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Chemical Modification of Polymer Surface Using Large-area Plasma Excited by 915MHz UHF Wave
915MHzUHF波励起大面積プラズマを用いたポリマー表面の化学修飾

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In this study, we developed the large-area surface-wave plasma device with a resonance cavity at 915MHz, where we investigated the optimization of launcher structure for achieving uniform plasma by making use of the 3D finite difference time-domain(3D-FDTD) method and carried out the Langmuir probe measurements of plasma density distribution. The preliminary results of the amino group addition onto polymer surface by Ar and NH_3 gas mixture plasma were also given.

1. Introduction

Recently, the development of the plasma equipment for the large-area process is strongly demanded because of an increase in demand for large-scale display panel and solar battery and also the enlargement of processing size for improving productivity and lowering the cost. The surface wave plasma using 2.45 GHz microwave has great advantages for making high-density plasma without magnetic field, but it is often difficult to make uniform plasma in a large-area. Here, we used 915 MHz UHF wave which has some advantages. First, the free space wavelength ratio increases by a factor of about 2.7 compared with the 2.45 GHz microwave, so making large-area plasma will be easy. Second, it is possible to control plasma from lower electron density, owing to the cutoff density (1.0×10^{10} cm^{-3}) can be lowered by a factor of 7 compared with the 2.45 GHz microwave (7.0×10^{10} cm^{-3}).

To enlarge plasma size, there is a problem of dielectric window plate to avoid it braking by a huge mechanical force between low pressure and atmospheric pressure. To overcome this issue, we proposed to use smaller dielectric windows which are arranged at appropriate positions as UHF wave launcher.

In this study, we developed the 915MHz UHF wave excited large-area surface-wave plasma device with a resonance cavity. To optimize the launcher structure for achieving large-area, uniform plasma, we carried out the field distribution analysis using the 3D finite difference time-domain(3D-FDTD) method and the Langmuir probe measurements to study the density profiles.

2. Experimental setup

A schematic drawing of 915 MHz surface wave plasma device is shown in Fig. 1. The resonance cavity was 800 mm in diameter and 60 mm in height. The dielectric window plates made of quartz were separately located on bottom of the resonance cavity as shown in Fig. 1.

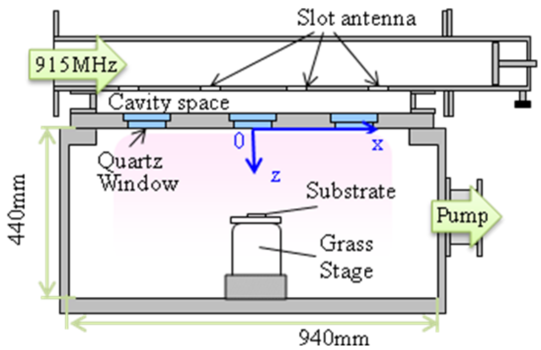

Fig. 1 Schematic diagram of 915 MHz surface wave plasma device.

The numerical analysis of electromagnetic-field in the resonance cavity was carried out with 3D-FDTD calculation code which we had developed [1]. The wave guide and the resonance cavity were defined by the space steps Δx, Δy and Δz as 5 mm to satisfy the convergence conditions of FDTD analysis.

The distributions of the ion saturation current in Ar/NH_3 gas mixture plasma were measured along the radial direction of 45 degrees against the x axis for z=240 mm at different gas mixture ratios.

The polyethylene (PE) sheets were placed on the stage inside chamber at z=240 mm. The total gas pressure and flow rate of Ar/NH_3 were kept at 8 Pa and 100 sccm, respectively. NH_3 gas was introduced to introduce the amino group on the surface. The surfaces of treated samples were analyzed by XPS. Amino group introduced on polymer surface was estimated by chemical derivatization method using 3-trifluoromethyl benzaldehyde (TFBA) of methanol solution (0.1 M/15ml). Fluorine atoms of TFBA have been utilized to label of primary amino group ($-NH_2$) among other groups [2].

3. Results

Figure 2 shows the 3D-FDTD calculation results of the spatial distributions of electric field intensity along z axis on bottom of the resonance cavity. Here, 915 MHz UHF wave introduced through the slot antennas from the waveguide to a resonance cavity distributed certain mode pattern with the azimuthal mode number of m=4, radial mode number of n=1 and axial mode number of p=0 inside the resonance cavity, which is identified as TM_{410} mode. Moreover, we also confirmed that the resonant mode of the present cavity structure was TM_{410} mode according to the resonance cavity theory. From these theoretical expectation, the quartz plates were arranged on the cavity bottom plate to fit TM_{410} mode, as shown in Fig. 2.

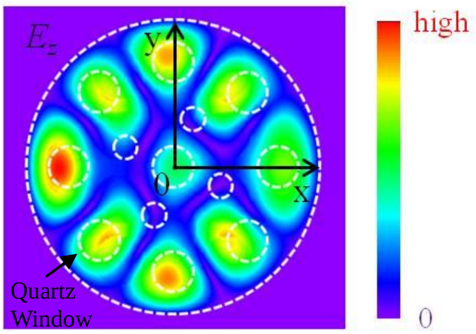

Fig. 2 The electric field intensity on cavity bottom plane calculated by using 3D-FDTD.

Figure 3 shows the distributions of the ion saturation current along the radial direction in Ar/NH_3 plasma. In the case of 100% Ar gas, the ion saturation current was higher than that of gas mixture case, and the electron temperature was about 1.5 eV along the radial direction. When NH_3 gas ratio was set to 3%, the uniform plasma was obtained within a radius of roughly 25 cm. Furthermore, when NH_3 gas ratio was increased to 5%, uniformity of the density profile slightly became better, while the ion saturation current decreased.

Figure 4 shows the XPS result in wide spectra for derivatized PE samples. F 1 peak (around 690 eV) was observed on the plasma treated surface.

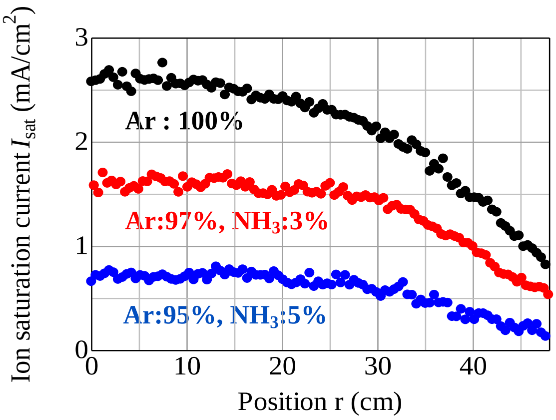

Fig. 3 The distributions of the ion saturation current along the radial direction in $Ar+NH_3$ plasma.

This peak was resulted from the introduced primary amino groups. The relative concentration of primary amino group ($-NH_2/C$) and the selectivity ($-NH_2/N$) was estimated from F 1s peak. [2]. The estimated $-NH_2/C$ and $-NH_2/N$ was 0.88% and 24.5% respectively.

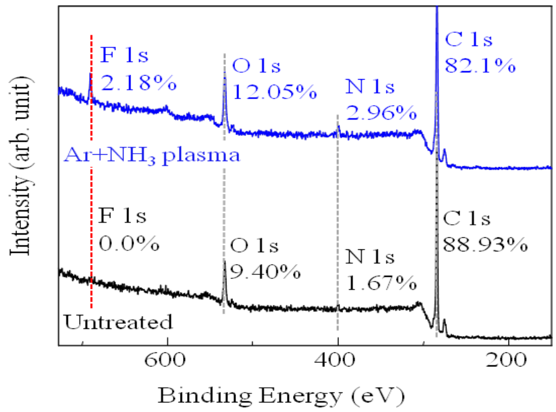

Fig. 4 Wide XPS spectra of untreated (bottom) and Ar/NH_3 plasma treated (top) samples.

4. Conclusion

In this study, we developed the large-area surface-wave plasma device with a resonance cavity at 915MHz. We investigated the optimization of launcher structure for achieving uniform plasma by making use of the 3D-FDTD method and carried out the Langmuir probe measurements of plasma density distribution. After optimizing the launcher structure, we obtained the large-area uniform plasma within a diameter of roughly 25 cm. We also presented the preliminary results of the amino group addition onto polymer surface.

References

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