Local Surface Modification of Polymer Material using Low-temperature Microplasma

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Low-temperature NH\textsubscript{3}/He-microplasma under a high-pressure environment close to atmospheric pressure (720-730 Torr) has been employed for local surface modification of nitrogen groups on the surface of plasma-polymerized styrene (pp-styrene). As a result of optical emission spectroscopy (OES) measurement, the gas temperature of low-temperature NH\textsubscript{3}/He-microplasma was $T_g \approx 290$ K and proved the treatment to be less thermal damage for the polymer. Also, from the measurement of Lissajou figure, the estimated electron temperature and the mean electron density was $T_e \approx 10^5$ K and $N_e \approx 10^7$ cm$^{-3}$, respectively. X-ray photoelectron spectroscopy (XPS) measurement results show that the nitrogen and oxygen groups were modified locally on the surface of pp-styrene film by the treatment of NH\textsubscript{3}/He-low-temperature plasma. The diameter of modified nitrogen groups' area corresponds to that of the glass capillary (500\textmu m) at the end of microplasma torch. Furthermore, the resonant frequency decline of the treated pp-styrene-coated surface transverse wave (STW) acoustic device suggested that NH\textsubscript{3}/He-low-temperature plasma raised the water adsorption on the surface of pp-styrene film. In maximum, the water adsorption increased 2.63 times compared to untreated one.

Keywords: low-temperature microplasma, ammonia, plasma-polymerized styrene (pp-styrene) film, localized treatment, optical emission spectroscopy (OES), Lissajou method, x-ray photoemission spectroscopy (XPS), surface transverse wave (STW) acoustic device

1. Introduction

Recently, plasma process on micron scale, which promotes the development of micro/nanotechnology, has become the worldwide topic and studied intensively [1].

The low-temperature (several hundred K for the gas temperature) microplasma employed in this study can be generated in high-pressure environment with low power and a small amount of gas source, which leads to wide range of applications [2]. The low-temperature microplasma can easily control the modification point in limited space (diameter of \textmu m scale) both two dimensionally and three dimensionally without masking. Moreover, due to the miniaturization of the plasma, microplasma has large surface area and small heat capacity. This fact suggests the possibility of controlling plasma gas temperature accurately including below the zero point.

On the other hand, biosensor field is one of the
application fields for this low-temperature microplasma, since the biosensor using polymer substrate is expected for its convenience and inexpensiveness in near future [3-4]. In order to immobilize biomacromolecular on the polymer surface without inactivating, it is necessary to raise biocompatibility of the polymer surface. Depending on the kind, size, and number of immobilizing biomacromolecular, one needs to fabricate micro interaction-field on polymer surface with desired properties such as hydrophilicity, biocompatibility, and so on [5]. However, the existing biomacromolecular immobilizing method, such as photolithography, takes too many steps to complete such micro interaction-field fabrication. Moreover, there lies a problem in fabricating multi-interaction-field on the local polymer surface at the same time.

In this study, we focus mainly on on-demand locality and the temperature of the microplasma, and aim to develop basic technology for the field such as biosensors, which the fabrication of micro interaction-field on thermally sensitive polymer is necessary.

Toward the final goal mentioned above, we firstly generated low-temperature NH$_3$/He-microplasma, and then diagnosed the characteristics of the plasma. Secondly, we locally (several hundred μm in diameter corresponding to the width of lab-on-a-chip) treated plasma-polymerised styrene (pp-styrene) film coated silicon substrates with NH$_3$/He-low-temperature plasma and modified nitrogen groups on the surface. Finally, we measured the resonant frequency change of the treated pp-styrene-coated surface transverse wave (STW) acoustic device to calculate the water adsorption rate, and compared with that of untreated one.

2. Experimental

2.1 Generation and diagnosis of low-temperature NH$_3$/He-microplasma

2.1.1 Generation

Fig.1 shows a schematic of our system to generate low-temperature NH$_3$/He-microplasma. The system consists of a function generator, an amplifier, a main chamber, a microplasma torch, and a rotary pump. To keep the gas isolated from the air outside, the pressure of the main chamber is maintained at 720-730 Torr. The holder is set in front of the torch, and the distance between the torch and the treating substrate is controlled by a micrometer.
2.1.2. Optical emission spectroscopy
To study the characteristics of the low-temperature NH₃/He-microplasma (excited molecules and atoms), optical emission spectroscopy (OES) was performed with monochromator with a focal length of 300 mm equipped with 1200 grooves/mm grating (Acton Research Corporation SpectraPro-300i, USA), and photons were detected with a CCD detection system (Acton Research Corporation, USA) for analysis of the 310-360 nm domain.

Also, OES measurement of the N₂ 2nd positive system was performed to estimate N₂ rotational temperature. Theoretical N₂ 2nd positive system spectrum was calculated in advance for the fitting the measured spectrum. In the atmosphere, it is well known that rotational temperature easily reaches the equilibrium and can be approximated with gas temperature of the plasma.

2.1.3 Electron temperature and electron density estimation
Electron temperature and electron density of the low-temperature NH₃/He-microplasma were estimated by using swarm data [6]. Note that this estimation is effective for the DBD part of our microplasma, and not the discharge part at the tip of the stainless wire where strong electric field occurs. The power consumption of the low-temperature NH₃/He-microplasma can be measured with Lissajou method, which is illustrated in Figure 3. The voltages across the discharge electrodes from the digital oscilloscope (TDS 5104 digital phosphor oscilloscope, Japan) are plotted as a function of the voltage across the test capacitor Ctest. The power consumption of the DBD part is obtained by measuring the area of the Lissajou curve and multiplying it to capacitance Ctest and the frequency of the applying voltage V [7].

2.2 Surface modification of pp-styrene film treated by low-temperature NH₃/He-microplasma and its characterization
2.2.1 Surface modification
Fig. 4 is a schematic of the RF capacitively coupled plasma reactor to synthesize pp-styrene film on the silicon substrate. In the reactor chamber, two electrodes are horizontally arranged above each other. Silicon substrates prepared in the form of 0.5 mm thick square-shaped coupons (10 × 10 mm) are put on a bottom electrode. The low-temperature plasma of the styrene monomer generates between the electrodes, and thus the pp-styrene layer is synthesized on a silicon substrate. Other specific condition for the fabrication of pp-styrene film is shown in Table 1.

![Fig. 4. Experimental setup for synthesizing pp-styrene film on a Si substrate.](image)

<table>
<thead>
<tr>
<th>Plasma process condition</th>
<th>Applied power (W)</th>
<th>Frequency (MHz)</th>
<th>Pressure (Pa)</th>
<th>Treated time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>13.65</td>
<td>100</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 1. Specific condition for fabrication of the pp-styrene film.
2.2.2 Characterization

2.2.2.1 XPS analysis of treated pp-styrene film surface

The local incorporation of the low-temperature NH$_3$/He-microplasma treated pp-styrene film surface is identified by XPS (PHI Quantum2000, USA) measurements. Monochromated AlK$_x$ (1486.7eV) radiation was used and the analysis area was 200 µm in diameter in this experiment. The electron take-off angle used is 45°. To avoid differential charging effects of nonconducting pp-styrene film samples, an electron flood gun is used for neutralizing the surface. The binding energy analysis was referenced to the C1s signal of the aliphatic hydrocarbon at 285 eV. The peak fitting was done by using Multipak V6.1A software and for the peak shape, a mixture of Gaussian and Lorentzian was chosen. Furthermore, by measuring the atomic concentrations of N$_{1s}$ and O$_{1s}$ on 49 points over the low-temperature NH$_3$/He-microplasma treated area, we have succeeded to map and visualize the locality of the low-temperature NH$_3$/He-microplasma treatment. The distance between the nearest measurement points is 200 µm. Moreover, angle dependant XPS analysis was performed for each treated pp-styrene film in order to achieve depth profile.

2.2.2.2 Resonant frequency measurement of treated pp-styrene film deposited on STW device

Surface transverse acoustic wave (STW) device can detect the elastic or electrical change caused by the adsorption on the device surface with high sensitivity [8]. The sensitivity of the STW device is inverse proportion to the surface area of the device. When the same amount of adsorption occurs, the resonant frequency change of the device becomes larger in the smaller device, which leads to the higher the sensitivity. Microplasma will be a suitable tool for modifying surface, which leads to a fabrication of micro interaction-area such as hydrophilic, hydrophobic or biocompatible area on GHz range STW device, which will become general-purpose sensor device in near future. In this study, the 600 MHz STW devices (Japan Radio Co., Japan) were used. Mass increase of 2.75 pg per square centimetres on the surface of the device gives resonant frequency decrease of 1Hz [9]. We measured the resonant frequency change of the treated pp-styrene-coated 600MHz STW devices under the humid condition (RH 9%) to calculate the water adsorption rate, and compared with that of untreated one. Note that to detect the resonant frequency of the low-temperature NH$_3$/He-microplasma treated pp-styrene coated STW devices accurately, it is necessary to treat uniformly, and therefore we took long treatment time (300 s).

3. Results and discussion

3.1. Generation and characterization of low-temperature NH$_3$/He-microplasma

3.1.1. Optical emission spectroscopy

Fig. 5 shows the example of actual generation of the low-temperature NH$_3$/He-microplasma. The condition for the generation was $V = 1.9$ kV, $f = 7$ kHz, $Q_{NH_3} = 5$ sccm, $Q_{He} = 200$ sccm respectively.

![Fig. 5. The low-temperature NH$_3$/He-microplasma ($V = 1.9$ kV, $f = 7$ kHz, $Q_{NH_3} = 5$ sccm, $Q_{He} = 200$ sccm).](image)

In this study, we focused on NH radicals, which play an important role in functionalization of nitrogen groups on pp-styrene film surface with our system. Fig. 6 is the optical emission spectra of NH radicals as a function of applying voltage. It shows that as the applying voltage increases, the intensity of the radicals increases. However, 1.9 kV is the maximum limit of applying voltage in our system because the discharge mode transit to arc and ends up destructing the electrode part.

On the other hand, Fig. 7 is the optical emission spectra of NH radicals as a function of NH$_3$ gas flow rate. Note that the He gas flow rate is constant at 200 sccm. It shows that as the NH$_3$ gas flow rate increases, the intensity of the radicals decreases. This can be explained by the Penning effects of helium metastables. He metastable particles consume their energy by dissociating and ionizing ammonia. When NH$_3$ gas flow rate increases, NH$_3$ particles receiving energy from He metastables increase although the He gas flow rate does not change. Hence the mean energy that NH$_3$
particles get from He metastables decreases, and dissociated and ionized NH$_3$ particles decrease. Taking into account that formation of NH radicals involves dissociation and ionization, the explanation agrees well with the result. We must also note that in our system, 5 sccm was the minimum limit of the stable NH$_3$ gas flow.

The N$_2$ rotational temperature calculation of the low-temperature NH$_3$/He-microplasma at the jet region in Fig. 8 suggested that the gas temperature was $T_g \approx T_e \approx 290$ K and proved the treatment to be less thermal damage for the polymer.

3.1.2. Electron temperature and electron density estimation

The Lissajou curve obtained under the condition of $V = 1.9$ kV, $f = 7$ kHz, $Q_{NH_3} = 5$ sccm, $Q_{He} = 200$ sccm, is shown in Fig. 9. Under the condition mentioned above, the power consumption of the low-temperature NH$_3$/He-microplasma was 6.2 mW, and 2.1 W/cm$^2$, respectively. This power consumption density value is about the same as the other conventional plasmas employed in the surface treatment system.

Moreover, an electron temperature $T_e$ and an electron density $N_e$ can be estimated using the Lissajou curve [10,11]. The estimated $T_e$ and the mean $N_e$ were $T_e \approx 10^5$ K and $N_e \approx 10^7$ cm$^{-3}$, respectively. Both values are about the same as that of DBD generated in other systems.
Table 2. Specific condition for the low-temperature NH3/He-treatment of the pp-styrene film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Applied Voltage (kV)</th>
<th>Frequency (kHz)</th>
<th>Pressure (Torr)</th>
<th>He flow rate (sccm)</th>
<th>NH3 flow rate (sccm)</th>
<th>Distance between the torch and the substrate (mm)</th>
<th>Treated time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>1.7</td>
<td>10</td>
<td>720</td>
<td>200</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>d</td>
<td>1.7</td>
<td>10</td>
<td>720</td>
<td>200</td>
<td>5</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>c</td>
<td>1.7</td>
<td>10</td>
<td>720</td>
<td>200</td>
<td>5</td>
<td>6</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3. XPS results of the untreated and treated pp-styrene film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>95.24</td>
<td>0.00</td>
<td>4.76</td>
</tr>
<tr>
<td>b</td>
<td>90.52</td>
<td>1.35</td>
<td>8.13</td>
</tr>
<tr>
<td>d</td>
<td>81.65</td>
<td>5.64</td>
<td>12.71</td>
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<tr>
<td>c</td>
<td>90.32</td>
<td>1.71</td>
<td>7.97</td>
</tr>
</tbody>
</table>

Table 4. Specific condition for the low-temperature NH3/He-treatment of the pp-styrene film coated on STW devices.

<table>
<thead>
<tr>
<th>Applied Voltage (kV)</th>
<th>Frequency (kHz)</th>
<th>Pressure (Torr)</th>
<th>He flow rate (sccm)</th>
<th>NH3 flow rate (sccm)</th>
<th>Distance between the torch and the substrate (mm)</th>
<th>Treated time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>10</td>
<td>720</td>
<td>200</td>
<td>5</td>
<td>4</td>
<td>300</td>
</tr>
</tbody>
</table>

3.2. Characterization of pp-styrene film treated by low-temperature NH3/He-microplasma

3.2.1. XPS analysis of treated pp-styrene film surface

Three kinds of surface treated pp-styrene film samples by the low-temperature NH3/He-microplasma under the condition shown in Table 2 were measured by XPS. They differ in the treatment time and the distance between the microplasma torch and the substrate (a. untreated, b. t = 1 s and d = 4 mm, c. t = 10 s and d = 4 mm, d. t = 10 s and d = 6 mm). In Table 3, the results show that the longer microplasma treatment time and shorter the distance between the microplasma torch and the substrate, the more N and O components get incorporated on the treated area.

Although the pp-styrene film was exposed to the NH3/He-microplasma, oxygen was observed in the XPS spectrum. The origin of the incorporated oxygen in the surface may be the gaseous oxygen or water dissolved in the polymer or desorbed from the walls of the plasma reactor, or it could be from the reaction of residual radicals with the atmosphere during the transfer of the sample for XPS analysis.

Fig. 10 is the results of localization mapping of N1s and O1s XPS signal counts for pp-styrene film coated silicon substrate treated under each condition. It shows that the nitrogen and oxygen groups were modified locally on the surface of pp-styrene film by the treatment of low-temperature NH3/He-microplasma. Especially, under the condition of d = 4 mm and t = 1, 10 s, the diameter of modified nitrogen groups’ area corresponds to that of the glass capillary (500μm) at the end of microplasma torch. Also, the O1s modified area spread faster than N1s modified area. This result can be explained by the binding energy that includes oxygen. Oxygen-carbon binding energy such as C-O and C=O is higher than Nitrogen-carbon binding energy such as C-N, and therefore, more stable Oxygen-carbon binding spread faster.

In Fig. 11, the angle dependant XPS analysis shows that nitrogen groups are modified only in the depth of nm range.
Fig. 10. N1s and O1s intensity mapping of locally modified area measured by XPS 
(a. $t=1$ s and $d=4$ mm, b. $t=10$ s and $d=4$ mm, c. $t=10$ s and $d=6$ mm).

![XPS mappings](image)

under the treatment condition of $d=4$ mm and $t=300$ sec, the water adsorption increased 2.63 times compared to untreated one. This suggests that the low-temperature NH$_3$/He-plasma raise the water adsorption of the surface of pp-styrene film. Therefore, we may conclude that the water adsorption rate rise locally under the treatment condition of $d=4$ mm and $t=1$ s, which both nitrogen and oxygen groups modified locally in the size of a glass capillar diameter. For further investigation, the treatment of pp-styrene film coated GHz range STW device is necessary.

![Graph](image)

**Fig. 11. Angle dependant XPS analysis of nitrogen group**

3.2.2. Resonant frequency measurement of treated pp-styrene film deposited on STW device

The specific condition of the pp-styrene film coated STW devices treated by the low-temperature NH$_3$/He-microplasma under humid condition (RH 9%) is shown in Table 4. From a resonant frequency decrease of the device, one can estimate mass increase due to water adsorption. Fig. 12 shows that

![Graph](image)

**Fig. 12. Frequency change of untreated (A) and treated (B $d=4$ mm and $t=300$ s, C $d=6$ mm, $t=300$ s) STW devices coated with pp-styrene film on the surface under humid condition**
4. Conclusion
In this study, we focused mainly on on-demand locality and temperature of the microplasma, and aimed to develop basic technology for the field such as biosensors, which the fabrication of micro interaction-area on thermally sensitive polymer is necessary. First, we generated and characterized a low-temperature NH₃/He-microplasma. Then treated pp-styrene film locally with a low-temperature NH₃/He-microplasma and evaluated the local treated surface. As a result of optical emission spectroscopy (OES) measurement, the gas temperature of NH₃/He-low-temperature plasma estimated from N₂ rotational temperature was $T_e \approx 290$ K and proved the treatment to be less thermal damage for the polymer. Also, from the measurement of Lissajou figure, the calculated electron temperature and the mean electron density was $T_e \approx 10^5$ K and $N_e \approx 10^7$ cm⁻³, respectively. X-ray photoelectron spectroscopy (XPS) measurement results show that the nitrogen and oxygen groups were modified locally on the surface of pp-styrene film by the treatment of NH₃/He-low-temperature plasma. The diameter of modified nitrogen groups’ area corresponds to that of the glass capillary (500µm) at the end of microplasma torch. Furthermore, the resonant frequency decline of the treated pp-styrene-coated STW acoustic device suggested that NH₃/He-low-temperature plasma raised the water adsorption of the surface of pp-styrene film. In maximum, the water adsorption increased 2.63 times compared to untreated one. All the results mentioned above provide evidence that we succeeded in a modification of polymer using low-temperature microplasma.

5. Acknowledgement
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References