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Plasma surface treatment of polymers with inductivity-coupled RF plasmas driven by low-inductance antenna units

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ABSTRACT

Plasma surface treatment of polymers has been carried out with argon/oxygen mixture plasmas driven by multiple low-inductance antenna units. Kinetic energy distribution of argon ions from the argon/oxygen mixture plasmas onto polymers showed considerable suppression of ion energies sufficiently less than 10 eV. Polyethyleneterephthalate (PET) films were exposed to argon/oxygen mixture plasma for 1–5 min on a water-cooled substrate holder. The etching depth of PET surface increased with increasing plasma-exposure time and the etching rate was 118 nm/min. Surface roughness of PET surface (root-mean-square value) increased from 0.5 nm to 2.7 nm with increasing plasma-exposure time from 0 min (original sample) to 5 min. Hard X-ray photoelectron spectroscopy (HXPES) was carried out for analysis of chemical bonding states of the PET surface. The HXPES analyses exhibited nano-surface modification of the PET surface without suffering degradation of molecular structures beneath.

1. Introduction

Polymer materials have been applied in a variety of engineering fields including organic–inorganic hybrid modules [1–3], biomaterials [4,5] and flexible displays [6]. For successful development of functional devices in these applications, optimization of surface properties and/or properties at the interface between polymers and inorganic materials is required in terms of chemical and physical properties. In order to satisfy these requirements, polymer modifications with plasmas have been widely employed as one of the promising techniques for a variety of engineering applications [7].

For successful modifications of polymer surface with plasma processes, however, it is of great significance to avoid unwanted degradation of chemical bonding structures of polymers beneath the surface and/or the organic–inorganic interface due to exposure of polymer surface with ions, radicals, photons and electrons. So far polymer degradation processes have been reported for a) bond-dissociation process via ion bombardment [8], b) photochemical reactions [9], c) chain scission processes associated with electron irradiation via electron-induced dissociation [10] and d) thermal degradation process [11]. In the plasma processing of polymers, these fundamental processes contribute to modification and/or degradation of the polymers in complex synergetic manners. Thus it is required to develop plasma-processing technologies, which can lower ion damage and/or avoid exposure with UV photons and electrons. However, the methods to reduce irradiation flux of UV photons and/or electrons generally require processing of polymer materials in lowered plasma-density condition, in which processing throughput should also be degraded. Therefore, it is considered that the plasma-processing technologies with reduced ion-damage while maintaining the process throughput may be attractive from the practical viewpoints.

Furthermore, the polymer degradation due to ion bombardment is closely related with bond-dissociation energies of polymers via nuclear collision processes of ions impinging onto polymer surface. Typical bond-dissociation energy ranges from 3.6 eV for C–CH_3 bond, 4.3 eV for O–C=O bond to 8.4 eV for C=O bond [11]. Assuming elastic collision of Ar^+ ions with carbon atoms to attain the recoiled energy of carbon atoms equivalent to the bond-dissociation energy in the polymer, it is significant to lower the average ion energy as low as or less than 10 eV in order to avoid bond dissociation of the ester group O–C=O bond.

In order to overcome these constraints, we have developed low-damage plasma processing technologies with low-inductance antenna

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(LIA) units to sustain inductively-coupled RF discharge [12]. Previous studies have demonstrated feasibility of high-density plasma productions with low sheath-edge potential plasmas and capabilities in active control of the plasma distributions have also been exhibited by adjusting power deposition profiles over large area [12–20]. Experiments using the plasma source with multiple LIA units resulted in stable source operation to attain high densities 10^{11}–$10^{12}\,cm^{-3}$ in argon. Ion energy distributions measured with a mass-separated ion energy analyzer showed significantly reduced ion energy at the sheath edge as low as 5 eV [19]. Furthermore, deposition of highly crystallized μc-Si films with a crystalline volume fraction of over 90% was demonstrated on glass substrates at the substrate temperature of 300 °C with deposition rate as high as 70 nm/min using rectangular reactor with multiple LIA units [20]. These results indicate that the plasma production technologies with the LIA units are quite attractive as deposition technology of microcrystalline silicon (μc-Si) films for thin-film transistor liquid-crystal displays (TFT-LCD). From these results, the ICP sources with LIA units are considered to be one of the most promising candidates as plasma sources for low-damage and high-quality processes.

In this paper, properties of argon/oxygen mixture plasmas driven by multiple LIA units are presented and nano-surface modification of polyethyleneterephthalate (PET) films using argon/oxygen mixture plasmas is evaluated in terms of surface morphology and the chemical bonding states.

2. Experimental

Schematic diagram of the chamber installed with a set of 8 LIA units is shown in Fig. 1. The LIA unit consisted of a U-shaped antenna conductor, which was fully covered with dielectric tubing for complete isolation from the plasma [12]. Eight LIA units with a 70-mm width and a 160-mm height were mounted on the top flange of the discharge chamber and were coupled to a 1000-W RF power generator at 13.56 MHz via a matching network for sustaining inductively-coupled discharge. Each LIA unit was connected in parallel to the matching network. The plasma 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 water-cooled substrate holder was placed at a distance of 297 mm from the top flange. The base pressure of the chamber evacuated with a turbo-molecular pump was 3×10^{-4} Pa and argon/oxygen mixture plasmas were produced at a total pressure of 2.6 Pa.

Plasma parameters were measured with a cylindrical Langmuir probe which was inserted radially at an axial position of 280 mm below the top flange. The probe tip made by platinum was used to avoid oxidation. Kinetic energy distributions of ions impinging onto the ground potential (ion energy at the sheath edge) from the plasmas were measured using a mass separated ion energy analyzer (Hiden, EQP500), which was mounted on the sidewall as illustrated in Fig. 1.

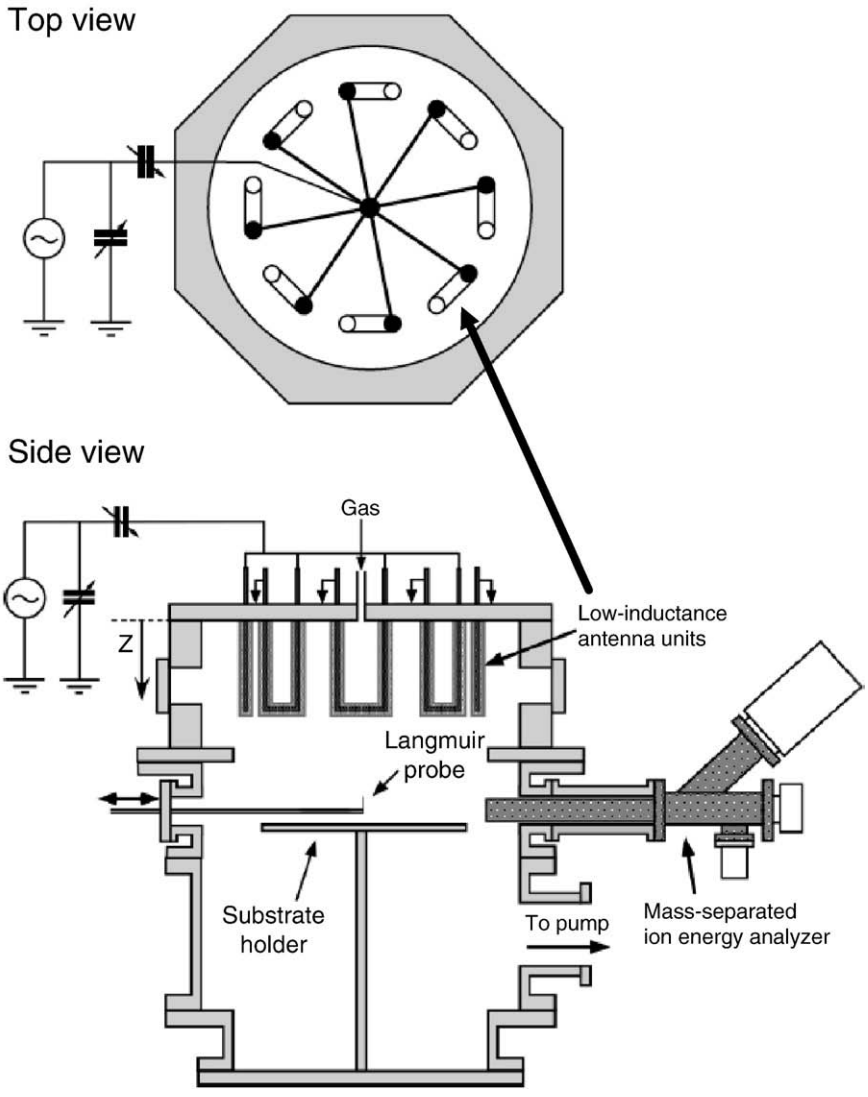

Fig. 1. Schematic diagram of discharge chamber with set of LIA units.