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Maskless Ultrafine Surface Modification onto Polymer Substrate by Atmospheric Pressure Plasma Jet with Nanocapillary

ナノキャピラリー大気圧プラズマジェットを用いた
ポリマー基板上へのマスクレス微細表面修飾

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The nano-sized low frequency driven atmospheric pressure plasma jet (APPJ) has been developed to apply it to the maskless ultrafine process. In this study, we tried to apply it for the maskless micro-sized surface modification onto polymer surface. From the optical emission spectroscopy of He/NH_3 mixture plasma jet, we observed the emission spectrum of NH (336.0 nm), which is considered to be a possible precursor of amino group addition. Using the APPJ with a 1 μmϕ capillary, we demonstrated the amino group modification with a dot size of about 20 μm onto the polymer surface.

1. Introduction

Recently, many researches of various processes using atmospheric pressure plasma jet (APPJ) have been extensively carried out. This low-frequency (LF) driven APPJ shows an interesting plasma characteristic, known as “plasma bullet” [1]. Furthermore, owing to the non-thermal equilibrium property, many applications to low-temperature material processing are expected under atmospheric pressure [2, 3]. The size of an APPJ generally ranges from mm order to hundreds nm. In this study, the selective small area processing was performed using an APPJ with a 1 μm or 100 nmϕ capillary [4].

So far, we have investigated the property of atmospheric pressure helium (He) plasma jet with the 100 nmϕ capillary using an electrostatic probe technique. We observed the propagation velocity of the plasma bullet ejected from the capillary. The size of the plasma bullet was evaluated by the etching pattern of photoresist film, which was about 500 nm from the results of the AFM analysis [4].

In this study, we aim at developing the maskless ultrafine surface chemical modification processing on the polymer surfaces using APPJ with a micro or nano-capillary under atmospheric pressure.

2. Experimental setup

The schematic drawing of the experimental setup is shown in Fig. 1. A thin copper plate wound on the glass capillary was used as a powered electrode, which was connected to a high voltage pulse power supply. In order to generate the plasma jet in a 0.6 mm inner diameter glass capillary with a thickness of 0.2 mm, He/NH_3 mixture gas was flowed as the working gas. The rectangular pulsed voltage at the duty ratio of 50% was applied on the electrode with maximum voltage of ～±7.5 kV, and a frequency of 5 kHz. The capillary used in this experiment were fabricated by micropipette puller [4]. In the present experiments, the capillaries with the aperture size of 1 μm ϕ and 100 nm ϕ were used. The ultrafine plasma jet was ejected in the atmosphere by attaching micro- or nano-capillary structure to a tip. In this experiment,

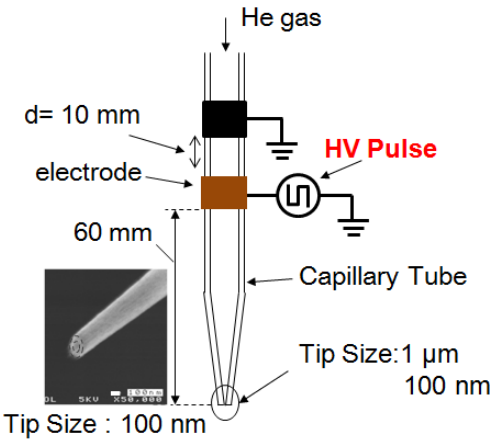

Fig.1. The schematic of the experimental setup

we irradiated the plasma to the silicon substrate which coated the photo-resist film (OEBR-1000) which was acrylic resin, and evaluated about the functional group modification by surface observation using fluorescence micro microscope.

3. Result

Figure 2 shows the experimental result of optical emission spectroscopy (OES) measurement. Plasma jet was generated on the condition of applied voltage: ±6.5 kV, frequency: 5 kHz, pulse duty ratio: 50%. It is noted that we used a larger size of capillary to get enough emission intensity to confirm the emission spectrum in the OES measurement. Optical fiber for collecting emission was located at 1mm from the tip of glass tube with 0.6 mm in diameter. From Fig. 2, the emission spectrum of NH (336.0 nm) was clearly seen. It is speculated that the emission spectrum for micro-capillary APPJ is almost same as the spectrum shown in Fig. 2. Therefore, the amino group introduction by NH and NH_2 fragments are expected in a micro-sized small area irradiated by micro-capillary APPJ.

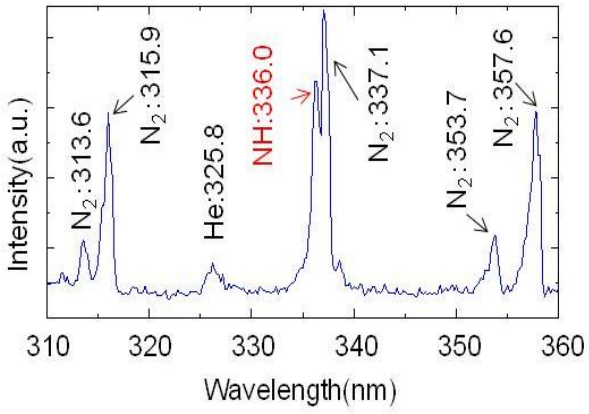

Fig.2. Spectrum characteristic of He/NH_3 mixture gas plasma jet

To confirm the amino group introduction on the surface, the fluorescence microscope observation was carried out. In this measurement, fluorescent dyes are selectively grafted with amino group. The grafted dye emits fluorescent light of a specific wavelength of 520 nm excited by a light of shorter wavelength of 494 nm. The used fluorescent dye for amino group confirmation is sulfodichlorophenyl ester.

Figure 3 shows the results of fluorescent observation of the treated surface. The surface was prepared by 2 step plasma treatments. In the first step of treatment, the surface was biased at DC -500 V, and then He plasma jet was irradiated for 0.1s. After the first treatment, He/NH_3 mixture gas plasma jet was irradiated for 3 s to introduce amino groups on the surface. The distance between the capillary tip and the substrate was kept at 250 μm. Figure 3(a) and 3(b) shows the aminated dot pattern when we used the APPJ with a single electrode and double electrodes, respectively. From the present result, it is confirmed that maskless amino group modification onto the polymer surface was selectively made by a micro-capillary APPJ plasma jet with double electrodes.

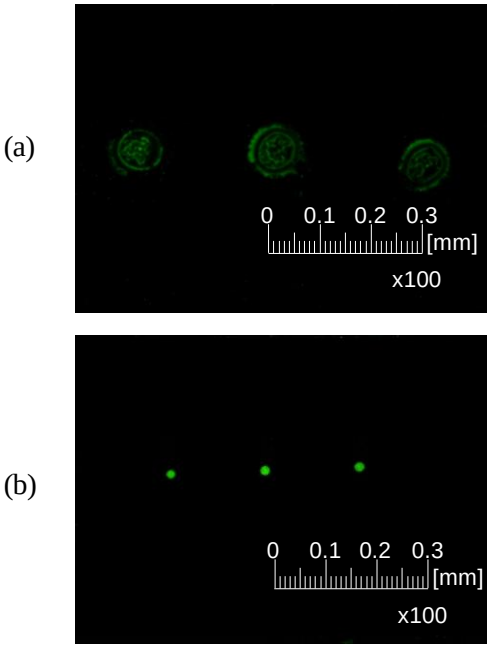

Fig.3. Fluorescent patterns of aminated area treated with 1 μmϕ capillary plasma jet with (a) a single electrode and (b) double electrodes.

4. Conclusion

We carried out the experiment of ultrafine functional group modification onto the polymer surface using APPJ with a micro-capillary. From the OES results for He/NH_3 mixture plasma jet, the emission spectrum of NH(336.0 nm) was observed in the downstream region. Moreover, the maskless amino group introduction onto the surface of photoresist film in a selected small area was demonstrated. The size of aminated area treated by 1 μmϕ capillary APPJ with double electrodes was about 20 μm.

References

[1] M. Teschke, J. Kedzierski, E.G. Finatu-Dinu, D. Korzec and J. Engemann., IEEE trans. Plasma Sci. 33 (2005) 310.
[2] C. Tendero, C. Tixier, P. Tristant, J. Desmaison, P. Leprince, Spectrochimica Acta Part B 61 (2006) 2.
[3] Z. Yang, H. Shirai, T. Kobayashi, Y. Hasegawa, Thin Solid Films 515 (2007) 4153.
[4] R. Kakei, A. Ogino, F. Iwata and M. Nagatsu: Thin Solid Films, Vol.518 (2010) 3457.