Condition and Effects of Various Plasmas after Passing through the Slits

Masaaki Katoh, Masaki Shibata, Akira Kojima and Takeo Ohte

Gunma National College of Technology, 580 Toriba-cho, Maebashi, 371-8530, Japan

The conditions and effects of various plasmas after passing through narrow slits have been investigated. It is important to know them in order to improve solid materials of complex structure. We have studied them, using a sample which simply represents the complex solid materials. This sample consists of slit plates, spacers and a base plate. Modification sources, which modify the material, were introduced into the sample through the slit plates. The conditions and effects of various plasmas were estimated by measuring the change between the contact angles before the plasma improvement and those after the plasma improvement. The material was treated in oxygen plasma, argon plasma and nitrogen plasma mainly. These kinds of plasma were generated by a discharge reactor of induction (coil) type. It has been found that these plasma gases can pass through a very complex route with twists and turns and treat a part behind the material. However, the processing effect is different with every plasma. Oxygen plasma's effect was the strongest of the gases that we used. Argon plasma’s effect was not very strong in the condition of our experiment. In case of nitrogen plasma, its effect became low rapidly near the slits.

Keywords: plasma improvement, plasma treatment effects, complex surface, slit, plasma condition

1. Introduction

Surface modification of various materials with plasma has been used widely and applied to many industrial fields [1] [2]. That can improve characteristics of material surfaces [3]. The material surface treatment can be done in a low temperature and in a short time. Most materials are solids with complicated inner structures and surfaces. Modification of such materials is a very important subject. However, the theme has not been investigated in detail. In case of plasma improvement of complicated solid-type materials, it is important to investigate the action of plasma on their surfaces and whether the surfaces are reformed uniformly and fully.

In this study, we have examined conditions and effects of plasma on the surfaces after passing narrow slits when the surface modification by plasma is carried out. We paid attention to a very complex route of plasma with twists and turns in particular. The simple model [4] (sample) representing this phenomenon has been developed successfully, and for investigating this phenomenon in detail, the sample was modified by plasma in case that discharge of a plasma apparatus is raised with a coil [5] [6]. The self-bias in this discharge type is not very large [7].

2. Method

2.1. Sample

The solid material used in this experiment is shown in Fig.1. This represents real complex materials simply. We call it the sample. It consists of slit plates, spacers and a base plate. The slit plates have narrow gaps. The spacers, the base plate, and the slit plates are made of aluminum.

A modification source, that is, plasma modifying the material, was introduced into the sample through the narrow gaps in the slit plates. The sides of the sample were covered with plates in order to prevent the plasma from intruding except their slits. The route of plasma is changed by modulating the length the spacers as shown in Fig.1. The thickness of the spacers and the slit gap can be changed, too. The number of steps in the sample is variable. All parts of this sample is tightly fixed to each other.

A glassy carbon (GC; Showa Denko, SG-3) were used in order to estimate the effect of surface modification by plasmas. The plate is 25 mm in length, 50 mm in width and 0.6 mm in thickness. It was washed with ethyl alcohol and water, and then
was dried before plasma treatment.

2.2. Plasma improvement

Plasma improvement was carried out by R.F. glow discharge plasma. As shown in Fig.2, the plasma treatment apparatus of induction type was used for treatment. This apparatus has a coil (3 in Fig.2; copper of \( \phi 123.5 \, \text{mm} \)), and an earth electrode (5; stainless steel of \( \phi 100 \, \text{mm} \)) in a pyrex glass discharge vessel (4; inside diameter of 250 mm). R.F. power from a R.F. electric power source is supplied to the coil through a matching box (2 in Fig.2). The characteristic of the induction type discharge is different from that of the discharge type of parallel plate electrodes. RF power is supplied to plasma through a glass vessel. The plasma sheath voltage between the surface of an electrode and plasma is low. The sample was put on the earth electrode. The discharge (treatment) chamber was evacuated to a high vacuum in advance. The mass flow of gas was controlled in 15 ml/minute. Then a designated power (13.56 MHz) was supplied to the coil. R.F. discharge plasma was generated. Conditions for improvement were shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Treatment conditions</th>
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<tbody>
<tr>
<td>Pressure</td>
<td>26.6, 53.2 [Pa]</td>
</tr>
<tr>
<td>Frequency</td>
<td>13.56 [MHz]</td>
</tr>
<tr>
<td>Power</td>
<td>50 [W]</td>
</tr>
<tr>
<td>Gas</td>
<td>oxygen, nitrogen, argon</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>15 [ml/min.]</td>
</tr>
<tr>
<td>Treatment time</td>
<td>5 [min.]</td>
</tr>
<tr>
<td>Sample</td>
<td>Glassy carbon</td>
</tr>
</tbody>
</table>

2.3 Measurement of contact angles

The contact angle with water at room temperature on each plate surface before and after the plasma treatment was measured by a goniometer-type contact angle meter (Erma, G-1) in order to estimate plasma-treatment effects. A drop of water (approximately 10 \( \mu l \)) was put onto
each GC plate surface. GC is suitable for measuring the contact angle on its surface.

2.4 Mass analysis
The sample was placed on the earth electrode of plasma apparatus that has a parallel plate type electrode (Nichiden Anelva, the modified version of PIA-200). Then we generated plasma and measured the plasma composition elements in the sample by a quadruple mass spectrometer (Nichiden Anelva, AQA-360). The measurement system of mass spectra of the plasma composition elements in the sample is shown in Fig.3. The R.F. discharge plasma is generated between the power electrode and the earth electrode by these parallel plate electrodes. The plasma composition elements in the sample are introduced from the orifice, of the earth electrode, into the mass analyzer.

![Diagram of mass analyzer and plasma setup](image)

**Fig.3** Measurement system of mass spectra in the sample.

3. Results & Discussion
The contact angles of GC plate surface before plasma treatment were about 90°. In case of oxygen plasma (C in Fig.4), the contact angles at all points were about 15° and were improved largely. The contact angles were almost constant at the points 10mm to 120mm from the slit. The nitrogen plasma (B in Fig.4) improved GC greatly at points 10mm and 20mm from the slit. The contact angles suddenly increased. (This means that the effects of plasma become low rapidly) and after 60mm they were about 80° and they were constant even if the distant from the slit was increased. The improvement effect by argon plasma (A in Fig.4) was small. At the points more than 50mm from the slit the improvement was hardly done. The surfaces of the glassy carbons became hydrophilic by modification with plasma. As for ions, they may not be able to move in a complicated course because they are controlled by an electric field. Argon ions in the sample were not detected by measurement with a mass analyzer in this condition. It was found from our experiment that

![Fig.4](image)

**Fig.4.** Relation between the contact angle of water to GC surface and the measured position in case that the GC was treated by some kinds of plasmas. pressure: 53.2[Pa], power: 50[W] processing time: 5[min.]
A: argon, B: nitrogen, C: oxygen

![Fig.5](image)

**Fig.5.** Relation between the contact angle of water to a GC surface and the measured position in case that the GC was treated by nitrogen plasma. power: 50[W], processing time: 5[min.]
A: 53.2[Pa], B: 26.6[Pa]
the argon ions could hardly pass through the slit. In case that elements of the gas in the sample is ionized in the mass spectrometer, ions are detected by the mass spectrometer. It means that the elements of the gas could arrive at a part near the orifice. Therefore, modification sources in the sample are thought radicals. A hydrophilic group is necessary on materials surfaces in order to become hydrophilic on the surfaces. The oxygen plasma and nitrogen plasma have elements for making the hydrophilic group. Argon plasma is not thought to contain such elements. However, the contact angles decreased a little at points near the slit. This fact means that the argon plasma reached the near points even if the effect small is. Several reasons for the effect are thought. At first, oxygen remained in the sample. Another reason is as follows. An active radical which had a long life time was generated on the GC surface near the slit by argon ion bombardment. It is thought that there existed argon ions near the slit inside the sample. The activity radical reacted to oxygen in air when we took out materials from the chamber and the hydrophilic group was produced. As the third reason we guess that near the slit or in the sample the argon discharge might occur and the argon ions might generate. The forth reason is that the argon ions could pass through the slit owing to some cause.

Fig.5 shows the relation between the contact angle on the GC surface and the measured position for two values of pressure when the GC was treated by the nitrogen plasma. In both values of pressure, the modification effect became low rapidly when the distance was increased. The modification effect of ion was thought very small. Therefore, the quantity of radicals decreased rapidly.

As a result of mass analysis, no ions were detected. Therefore, any ion does not arrive at deep points in the sample. The ions are not related to the improvement of material surfaces in a sample.

4. Conclusion
Plasma can deeply intrude into a sample through a complicated and narrow course and can improve the material. The reform effect can be controlled by changing pressure or input power. Radicals play a great role when a solid material of complex structure is improved by plasmas. Its modification effect rapidly becomes low in the nitrogen plasma treatment near slit.

References