

Molecular-structure variation of organic materials irradiated with atmospheric pressure plasma

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Abstract. The effect of atmospheric pressure He plasma on the molecular structure of polyethylene terephthalate (PET) has been investigated. The plasma composition was analyzed using optical emission spectroscopy. In addition to strong He emission lines, lines due to O and N radicals were also detected. The change in the molecular structure of the PET film surface was investigated using Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. It was found that plasma irradiation led to oxidation and degradation of the surface due to chemical and physical effects of the active species. The results demonstrate the feasibility of observing the interaction of plasma with organic material on a local scale.

1. Introduction

Atmospheric pressure plasma is attractive for a variety of processes used in the fabrication of microelectronic devices, such as chemical vapor deposition (CVD), etching and ashing. It is a dense plasma that contains more activated species (ions, radicals) than conventional low-pressure plasma, and so can speed up plasma processes. Its application in the fields of medicine and biology has also expanded remarkably [1-11]. For medical applications, it is essential to perform fundamental studies at the molecular or atomic level in order to clarify the complex interactions of plasma, which contains ions, radicals, electrons and photons, with biomolecules such as DNA, amino acids and proteins. In previous studies, we have investigated physical and chemical interactions of plasma with the surface of soft materials, including biomolecules, using X-ray photoelectron spectroscopy (XPS). The plasmas studied were generated using low-inductance antenna (LIA) modules at low pressures of 0.13-13 Pa [12-25]. The present study extends this work by considering the interactions of atmospheric pressure He plasma generated in air with polyethylene terephthalate (PET) films. The chemical composition of the plasma was analyzed using optical emission spectroscopy (OES). The effect of the plasma on the PET films was investigated using XPS and Fourier transform infrared (FTIR) spectroscopy.

2. Experimental

The atmospheric pressure He plasma was generated using a micro-hollow cathode source, as shown in figure 1. The cathode had a hole diameter of 0.3 mm and was operated at a DC voltage of 1000 V. He gas was supplied at a flow rate of 1 slm. The OES analysis was carried out using a high-resolution fiber-optic spectrometer (Ocean Optics HR-4000). PET films with a thickness of 100 μm were exposed to the plasma. The change in the chemical bonding state of the nanoscale



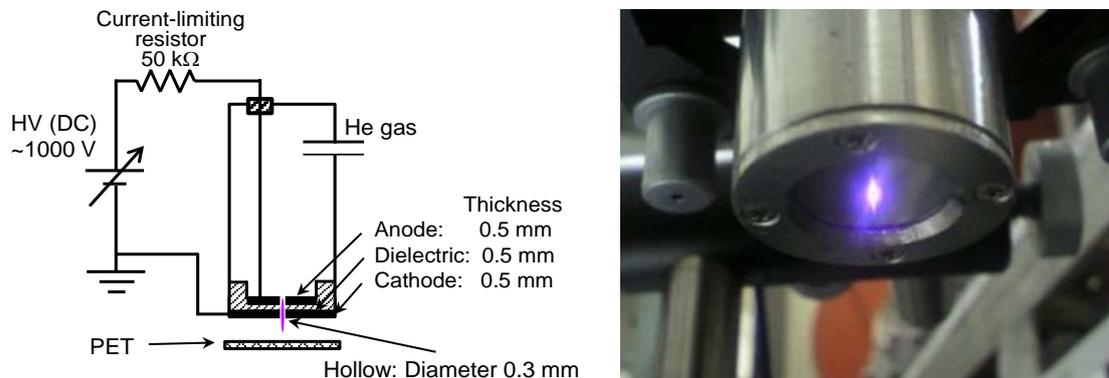


Figure 1. Schematic diagram and photograph of micro-hollow cathode plasma source.

surface layer exposed to the plasma was investigated using XPS (AXIS-165x, Shimadzu) with non-monochromatized Mg K α radiation (photon energy 1253.6 eV), and an FTIR system (Nicolet iS50, Thermo Scientific) equipped with an infrared microscope (Continuum, Thermo Scientific) with an attenuated total reflection (ATR) accessory.

3. Results

3.1 Optical emission spectroscopic analysis in atmospheric pressure He plasma

Figure 2 shows a typical OES spectrum of the atmospheric pressure He plasma. In addition to strong He lines, emissions due to O and N radicals and N₂ molecules can be observed. Furthermore, a broad peak attributed to NO_x is observed from 400 nm to 700 nm. The radicals are considered to be produced by excitation and dissociation of N₂ and O₂ when the plasma comes into contact with air.

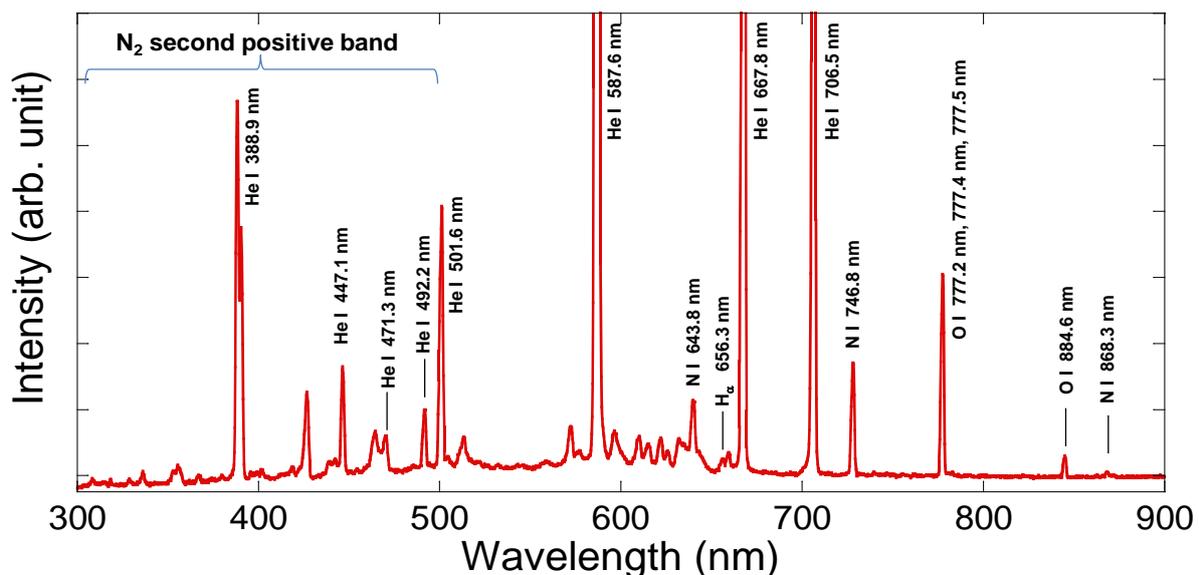


Figure 2. Optical emission spectrum of atmospheric pressure He plasma.

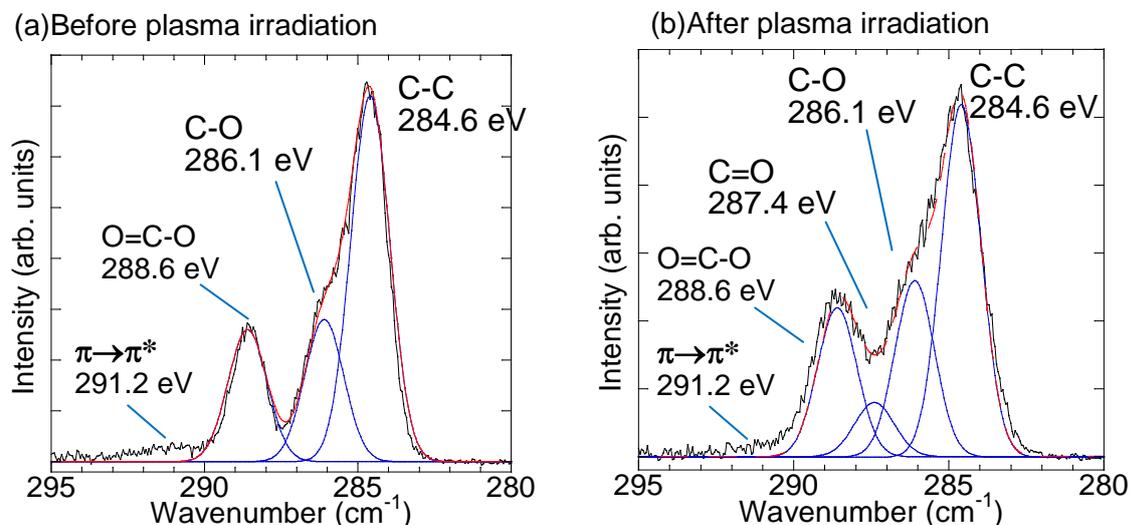


Figure 3. XPS C 1s spectra of PET films (a) before plasma irradiation and (b) after plasma irradiation.

3.2 XPS analysis of nano-surface on PET films

Figure 3 shows typical XPS C1s spectra of a PET film before and after irradiation with atmospheric-pressure He plasma. The spectra are normalized using the intensity of the C-C bond peak. The spectrum of the unirradiated PET sample in figure 3 (a) can be decomposed into four main components: a component at 284.6 eV due to C-C bonds, a component at 286.1 eV due to C-O bonds, a component at 288.6 eV due to O=C-O bonds and a component at 291.2 eV due to the $\pi \rightarrow \pi^*$ shake-up satellite of the phenyl group [26]. As seen in figure 3 (b), following plasma exposure, the intensity of the peaks due to O=C-O and C-O bonds increased, and a new peak due to C=O bonds (287.4 eV) appeared. This indicates that a nanoscale surface region of the PET is oxidized by the reactive oxygen species, and/or the molecular structure is degraded.

3.3 FT-IR analysis of PET films

Figure 4 shows FTIR spectra (normalized at 1250 cm^{-1}) of the PET surface before and after plasma treatment, in the narrow wavenumber range $700\text{--}2000 \text{ cm}^{-1}$. The main absorption bands appear at 1712 cm^{-1} (C=O stretching), 1250 cm^{-1} (ring O=C-O, glycol O-C-H bending), 1123 and 1113 cm^{-1} (CH_2 twisting or ring mode, ring O=C-O), and 725 cm^{-1} (ring C-H) [27-31]. A broad peak also appears at about $900\text{--}1000 \text{ cm}^{-1}$, and is attributed to C-C and C=C groups that was responsible for the soot structure [32,33]. Following plasma irradiation, the spectrum in figure 4 (b) contains peaks attributed to a part of oxidized and degraded PET surface. Following plasma irradiation, the intensity of the O=C-O peak is seen to decrease. Furthermore, oxidation of the PET surface is confirmed from the FTIR analysis. For low-pressure (about 1 Pa) plasma irradiation of PET, the intensity of the C=O peak (1712 cm^{-1}) tends to decrease relative to that for the O=C-O and O-C-H peaks in the glycol segment (1250 cm^{-1}) with increasing plasma density. This indicates that more C=O bond breaking is taking place due to plasma irradiation. For the atmospheric pressure He plasma, the FTIR results suggest that O=C bonds are broken by chemical and/or physical effects that occur in the deep-surface region.

The changes in the PET structure determined by the FTIR analysis are not consistent with the XPS results, which indicated oxidation occurring. This is because XPS is a surface-sensitive technique and FTIR is not. The plasma contains not only radicals that modify the top surface but also a significant number of photons that can penetrate deep into the PET, and the resulting modification effects can be

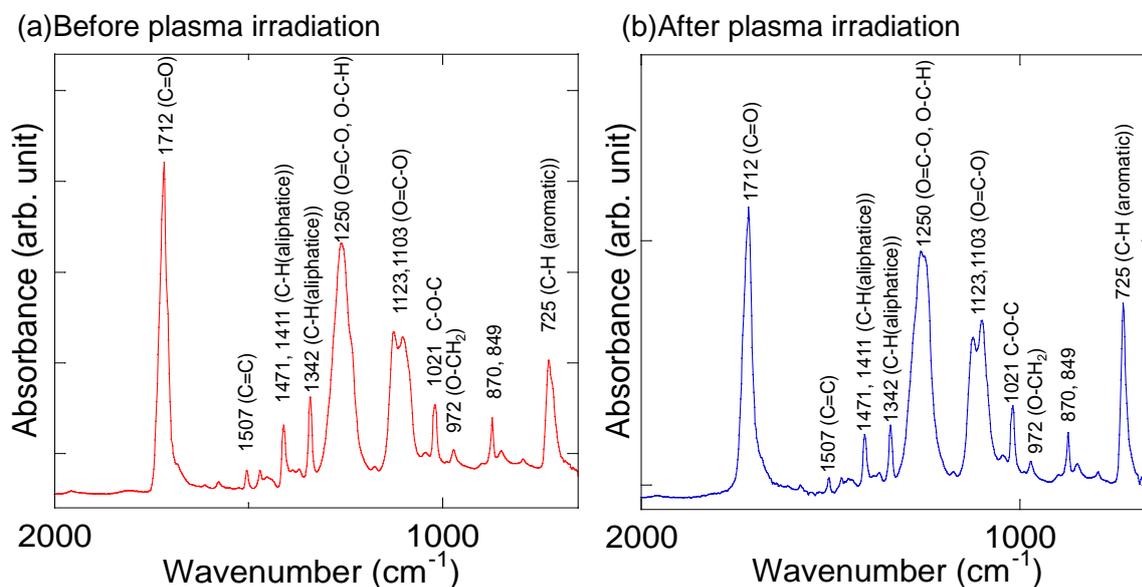


Figure 4. FTIR-ATR spectra of PET films (a) before plasma irradiation and (b) after plasma irradiation.

detected by FTIR. Therefore, the difference between the XPS and FTIR results is due to their being sensitive to different regions.

3.3 FT-IR mapping analysis of PET films

To investigate the variation of the chemical structure in the plasma irradiated area of the PET film, FTIR mapping was carried out. Figure 5(a) shows a plan-view optical micrograph of the PET surface,

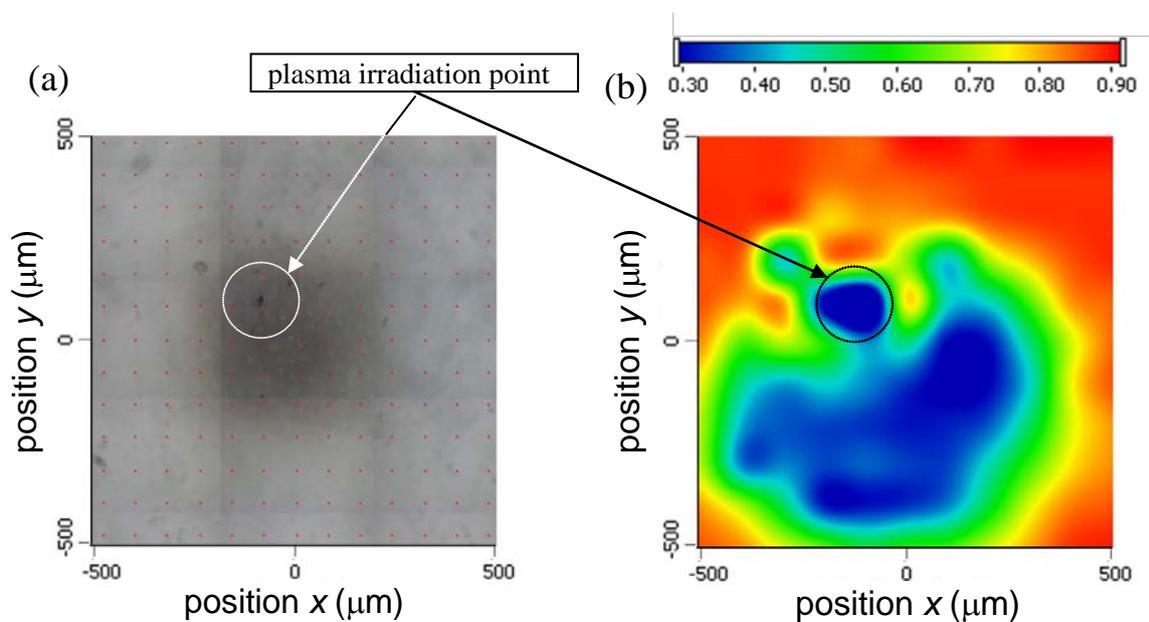


Figure 5. Plan-view (a) optical micrograph of PET surface and (b) FTIR map of intensity ratio of C=O peak (1712 cm^{-1}) to O=C-O peak (1250 cm^{-1}).

with the plasma irradiation point indicated. Figure 5(b) shows a FTIR map of the intensity ratio of the C=O peak (1712 cm^{-1}) to the O=C-O peak (1250 cm^{-1}). A large change in the intensity ratio is seen near the irradiation point, and the chemical structure gradually changes with distance from this point. The latter is considered to be due to a gas flow effect, which causes radial transport of the plasma across the PET surface. The resulting surface modification gives rise to the pattern shown in figure 5 (b). These results demonstrate the feasibility of observing the interaction of plasma with organic material on a local scale. A more detailed study of the interaction of atmospheric plasma He plasma and organic material will soon be carried out.

4. Summary

Plasma interactions with organic materials have been investigated by using atmospheric-pressure He plasma. Optical emission spectrum in the atmospheric-pressure He plasma has been measured. The spectrum shows considerable emissions of He lines, and the emission of O and N radicals attributed to air has been confirmed in the atmospheric-pressure He plasma. Variation in molecular structure of PET film surface irradiated with the plasma has been observed via FT-IR and XPS. These results via FT-IR and XPS indicate that the PET surface irradiated with the atmospheric-pressure He plasma was oxidized and/or degraded by chemical and/or physical effect due to irradiation of active species. These FT-IR mapping results exhibit the feasibility of observation of plasma/organic materials interaction in a small area due to local irradiation of atmospheric-pressure He plasma.

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References

- [1] Moisan M, Barbeau J, Moreau S, Pelletier J, Tabrizian M and Yahia L H 2001 *Int. J. Pharm.* **226**, 1
- [2] Laroussi M 2005 *Plasma Process. Polym.* **2** 391
- [3] Boudam M K, Moisan M, Saoudi B, Popovici C, Gherardi N and Massines F 2006 *J. Phys. D: Appl. Phys.*, **29** 3494
- [4] Weltmann K -D, Brandenburg R, Woedtke T, Ehlbeck J, Foest R, Stieber M and Kindel E 2008 *J. Phys D: Appl. Phys.*, **41** 194008
- [5] Raiser J and Zenker M 2006 *J. Phys. D: Appl. Phys.*, **39** 3520
- [6] Stalder K R and Woloszko J 2007 *Contrib. Plasma Phys.*, **47** 64
- [7] Yonson S, Coulombe S, Lveill V, Leask R L 2006 *J. Phys. D: Appl. Phys.*, **39** 3508
- [8] Coulombe S, Lveill V, Yonson S and Leask R L 2006 *Pure Appl. Chem.*, **78** 1147
- [9] Stoffels E, 2007 *Contrib. Plasma Phys.*, **47** 40
- [10] Fridman G, Friedman G, Gutsol A, Shekhter A B, Vasilets V N and Fridman A 2008 *Plasma Process. Polym.*, **5** 503
- [11] Morfill G E, Kong M G and Zimmermann J L 2009 *New J. Phys.* **11** 115011
- [12] Setsuhara Y, Cho K, Takenaka K, Shiratani M, Sekine M and Hori M, 2011 *Thin Solid Films* **519** 6721
- [13] Cho K, Setsuhara Y, Takenaka K, Shiratani M, Sekine M and Hori M, 2011 *Thin Solid Films* **519** 6810
- [14] Takenaka K, Setsuhara Y, Cho K, Shiratani M, Sekine M and Hori M, 2010 *Jpn. J. Appl. Phys.* **49** 08JA02
- [15] Setsuhara Y, Cho K, Takenaka K, Shiratani M, Sekine M and Hori M, 2010 *Surf. Coatings Technol.* **205** S355.

- [16] Setsuhara Y, Cho K, Takenaka K, Shiratani M, Sekine M and Hori M, 2011 *Surf. Coatings Technol.* **205** S484
- [17] Setsuhara Y, Cho K, Takenaka K, Shiratani M, Sekine M and Hori M, Ikenaga E, and Zaima S 2010 *Thin Solid Films* **518** 3561
- [18] Setsuhara Y, Cho K, Takenaka K, Shiratani M, Sekine M and Hori M, 2010 *Thin Solid Films* **518** 6320
- [19] Cho K, Takenaka K, Setsuhara Y, Shiratani M, Sekine M, Hori M, Ikenaga E, Kondo H, Nakatsuka O and Zaima S 2010 *Ceramic Transactions* **219** 183
- [20] Setsuhara Y, Cho K, Takenaka K, Ebe A, Shiratani M, Sekine M, Hori M, Ikenaga E, Kondo H, Nakatsuka O and Zaima S 2009 *Thin Solid Films* **518** 1006
- [21] Setsuhara Y, Cho K, Shiratani M, Sekine M, Hori M, Ikenaga E and Zaima S 2009 *Thin Solid Films* **518** 3555
- [22] Setsuhara Y, Cho K, Shiratani M, Sekine M and Hori M, 2009 *Thin Solid Films* **518** 6492
- [23] Cho K, Setsuhara Y, Takenaka K, Shiratani M, Sekine M and Hori M, 2012 *Jpn. J. Appl. Phys.* **51** 01AJ02
- [24] Takenaka K, Cho K, Setsuhara Y, Shiratani M, Sekine M and Hori M 2013 *J. Phys. Conference Series* **441** 012001
- [25] Setsuhara Y, Cho K, Shiratani M, Sekine M and Hori M 2013 *Current Applied Physics* **13** S59
- [26] Miyayama T, Sanada N, Iida S-I, Hammond J S and Suzuki M 2008 *Appl. Surf. Sci.* **255** 951
- [27] Lee C-T, Wu C-H and Lin M-S 2004 *Polym. Degrad. Stab.* **83** 435
- [28] Jaško M, Krump H, Hudeca I, St'ahel' P, Kováčik D and Šíra M, 2006 *Surf. Coatings Technol.* **201** 57
- [29] Patel M R, Patel J V and Sinha V K, 2005 *Polym. Degrad. Stab.* **90** 111
- [30] Fávoro S L, Rubira A F, Muniz E C and Radovanovic E 2007 *Polym. Degrad. Stab.* **92** 1219
- [31] Kormunda M, Pavlik J 2010 *Polym. Degrad. Stab.* **95** 1783
- [32] Kirchner U, Scheer V and Vogt R 2000 *J. Phys. Chem. A* **104** 8908
- [33] Armand X, Herlin N, Voicu I and Cauchetier M 1997 *J. Phys. Chem. Solids* **58** 1853