Shimizu\*, Akira Umeda , Marius Blajan

*Innovation and Joint Research Center, Shizuoka University,*

*Hamamatsu, 432-8561, Japan*

\*E-mail address : [shimizu@cjr.shizuoka.ac.jp](mailto:shimizu@cjr.shizuoka.ac.jp)

Surface treatment of a polyethylene naphthalate (PEN) film by atmospheric pulsed microplasma with humid Ar gas was experimentally investigated. A Marx generator with metal-oxide semiconductor field-effect transistor (MOSFET) switches that generates negative pulses was used for generating microplasma. Hydrophilization was estimated by measuring contact angle before and after the microplasma surface treatment by a remote process. The initial contact angle was about 76°. The minimum contact angle of about 20° was obtained after a treatment, a discharge voltage of -1.3 kV negative pulse, a frequency of 24 kHz, a gas relative humidity of about 60%. Analysis by X-ray photoelectron spectroscopy (XPS) showed a decrease in the C 1s peak corresponding to the C-H bond or C-C bond, and increases in the O 1s peaks corresponding to the C=O bond or O-H bond.

## 1. Introduction

Polymer materials have a wide field of applications, for example, in food industry, medical equipment, electronic components, and information technology industry. The surface of polymer materials is chemically stable, but this characteristic makes it difficult to paint on it or to adhere for practical usage. Plasma treatment has been studied to modify polymer surface characteristics<sup>1-7)</sup>. Introduction of hydrophilic functional groups on the polymer surface is an important factor for the improvement of hydrophilic property; therefore, a chemically reactive gas such as O<sub>2</sub><sup>8)</sup>, acetic acid<sup>9)</sup>, acrylic acid<sup>10)</sup>, or water vapor<sup>11)</sup> was used as a discharge gas in surface treatment. Also, gas humidity effect for polymer film surface treatment was investigated<sup>12)</sup>.

A polyethylene naphthalate (PEN) film was used as a target material in this study. PEN has superior mechanical, chemical, and electrical properties among polymers<sup>13)</sup>. Therefore, the PEN film has a wide field of applications such as magnetic recording tapes for computers, capacitors and artificial skin.

For industrial applications, a plasma process in atmospheric pressure is desired to minimize the cost and process time. The microplasma studied in our group is atmospheric pressure non-thermal plasma, which requires a relatively low discharge voltage. Atmospheric microplasma is a type of dielectric barrier discharge.

The remote microplasma method, which we propose to be applied for the treatment of PEN film, removes the probability of damaging the exposed polymer by the formation of micro discharges; thus, the film will be exposed only to various active species<sup>14)</sup>. The discharge gap is set to an order of micrometers, which is extremely low, enabling the plasma to start at discharge voltage of approximately 1 kV.

In this study, the surface treatment of a PEN film was experimentally investigated using pulsed atmospheric microplasma with humid Ar gas compared with dry Ar gas.

## 2. Experimental Method

### 2.1 Microplasma electrodes

A schematic image of the microplasma electrodes and surface treatment of the PEN film is presented in Fig. 1. The electrodes have holes with a diameter of 1.1 mm for the gas to flow. The metallic electrodes used were covered with a dielectric layer. The electrodes were placed facing each other with a spacer (thickness 100  $\mu\text{m}$ ) in between. Owing to small discharge gaps (0-100)  $\mu\text{m}$  and to the assumed specific dielectric constant of  $\epsilon_r = 10^4$ , a high-intensity electric field ( $10^7$ - $10^8$  V/m) could be obtained with a relatively low discharge voltage of approximately 1 kV. Streamers were generated between the electrodes, which generate various radicals and ions that could affect a target surface<sup>15, 16)</sup>.

## 2.2 Marx generator

The Marx generator with MOSFET switches, which generates a negative pulse was used for generating microplasma at atmospheric pressure. Figure 2 shows a Marx generator circuit for an experiment. When the MOSFET switches ( $Tr_2$ ) are opened, the capacitors linked in the parallel connection are charged at a given voltage  $V_{DC}$ . By turning on the switches, the capacitors discharge in a series connection. The output voltage is  $V_{DC}$  multiplied by the number of capacitors<sup>17)</sup>.

An experimental Marx generator with MOSFET switches was developed as a high-voltage supply generating microplasma. It has an output voltage of up to -2.0 kV peak (negative pulse; rise time, 40 ns; pulse width, 3  $\mu$ s; frequencies, 8-24 kHz).

Figure 3 shows the discharge voltage and discharge current waveforms at a discharge voltage of -1.3 kV and a discharge current of -2 A. Discharge current was observed at the rising part of discharge voltage. The discharge voltage and the corresponding discharge current were measured using a high-voltage probe (Tektronix P6015), a current probe (Tektronix P6022) and a digital oscilloscope (Tektronix TDS2024B).

## 2.3 Experimental setup

The experimental setup for surface treatment is presented in Fig. 4.

Ar gas was supplied from a gas cylinder as a process gas. Control of the gas humidity was performed by mixing dry Ar gas with humid Ar gas that passed through distilled water (an electric conductivity of 0.67  $\mu\text{S}/\text{cm}$ ). The humidity of process gas was changed from 0 to 60% relative humidity (RH) at room temperature and measured at the gas outlet of electrodes by a hygrometer. The contact angle of the water droplet on the PEN film was measured by a contact angle meter (Kyowa PCA-1). Chemical bonds after microplasma treatment were analyzed by X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-3400).

The emission spectra were measured using an intensified charge coupled device (ICCD) camera (Ryoshi giken SMCP-ICCD 1024 HAM-NDS/UV), a spectrometer (Ryoshi-giken VIS 351), and a photomultiplier tube (Hamamatsu Photonics R3896). A pulse generator (Tektronix AFG 3102) was used to trigger the Marx generator consisting of semiconductor switches and the ICCD camera. The obtained data were transferred to a computer (Fig. 5).

### **3. Results and Discussion**

#### **3.1 Contact angle measurement**

Surface wettability was evaluated by measuring static contact angle with a drop of distilled water on the sample PEN film surface. The contact angle was calculated by the

$\theta/2$  method. A change in contact angle was observed; the angle considerably decreased after 5 s of treatment using Ar with water vapor (60% RH), as shown in Fig. 6.

Figure 7 shows contact angle versus discharge voltage and discharge power at a frequency of 24 kHz, a distance of 1 mm between the electrode and the PEN film, a treatment time of 5 s and gas flow rate of 5 L/min.

The power was calculated using the following equation:

$$P = f \int V \cdot Idt \quad (1)$$

The energy consumption per pulse was about 92  $\mu$ J at a discharge voltage of -1.3 kV.

The energy consumption contained loss of displacement current and loss of pulse power supply. A decrease in contact angle was observed with the increases in discharge voltage and discharge power.

Figure 8 shows the gas humidity dependence of surface treatment at a discharge voltage of -1.3 kV and treatment time of 5 s.

A decrease in contact angle was observed with the increase in process gas humidity. A contact angle of about 20° was obtained at a process gas humidity of about 60% RH and a decrease of 10° was obtained at a process gas humidity of 0% RH.

Figure 9 shows the relationship between contact angle and treatment time, at a discharge voltage of -1.3 kV and gas humidities of 0% RH and about 60% RH.

The initial contact angle of the PEN film was about 76°. A decrease in contact angle was observed with the increase in treatment time. Also, we observed that using humid Ar plasma was more effective than using dry Ar plasma for surface treatment. Under both conditions, contact angle change was saturated at a treatment time of 5 s.

### 3.2 Emission spectroscopy

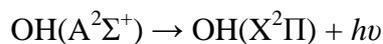
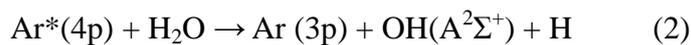
A higher humidity leads to an improvement of PEN film wettability. That could be explained by the role of OH radicals in the process. Figures 10 and 11 show the emission spectra of dry Ar plasma and humid Ar plasma, respectively at a gas humidity of about 60% RH.

Figure 10 shows the intensity of excited Ar atoms generated by electron collision<sup>18</sup>.

The decrease in excited Ar atom peaks was observed by humidification of Ar gas.

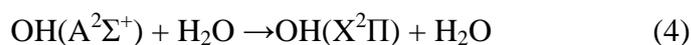
The presence of OH radicals was observed in dry Ar plasma and humid Ar plasma (Fig.

11) in accordance with reactions (2) and (3) of spontaneous emission.



spontaneous emission (3)

The intensity of OH radicals and excited Ar atoms was higher for dry Ar but the effect on the PEN film was stronger at a high humidity. In dry Ar, the emission of OH is attributed to the presence of water vapor in the reactor. According to Hilbert *et al.*,<sup>19)</sup> the intensity of OH(A<sup>2</sup>Σ<sup>+</sup>) emission increases as a function of water concentration up to 2000 ppm (=6.4% RH at 295 K) after which it starts to decrease because of the quenching effect of water (4):



The same authors<sup>19)</sup> measured the density of OH(X<sup>2</sup>Π) and they concluded that it is increasing with the increase in water density up to the saturation. Thus, a stronger effect on the PEN film surface at higher humidity is attributed to an increased density of OH(X<sup>2</sup>Π) regardless of reaction (3).

### 3.3 XPS analysis

Chemical bonds on the surface of the PEN film was analyzed by XPS. The untreated sample and treated samples, which were exposed to microplasma at a discharge voltage

of -1.3 kV, a frequency of 24 kHz, a distance of 1 mm between the electrode and the PEN film, a gas flow rate of 5 L/min, a treatment time of 5 s, and gas humidities of 0% and about 60% was analyzed.

Table I shows the elemental composition obtained using XPS of the PEN surface. The PEN surface is mainly composed of carbon and oxygen. We confirmed that the O/C ratio was increased by microplasma treatment.

Figure 12 shows C 1s peaks of the PEN surface. The decrease in the C 1s peak at 285 eV<sup>20,21)</sup>, which corresponds to the C-H or C-C bond was measured after microplasma treatment.

Figure 13 shows the O 1s peaks of the PEN surface. The increases in the O 1s peaks corresponding to the O-H bond (534 eV) and O=C bond (532 eV)<sup>22-24)</sup>, which are hydrophilic functional groups, were measured after microplasma treatment.

This could be the result of the excited Ar atoms responsible for attacking the C-H or C-C bond leading to the production of carbon radicals. These radicals could react with oxygen and water vapor in ambient air resulting in the incorporation of oxygen functional groups. The wettability of the PEN surface was improved by these reactions<sup>25)</sup>.

The peaks of the oxygen functional group after humid Ar treatment were higher than the

peaks of oxygen functional group after dry Ar treatment. This could be explained by the effect of the reactions of  $\text{OH}(X^2\Pi)$  and water vapors in the process gas. Water vapor on the PEN surface could be again reacted with the excited Ar atoms to produce  $\text{OH}(A^2\Sigma^+)$  radicals.

#### 4. Conclusions

The following conclusions were obtained from the series of experiments by atmospheric microplasma treatment.

- (1) The surface of the PEN film was modified by pulsed powered atmospheric microplasma.
- (2) A contact angle of about  $21^\circ$  was obtained at a discharge voltage of  $-1.3$  kV, a frequency of 24 kHz, a treatment time of 5 s with about 60% RH.
- (3) Humid Ar plasma was more effective than dry Ar plasma for improving the hydrophilic property of the PEN film surface.
- (4) XPS of the surface of the PEN film showed a decrease in the C 1s peak corresponding to the C-H or C-C bond and increases in the O 1s peaks corresponding to the O=C bond and O-H bond as a result of active species and radicals generated by microplasma.

- 1) T. Yuji, H. Akatsuka, N. Mungkung, B. W. Park and Y. M. Sung: *Journal of the Vacuum Society of Japan* **83** (2009) 124.
- 2) H. Yagi, A. Hatta and T. Ito: *Appl. Surf. Sci.* **137** (1999) 50.
- 3) J. F. Friedrich, R. Mix and G. Kühn: *Surf. Coat. Technol.* **200** (2005) 565.
- 4) L. J. Gerenser, J. M. Grace, G. Apai and P. M. Thompson: *Surf. Interface Anal.* **29** (2000) 12.
- 5) M. Okubo, M. Tahara, N. Saeki and T. Yamamoto: *Thin Solid Films* **516** (2008) 6592.
- 6) R. Prat, Y. J. Koh, Y. Babukutty, M. Kogoma, S. Okazaki and M. Kodama: *Polymer* **41** (2000) 7355.
- 7) C. Chaiwong, S. Tunma, W. Sangprasert, P. Nimmanpipug and D. Boonyawan: *Surf. Coat. Technol.* **204** (2010) 2991
- 8) Y. Setsuhara, K. Cho, K. Takenaka, A. Ebe, M. Shiratani, M. Sekine, M. Hori, E. Ikenaga, H. Kondo, O. Nakatsuka and S. Zaima: *Thin Solid Films* **518** (2009) 1006.
- 9) E. Anzawa, M. Kral, A. Ogino and M. Nagatsu: *Denki Gakkai Ronbunshi A* **129** (2009) 103 [in Japanese].
- 10) C. Vilani, D. E. Weibel, R. R. M. Zamora, A. C. Habert, C. A. Achete: *Appl. Surf. Sci.* **254** (2007) 131.
- 11) H. Xu, Z. Hu, S. Wu and Y. Chen: *Mater. Chem. Phys.* **80** (2003) 278.

- 12) T. Iijima, Y. Okita, T. Murata and E. Noda: *Denki Gakkai Ronbunshi A* **128** (2008) 251 [in Japanese].
- 13) L. D. Lillwitz: *Appl. Catal. A* **221** (2001) 337.
- 14) J. E. Gray, P. R. Norton and K. Griffiths: *Appl. Surf. Sci.* **217** (2003) 210.
- 15) K. Shimizu, T. Ishii and M. Blajan: *IEEE Trans. on Industry Applications Society* **3** (2010) 1125.
- 16) K. Shimizu, M. Yamada, M. Kanamori and M. Blajan: *IEEE Trans. on Industry Applications Society* **2** (2010) 641.
- 17) W. J. Carey and J. R. Mayes: *Conf. Re. Int. Power Modulator Symp.*, 2002, 625.
- 18) S. Iordanova and I. Koleva: *Spectrochim. Acta, Part B* **62** (2007) 344.
- 19) C. Hibert, I. Gaurand, O. Motret, and J. M. Pouvesle: *J. Appl. Phys.* **84** (1999) 7070.
- 20) J. E. Gray, P. R. Norton and K. Griffiths: *Thin Solid Films* **484** (2005) 196.
- 21) C. Cheng, Z. Liye and R. Zhan: *Surf. Coat. Technol.* **200** (2006) 6659
- 22) D. J. Upadhyay, N. Y. Cui, C. A. Anderson and N. M. D. Brown: *Polymer Degradation and Stability* **254** (2008) 2882.
- 23) N. De Geyter, R. Morent, C. Leys, L. Gengembre, E. Payen: *Surf. Coat. Technol.* **201** (2007) 7066.
- 24) M. Matsunaga and P. J. Whitney: *Polymer Degradation and Stability* **70** (2000) 325.

25) W. Chen, C. Jie-rong, L. Ru: *Appl. Surf. Sci.* **254** (2008) 2882.

Fig. 1 Schematic image of microplasma electrodes.

Fig. 2 Marx generator circuit.

Fig. 3 Discharge voltage and discharge current waveforms.

Fig. 4 Experimental setup for surface treatment.

Fig. 5 Experimental setup for emission spectroscopy analysis.

Fig. 6 Image of contact angle of a waterdrop on PEN film.

Fig. 7 Contact angle versus discharge voltage and discharge power.

Fig. 8 Contact angle as a function of process gas humidity.

Fig. 9 Relationship between contact angle and treatment time.

Fig. 10 Emission spectrum of excited Ar atoms.

Fig. 11 Emission spectrum of OH radical.

Fig. 12 C1s peaks of PEN films analyzed by XPS.

Fig. 13 O1s peaks of PEN films analyzed by XPS.

Table I Elemental composition on the PEN surface.

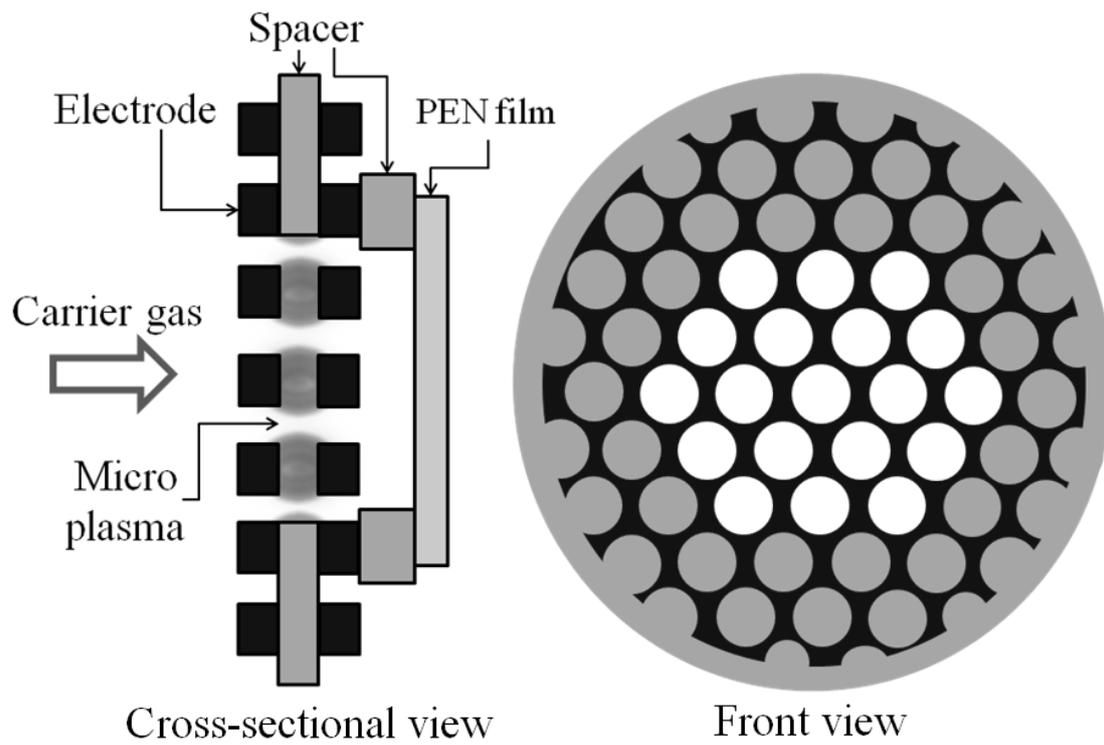


Fig. 1 Schematic image of microplasma electrodes.

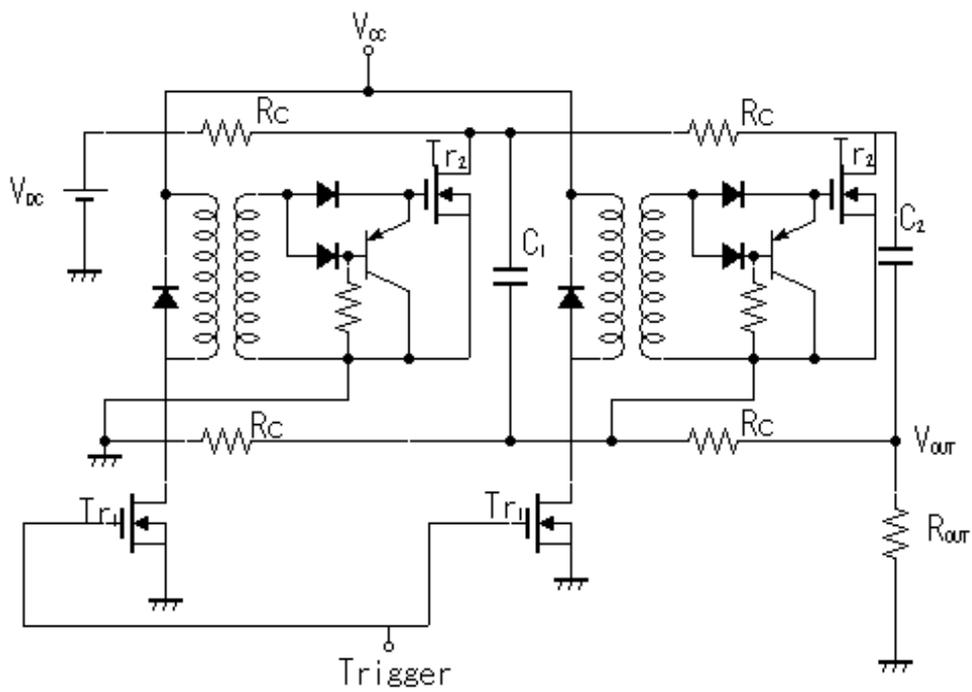
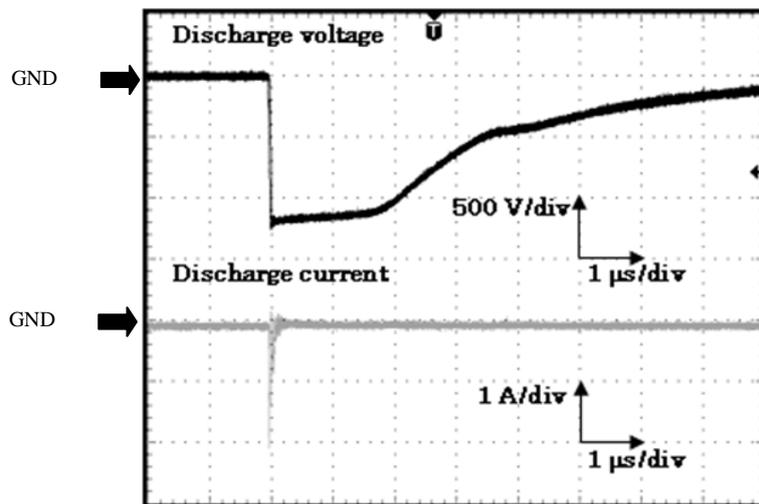
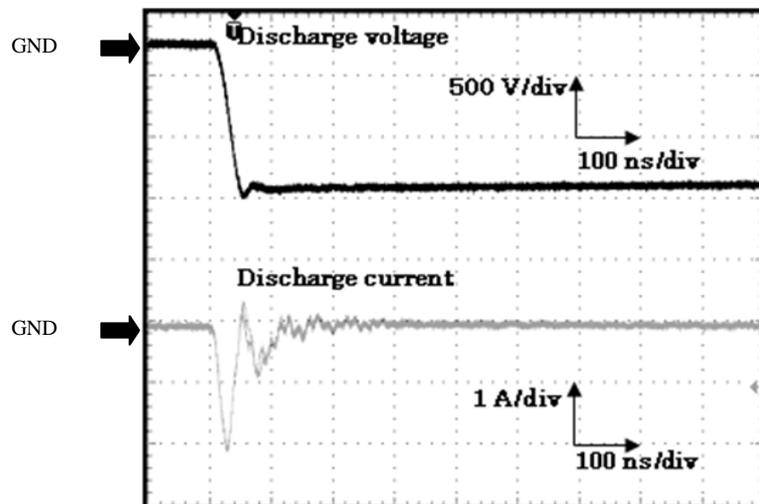


Fig. 2 Marx generator circuit.



(a) Time axis: 1.0  $\mu$ s



(b) Time axis: 100ns

Fig. 3 Discharge voltage and discharge current waveforms.

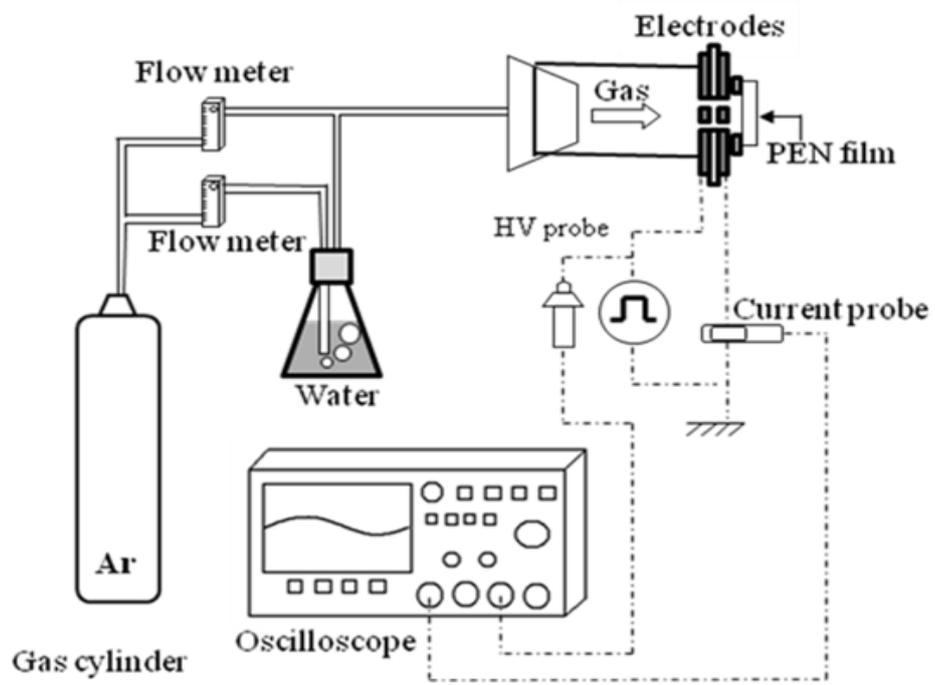


Fig. 4 Experimental setup for surface treatment.

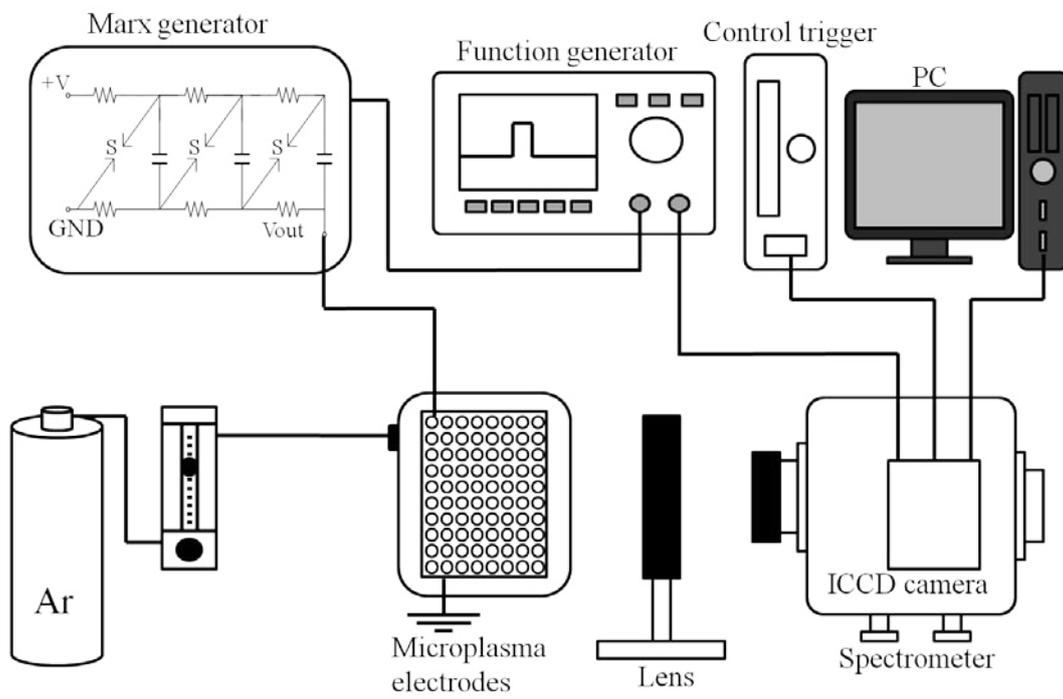


Fig. 5 Experimental setup for emission spectroscopy analysis.

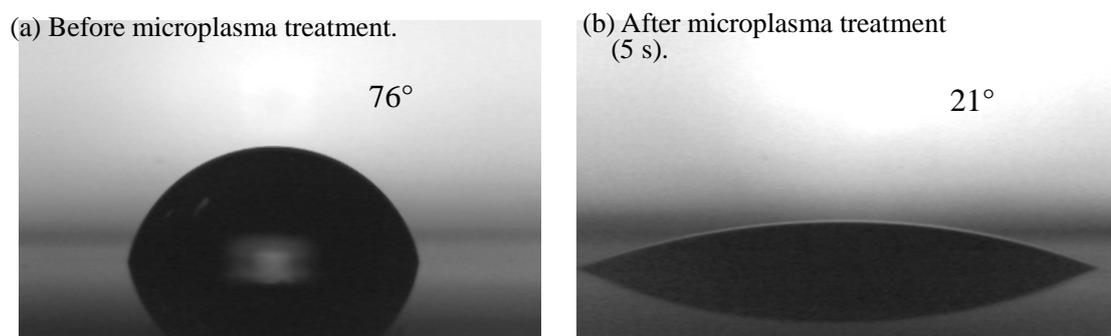


Fig. 6 Image of contact angle of a waterdrop on PEN film.

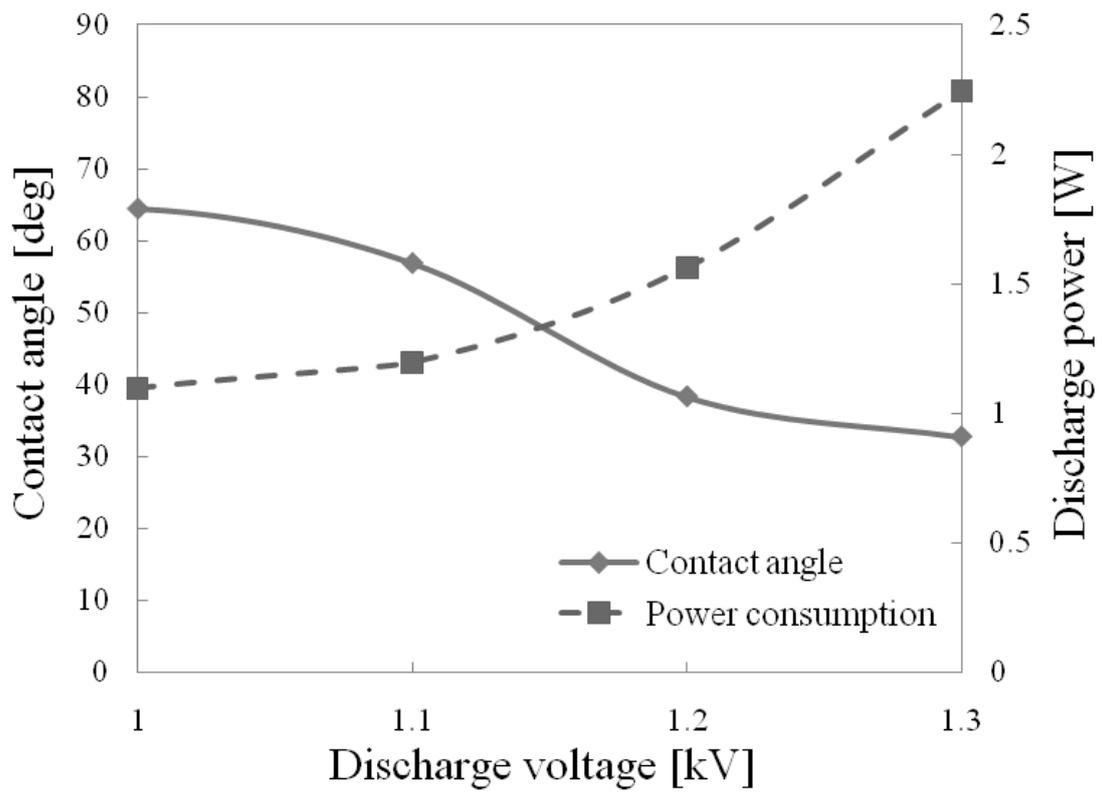


Fig. 7 Contact angle versus discharge voltage and discharge power.

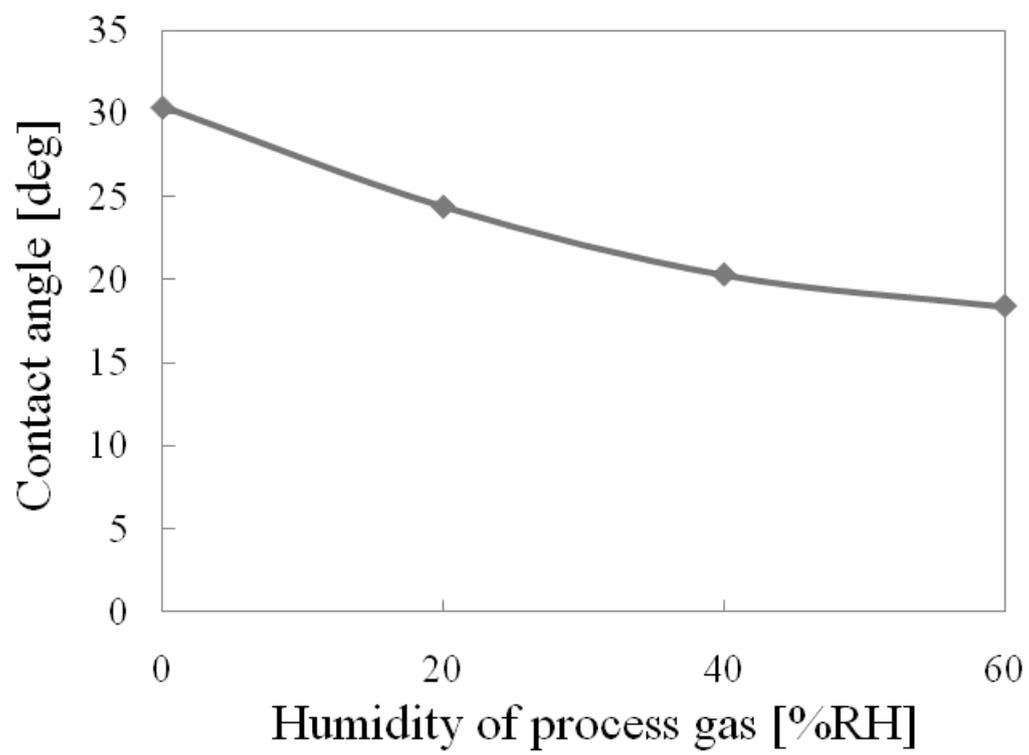


Fig. 8 Contact angle as a function of process gas humidity.

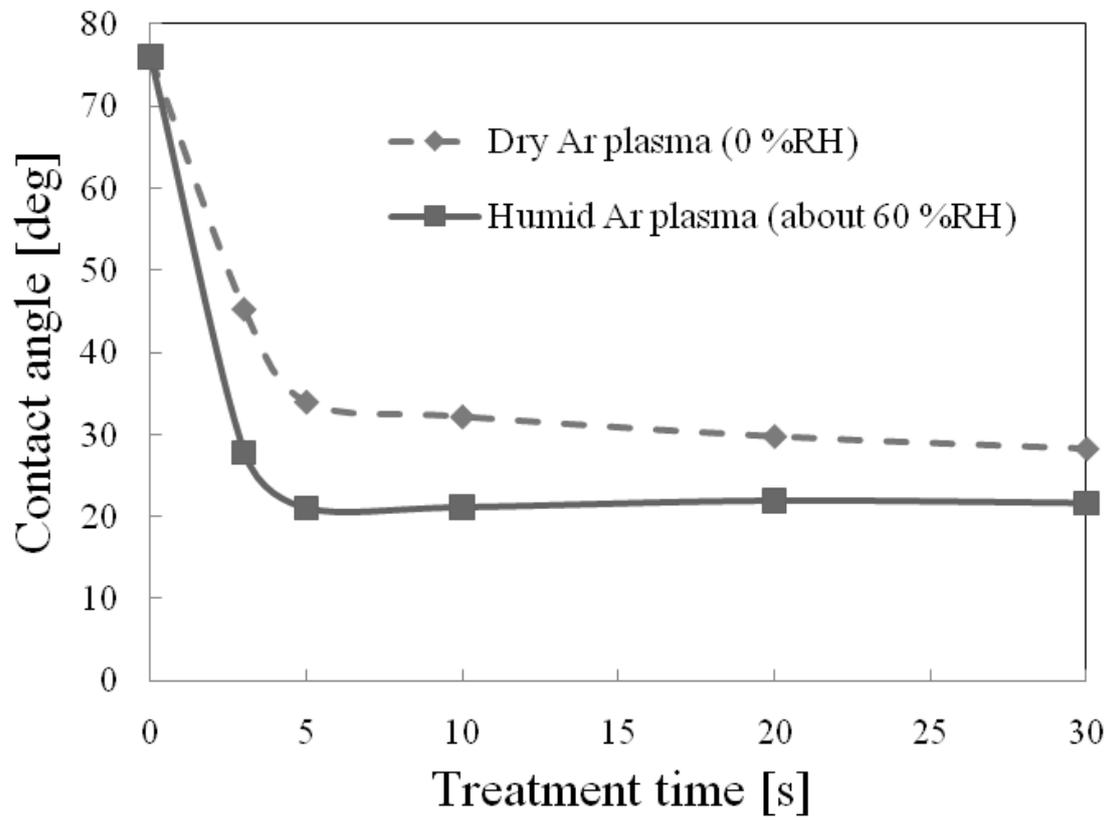


Fig. 9 Relationship between contact angle and treatment time.

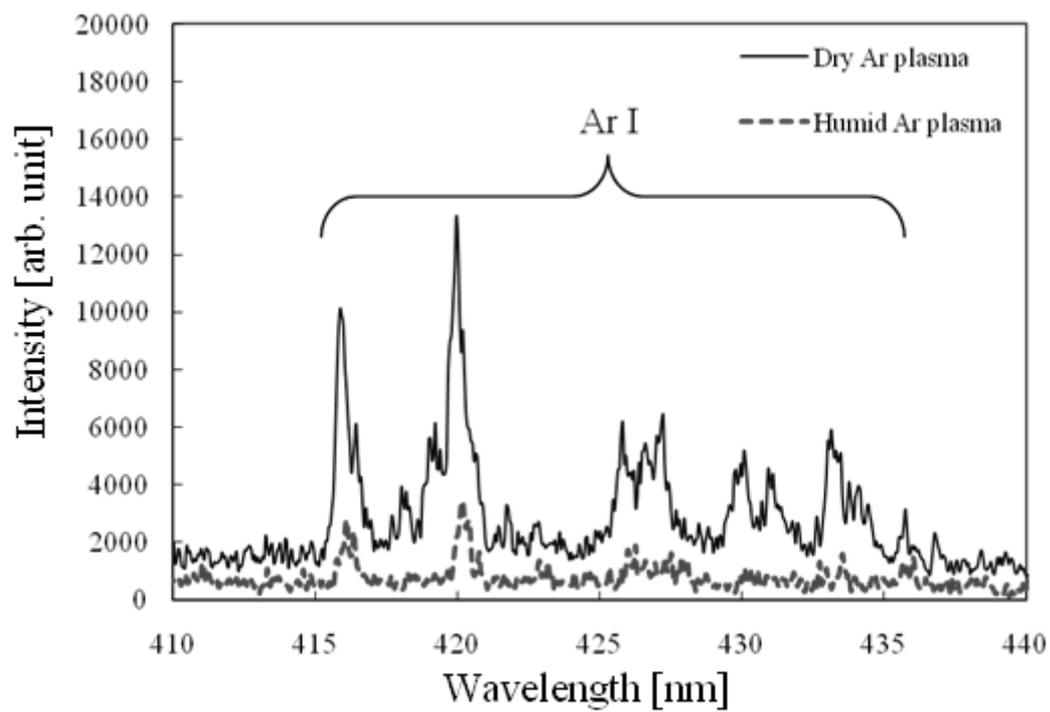


Fig. 10 Emission spectrum of excited Ar atoms.

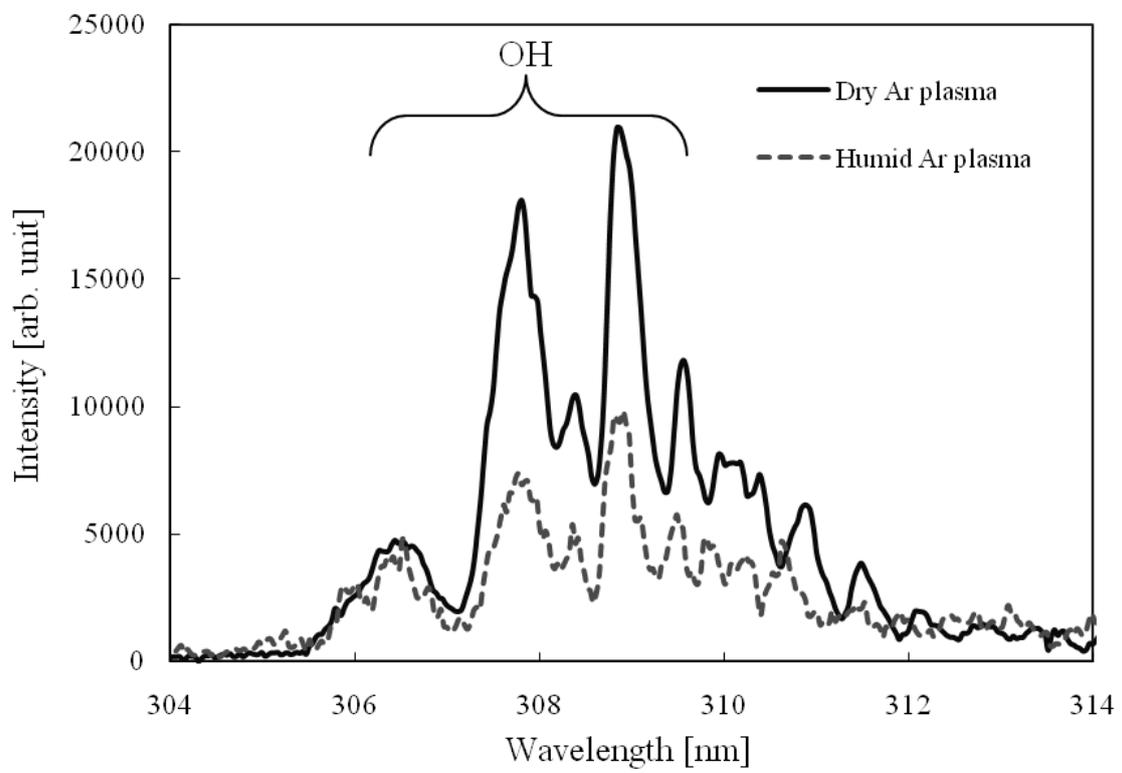


Fig. 11 Emission spectrum of OH radical.

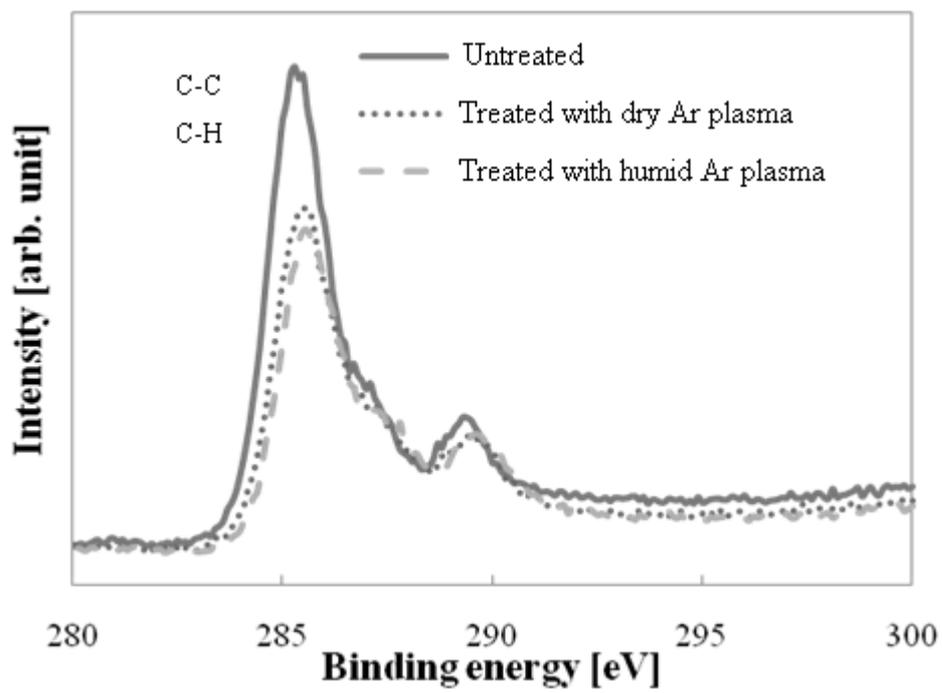


Fig. 12 C1s peaks of PEN films analyzed by XPS.

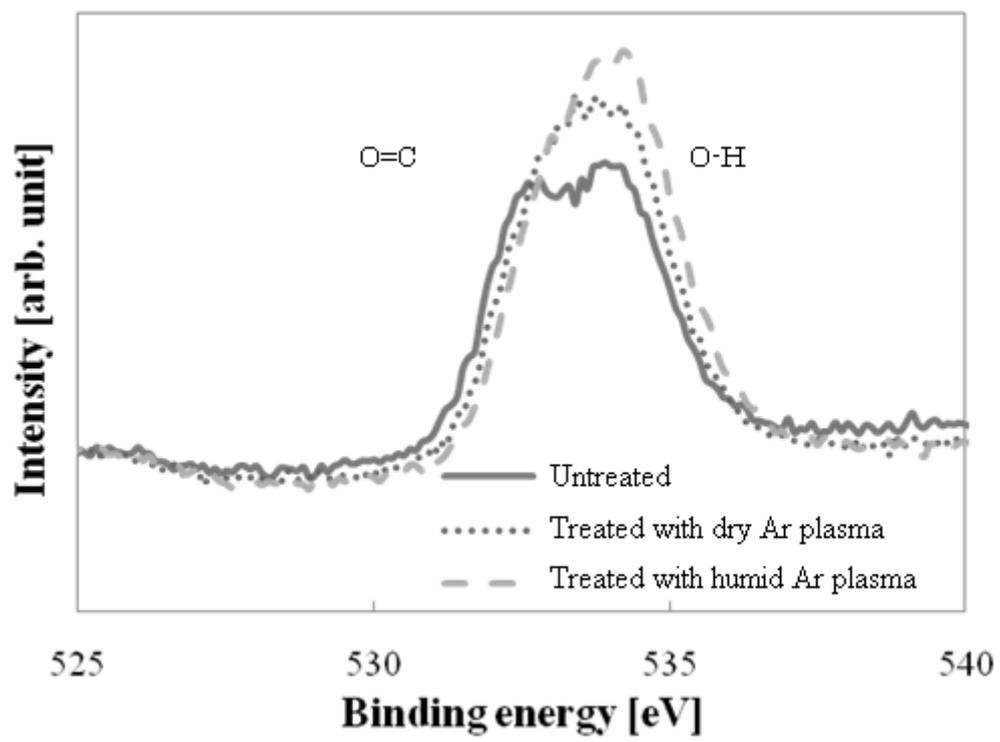


Fig. 13 O1s peaks of PEN films analyzed by XPS.

Table I Elemental composition on the PEN surface.

Sample	Atomic concentration (%)		O/C ratio
	C	O	
	Untreated	77.61	22.13
Treated with dry Ar	70.79	28.60	0.40
Treated with humid Ar	68.03	31.63	0.46