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Effects of photon irradiation in UV and VUV regions during plasma processing of organic materials[†]

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KEY WORDS: (Inductively-coupled plasma), (Low-inductance antenna), (Low-damage process), (Hard x-ray photoelectron spectroscopy)

1. Introduction

Next-generation devices including flexible displays, thin-film photovoltaic cells and advanced ULSIs (low-k interlayer and EUV lithography) are expected to occur in combination with polymer materials [1,2]. For successful development of these devices, therefore, it is of great significance to control polymer surface and/or interface with functional layers in terms of chemical and physical structures. In order to satisfy these requirements, it is necessary to use plasma processes, because plasma has high-reactivity due to ions and radicals. However, bond-dissociation energies of polymer materials for thermal decomposition are less than that of inorganic materials (3.4 eV for the O-C(=O) bond, 3.6 eV for the C-CH₃ bond and 8.4 eV for C=O bond). Thus, it is considered that ions, radicals, photons and electrons from plasma may give significant degradation in chemical bonding structures of soft materials beneath the surface and/or the inorganic/organic interface. Therefore, it is necessary to understand plasma-polymer interactions for development of low-damage and low-temperature plasma processes.

As one of the effective plasma sources for these processes, inductivity-coupled plasma sources have been developed with multiple low-inductance antenna (LIA) modules, which allowed low-voltage operation of high-density ICPs [3]. In terms of interactions of radiations from plasmas with organic materials surface, radiations in vacuum ultraviolet (VUV) and ultraviolet (UV) are significant in that the photon energies are higher than the bond dissociation energies. In this study, interactions of optical emissions from Ar-O₂ mixture plasmas with polymer surfaces have been investigated on the basis of surface morphological changes and non-destructive depth analyses of chemical bonding states in the nano-surface layer of polyethyleneterephthalate (PET) films via hard x-ray photoelectron spectroscopy (HXPES).

2. Experimental

A schematic diagram of the process chamber is shown in Fig. 1. The LIA units were mounted on the top flange of the discharge chamber and were coupled to a RF power

generator at 13.56 MHz via a matching network. Each LIA unit was connected in parallel to the matching network. The LIA unit consists of a U-shaped antenna conductor, which was fully covered with dielectric tubing for complete isolation from the plasma [4]. The chamber had a 500 mm inner diameter and a 200 mm height, which was connected to a diffusion chamber with a 500 mm inner diameter and a 400 mm height. The Ar-O₂ mixture plasma was sustained at an oxygen partial pressure (R_p) of 20% at a total pressure of 2.6 Pa at an RF power of 1 kW. Optical emission spectra in UV and VUV regions were measured with a VUV monochromator mounted on the sidewall of the chamber.

For evaluating the interactions of the polymer surface with UV and VUV photons from the plasmas, PET films (thickness 100 μ m) were exposed to photons from the Ar-O₂ mixture plasmas by covering the PET samples with a MgF₂ window. Here it is noted that thickness of the MgF₂ window is 2 mm. The MgF₂ window is transparent in UV+VUV regions (wavelength longer than 115 nm). Therefore, it is possible to evaluate the effects of photo-irradiation by comparing results of the sample with a plasma exposed sample [5].

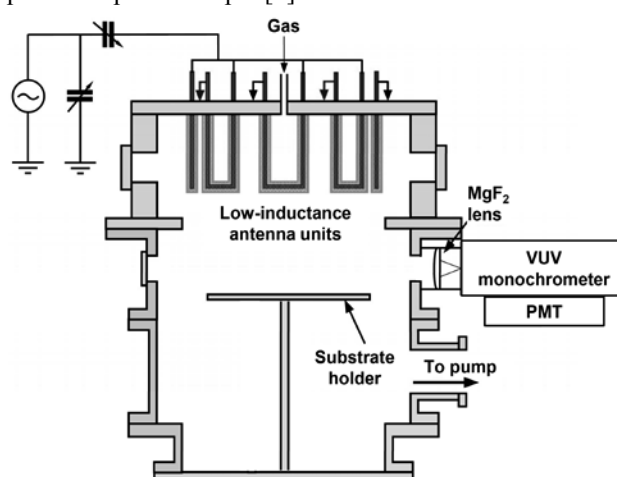


Fig. 1 Schematic diagram of the discharge chamber.

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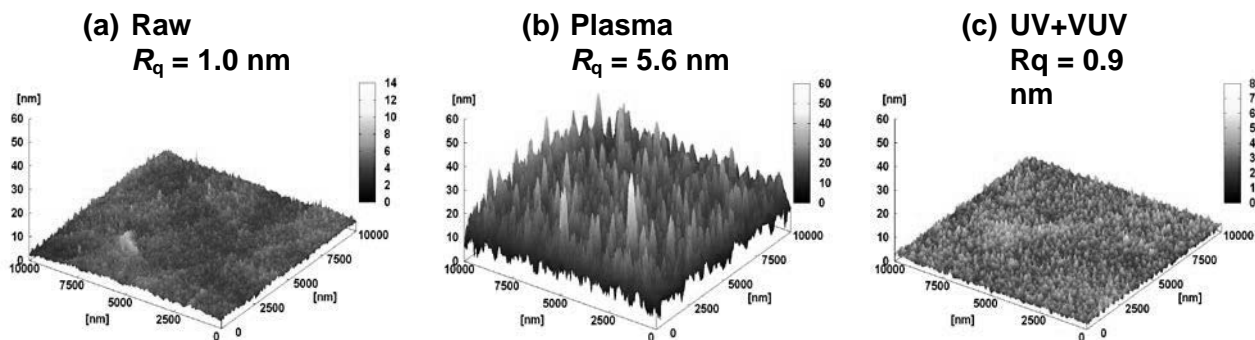


Fig. 2 Typical AFM images of the PET surface; (a) before and (b) after direct exposure to the plasma, (c) after irradiation with the UV+VUV photons from the plasma.

For investigation of surface morphological changes, the sample surface was observed with an atomic force microscope (AFM). The depth analysis of chemical bonding states was carried out by hard x-ray photoelectron spectroscopy (HXPES) and conventional x-ray photoelectron spectroscopy (XPS). The HXPES analysis was performed with x-rays from a synchrotron at a photon energy of 7940 eV at the national synchrotron radiation facility (SPring-8) of the Japan Synchrotron Radiation Institute [6]. The inelastic mean free path (IMFP) of 7940 eV electrons in polymers is approximately 18 nm [7]. Therefore, the probing depth of HXPES is about 50 nm for analysis of polymers. The XPS analysis was performed with non-monochromatized Mg K α radiation (photon energy of 1253.6 eV).

3. Results

Figure 2 shows typical AFM images of the PET surface (a) before and (b) after direct exposure to the plasma, (c) after irradiation with the UV+VUV photons from the plasma (with MgF₂ window). Surface roughness R_q (root-mean-square) of the raw PET film (Fig. 2(a)) was 1.0 nm. After the direct exposure to the Ar+O₂ mixture plasma for 1052 seconds, the roughness increased to 5.6 nm (Fig. 2 (b)). Whereas, the roughness was almost constant ($R_q = 0.9$ nm) even after exposure to UV+VUV photons from the plasma for 1052 seconds as shown in Fig. 2(c). These results suggest that the surface morphological change of PET films due to the Ar-O₂ mixture plasma exposure is not caused by only UV+VUV photons from the plasma.

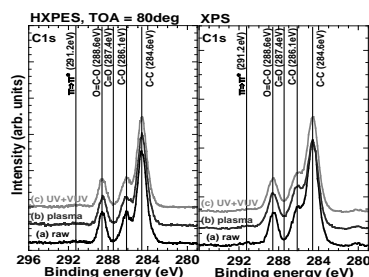


Fig. 3 HXPES and XPS C1s spectra for PET films; (a) before and (b) after direct exposure to the plasma, (c) after irradiation with the UV+VUV photons from the plasma.

The HXPES and XPS C1s spectra for PET films without and with direct exposure to the Ar-O₂ mixture plasma and irradiations with photons from the Ar-O₂ mixture plasma are shown in **Fig. 3**. The HXPES spectra showed insignificant change of the O=C-O bond and the C-O bond after the plasma exposure and the UV+VUV photo-irradiation. Whereas, in the XPS spectra, the samples exposed to the Ar-O₂ mixture plasma and the UV+VUV photons clearly exhibit significant increase in the oxygen functionalities (the O=C-O bond and the C-O bond). In particular, substantial increase is found for the C=O bond, which is not observed in the spectrum of raw PET film.

The UV+VUV photo-irradiation from the Ar-O₂ mixture plasmas resulted in insignificant change of the bond structures in deeper regions up to about 50 nm from the surface. However, in regions up to about 10 nm from the surface, the UV+VUV photo-irradiation resulted in increase of the oxygen functionalities.

4. Summary

Interactions of UV+ VUV photons from Ar-O₂ mixture plasmas with polymer surfaces were investigated using AFM, HXPES and conventional XPS analyses. The AFM images indicated that the surface morphological change of PET films due to Ar-O₂ mixture plasma exposure is not caused by only UV+VUV photons from the plasma. The HXPES analysis suggested that the effects of UV+VUV photons from the Ar-O₂ mixture plasmas on the chemical bonding states of polymer are insignificant in deeper regions up to about 50 nm from the surface. The XPS analysis shows that the formation of oxygen functionalities after UV+VUV photo-irradiation is localized in the vicinity of the surface regions as shallow as 10 nm. These results indicated that the UV and VUV photo-irradiation caused photodecomposition of the chemical bonds to create free radicals, which were terminated and/or chemically reacted with oxygen and/or OH species in the vicinity of the sample surface; oxygen molecules and radicals during plasma exposure and/or oxygen molecules and moisture after taking the PET samples out of the plasma reactor to the ambient air.

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References

- [1] M.-C. Choi, Y. Kim and C.-S. Ha, Prog. Polym. Sci. 33 (2008) 581.
- [2] K. L. Chopra, P.D. Paulson and V. Dutta, Prog. Photovolt: Res. Appl. 12 (2004) 69.
- [3] Y. Setsuhara, T. Shoji, A. Ebe, S. Baba, N. Yamamoto, K. Takahashi, K. Ono and S. Miyake, Surf. Coat. Technol. 174 - 175 (2003) 33.
- [4] Y. Setsuhara, K. Takenaka, A. Ebe and K. Nishisaka, Plasma Process. Polym. 4 (2007) S628.
- [5] S. Uchida, S. Takashima, M. Hori, M. Fukasawa, K. Ohshima, K. Nagahata, and T. Tatsumi, J. Appl. Phys. 103, 073303 (2008)
- [6] K. Kobayashi, Nucl. Instrum. Meth. Phys. Res. A 601 (2009) 32.
- [7] S. Tanuma, C.J. Powell and D.R. Penn, Surf. Interface. Anal. 21 (1994) 165.