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# Combinatorial analysis of plasma-polymer interactions for formation of inorganic-soft materials hybrid structure<sup>†</sup>

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**KEY WORDS:** (Plasma) (Polymer) (Combinatorial analysis) (Soft material) (Flexible electronics)

## 1. Introduction

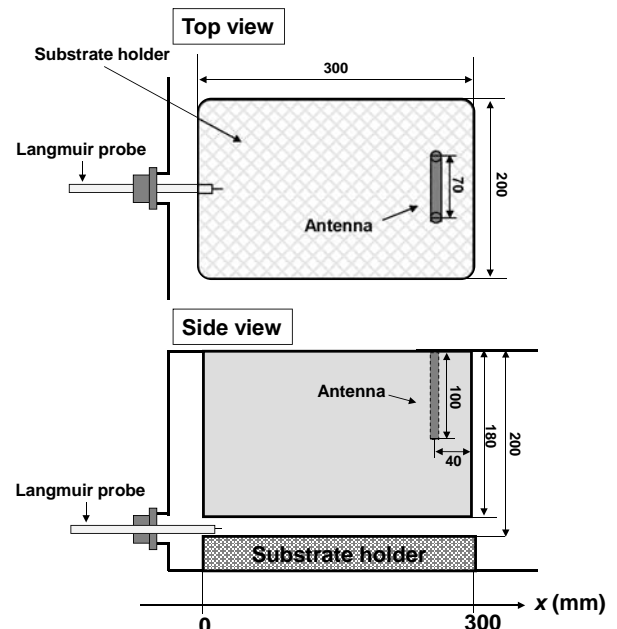
For fabrication of the future nano device using soft materials including next-generation ULSIs, MEMS, NEMS and bio-chips [1], plasma processes have played important roles as base technologies. It has become of key importance to develop process technologies with nano-sized structure control, which are required to be performed via plasma processing technologies. However, it is greatly anticipated that optimal process conditions can be attained at a pinpoint window of the process conditions, in which device structures and/or organic-inorganic interface should be controlled with a precision of nanometer size either via top-down or bottom-up process.

In order to overcome these constraints involved in next-generation plasma nano fabrication technologies, it is of great significance to establish "Plasma Nano Science", in which the process results are essentially characterized by the basic elements of processes rather than the conventional process parameters involved in the apparatus. For the breakthrough of the next-generation plasma nano technologies, we have developed a plasma-process analyzer based on the combinatorial methods, in which a variety of process results can be efficiently analyzed via inclination of process parameters (ion flux, radical flux) along the substrate. In this paper, combinatorial analysis of plasma-polymer interactions has been carried out in terms of etching characteristics and chemical bonding states of polymers to show efficiency and effectiveness for basic data acquisition.

## 2. Experimental

**Figure 1** shows the plasma reactor for sustaining plasmas with density gradient via localized power deposition of RF power through inductive coupling with a LIA module. The LIA module consisted of a U-shaped copper tube covered with a quartz tube, which allow low-voltage and high-density plasma production [2]. The LIA with 70 mm width and 100 mm length was located at  $x = 260$  mm on a top flange of the chamber with a horizontal length (in the direction of density inclination) of 300 mm and a width of 200 mm. The LIA was coupled to an RF power generator at 13.56 MHz via a matching network.

The working gas of argon-oxygen mixture was supplied to the discharge chamber through a gas inlet located at the top flange. The argon-oxygen mixture plasma was generated at a total pressure of 2.6 Pa and RF power of 88 - 350 W with an oxygen partial pressure of 20% in the total pressure. Ion-saturation current profiles along the substrate were measured with a cylindrical Langmuir probe at 5 mm above the substrate holder. Poly(ethylene terephthalate) (PET) films with a thickness of 100  $\mu\text{m}$  were exposed to argon-oxygen mixture plasmas on an electrically grounded substrate holder with and without water-cooling. In this investigation, five samples were located at substrate positions  $x = 40, 80, 120, 150,$  and  $220$  mm. Etching depth of the PC and PET films via plasma exposure was measured with stylus surface profiler. Surface roughness of the PC and PET films was observed with atomic force microscopy (AFM). Chemical bonding states of the nano surface layer of polymers exposed to plasmas were analyzed using x-ray photoelectron spectroscopy (XPS).



**Fig. 1** Schematic diagram of combinatorial plasma process chamber.

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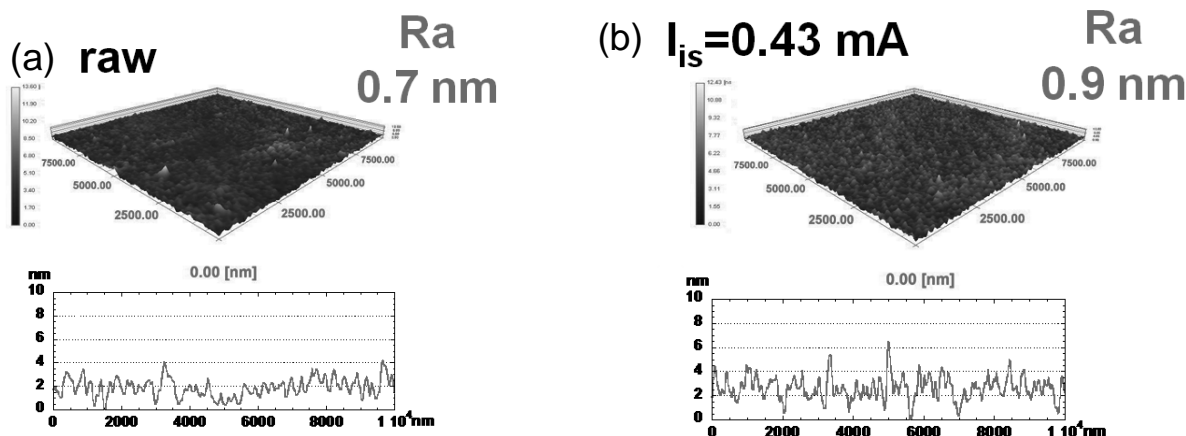


Fig. 2 Typical AFM images of polymers with and without argon-oxygen mixture plasma exposure.

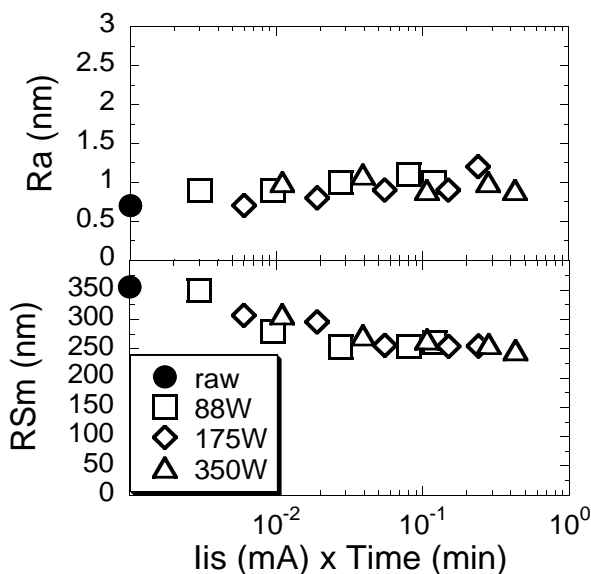


Fig. 3 Variation of surface roughness  $R_a$  and average peak interval  $R_{Sm}$  of polymers on the product of (ion saturation current  $I_{is}$ ) x (plasma exposure time  $T$ ) as a measure of the ion dose.

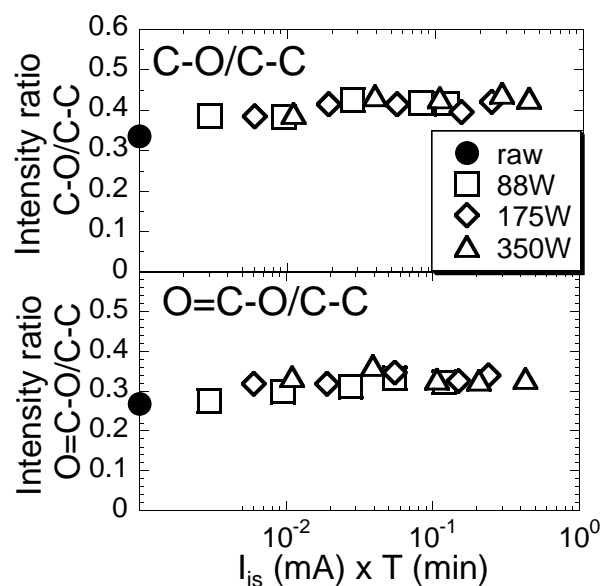


Fig. 4 Variation in deconvoluted peak-area ratio of  $I_{C-O}/I_{C-C}$  and  $I_{O=C-O}/I_{C-C}$  as a function of the product of (ion saturation current  $I_{is}$ ) x (plasma exposure time  $T$ ) as a measure of the ion dose onto the PET surface.

The XPS analyses were performed in AXIS-165x spectrometer (SHIMADZU corp., JAPAN) with non-monochromatized MgK $\alpha$  radiation (photon energy of 1253.6 eV).

### 3. Results and discussion

In order to investigate characteristics of argon/oxygen mixture plasmas, plasma parameters were measured for argon/oxygen mixture plasmas. Considerable gradients of plasma density were obtained by localized power deposition profiles (not shown here). Based on the results in terms of ion-saturation current density, analysis of plasma-polymer interactions has been carried out in terms of etching characteristics and chemical bonding states.

In order to examine the influence of plasma exposure time on morphological change of polymers, the plasma-exposed surface was imaged with AFM. Figure 2(a) and (b) shows typical AFM images of the original surface of the

PET films and the PET surface located at  $x = 220$  mm ( $I_{is} = 0.43$  mA) which was exposed to argon-oxygen plasma for 1 min. After exposure to the argon-oxygen plasma, the PET surface showed enhancement in surface roughness ( $R_a$ ) and suppression of average peak interval ( $R_{Sm}$ ) as can be seen in AFM images. Figure 3 shows dependence of the surface roughness ( $R_a$ ) evaluated from the AFM images on ion saturation current x exposure time corresponding to ion dose. The  $R_a$  of the PET surface after plasma exposure slightly increased with increasing ion dose, while the  $R_{Sm}$  considerably decreased with increasing ion dose.

The deconvoluted peak-area ratio of the C-O bond to the C-C bond ( $I_{C-O}/I_{C-C}$ ) and O=C-O bond to the C-C bond ( $I_{O=C-O}/I_{C-C}$ ) are evaluated and are summarized in Fig. 4 as a function of the product of the ion saturation current  $I_{is}$  and the plasma exposure time  $T$  as a measure of the ion dose onto the samples from the typical XPS C1s spectra of PET films. These results indicate that the increase of the peak-

area ratio  $I_{C-O}/I_{C-C}$  is considered to be due to C-O bond formation either via the side-band scission of the O=C-O bond and/or via the incorporation of oxygen radicals and/or ions through chemical reactions on the surface.

#### 4. Conclusions

Combinatorial analysis of plasma-polymer interactions with combinatorial plasma-process analyzer has been carried out in terms of etching characteristics and chemical bonding state of polymers. Surface roughness of the polymer slightly increased with increasing ion dose, while the average peak interval considerably decreased with

ion dose. The XPS results showed almost linear dependence with increasing ion dose. The data points obtained from three independent batches of experiments with 5 samples showed universal relations, indicating efficiency of the combinatorial method for effective basic data acquisition.

#### References

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