Gas Barrier Properties of Diamond-like Carbon Films
Synthesized by Using Remote Type Microwave Plasma CVD under Sub-ambient Atmospheric Pressure

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Abstract. Diamond-like carbon (DLC) films were synthesized on polyethylene (PE) substrates with a remote type microwave plasma chemical vapor deposition (MPCVD) apparatus at 10 kPa. We investigated the effect of source gas flow rate and microwave power on oxygen transmission rate of DLC films. Acetylene (C\(_2\)H\(_2\)) and argon (Ar) gas were used for source gas and carrier gas, respectively. From the result of contact-type profiler and atomic force microscope, oxygen transmission rate decreased as thickness increased and surface roughness decreased with increasing C\(_2\)H\(_2\) flow rate. The oxygen transmission rate of DLC film synthesized at the C\(_2\)H\(_2\) flow rate of 0.50 l/min and the microwave power of 1.0 kW on 300 \(\mu\)m thick PE substrates was 141 cc/m\(^2\)·day, while that of uncoated PE substrates was 247 cc/m\(^2\)·day.

1. Introduction
There has been a great attention about the study of diamond-like carbon (DLC). Several studies have reported that DLC films possess many excellent properties: low friction coefficient, low wear rate, high hardness, fine corrosion resistance and low gas permeability [1-3]. Because of these properties, DLC films have yielded practical applications in mechanical, electrical and medical fields [4,5]. This film has been synthesized inside polyethylene terephthalate (PET) bottles to improve gas barrier properties, and plasma enhanced chemical vapor deposition (PECVD) method is applied for commercializing this application [6]. However, since oxygen ingress through plastic caps causes deterioration of the contents as well as through bottles, high gas barrier films should be synthesized on caps to protect the contents.

Conventional PECVD method under low pressure is not suited to synthesis of DLC films on inexpensive products like caps due to unbearable cost resulted from the vacuum process. For this reason, we have studied synthesis methods at sub-ambient atmospheric pressure without high-vacuum technique and recently we have focused on CVD processes using a sub-ambient atmospheric microwave plasma generating device utilizing an annular wave guide.

Microwave plasma chemical vapor deposition (MPCVD) devices use induction coupled plasma and there is no necessity to make electrodes fit along substrates. Therefore MPCVD devices are adapted for application to three dimensional substrates. Over the past few years, many researchers have synthesized DLC films by using MPCVD devices under high vacuums or high temperatures [7,8]. However, there have been no noticeable studies on synthesis of DLC films by MPCVD devices on...
polymer substrates such as polyethylene (PE), which is common material of plastic caps, carrying out under sub-ambient atmospheric pressures at low temperatures. In recent year, novel MPCVD devices which can generate plasma at sub-ambient atmospheric pressure have been developed by irradiating surrounded microwaves through the annular wave guide to fused quartz cylinders [9,10].

The present study was undertaken in order to synthesize DLC films under sub-ambient atmospheric pressure and low temperature by a remote type MPCVD apparatus and to investigate the effect of source gas flow rate and microwave power on oxygen transmission rate of the DLC films and to clarify the factors influencing the decrease in the oxygen transmission rate.

2. Experiments

We employed a MPCVD device for the synthesis of DLC films under sub-ambient atmospheric pressures. Figure 1 shows a schematic view of the remote type MPCVD equipment with an annular wave guide for generating surface wave plasma (CYRANNUS I-6, iplas, Germany). The equipment excites carrier gases by irradiating the microwave of 2.45 GHz to the fused quartz cylinder whose diameter is 140 mm and height is 143 mm, and generates plasma. The generated plasma was exhausted as a jet stream generated by the pressure difference between an upper chamber with lower pressure and the fused quartz cylinder, and a source gas was introduced into the plasma jet and was excited.

Table 1 shows the experimental conditions. First, nitrogen (N$_2$) and argon (Ar) gas which have long lifetime of excited states were used as carrier gas and we investigated the effect of the carrier gases on substrate temperatures. The Microwave power was 2.0 kW, and the output wave, which decides the operation modes of the microwave generator, was continuous wave. Second, acetylene gas (C$_2$H$_2$) was used as the source gas and its flow rates were 0.10, 0.25, 0.50 l/min, and Microwave power were 1.0, 2.0, 3.0, 4.0 kW to investigate the effect of source gas flow rate and microwave power on oxygen transmission rate of the DLC films. PE sheets with a thickness of 300 μm were used as the substrates for oxygen transmission rate measurement system and single crystal Si (100) wafers were used for all the other analyses.

The substrate temperature was measured by a thermocouple thermometer. The structure of the films was determined by Raman spectroscopy (STR300, Seki Technotron Corp., Japan). The oxygen transmission rate was determined by an equal-pressure method of ISO 15105-2 (OX-TRAN Model 2/21, Mocon, Inc., USA). The film thickness was measured by a contact-type surface profiler (Dektak3030, Veeco, USA). The surface roughness was measured by an atomic force microscope (SPM-9600, SHIMADZU CORPORATION, Japan).

Table 1. Experimental conditions.

| Parameter                  | Conditions          |
|----------------------------|---------------------|
| Microwave power (kW)       | 1.0, 2.0, 3.0, 4.0  |
| Output wave                | Continuous wave     |
| Source gas                 | C$_2$H$_2$          |
| Source gas flow rate (l/min)| 0.10, 0.25, 0.50    |
| Carrier gas                | N$_2$, Ar           |
| Carrier gas flow rate (l/min)| 10                 |
| Substrates                 | PE, Si              |
| Synthesis time (min)       | 10                  |
| Synthesis pressure (Pa)    | $10^4$              |
3. Results and Discussions

3.1. Effect of carrier gases on substrate temperatures

Figure 2 shows the substrate temperatures using N\textsubscript{2} and Ar as the carrier gases at the microwave power of 2.0 kW with a function of synthesis time. The substrate temperature was exceeding 200\degree C when N\textsubscript{2} was used for a carrier gas though melting point of PE is 110-140\degree C. When Ar was used for a carrier gas, the substrate temperature was decreased to about 70\degree C. The substrate temperatures at 4.0 kW was kept a little below 110\degree C while it was higher than that at 2.0 kW.

3.2. Synthesis of DLC films using Ar carrier gas and measurement of oxygen transmission rate

Figure 3 shows Raman spectra of DLC films using Ar carrier gas when microwave power was 1.0 kW. Raman spectra of DLC-specific which had G band (1540 cm\textsuperscript{-1}) and D band (1380 cm\textsuperscript{-1}) were obtained. From Figure 3, the structure of the films did not depend on C\textsubscript{2}H\textsubscript{2} flow rate. The same spectra were observed with different microwave powers, which indicate the structure of the films is not affected by microwave power.
Figure 4 shows Oxygen transmission rate of DLC films on PE substrates as a function of the C$_2$H$_2$ flow rate. Oxygen transmission rate decreased with increasing C$_2$H$_2$ flow rate except the DLC film obtained at 4.0 kW. When microwave power was 4.0 kW, oxygen transmission rate decreased to about 190 cc/m$^2$·day in spite of no C$_2$H$_2$. This result indicates that higher substrate temperature closed to the melting point of PE accelerated crystallization of PE and decreased oxygen transmission rate.

3.3. Factors influencing the decrease in the oxygen transmission rate

Figure 5 shows thickness of DLC films as a function of the C$_2$H$_2$ flow rate at various microwave power. Thickness increased with increasing C$_2$H$_2$ flow rate and microwave power in the range of 1.0-3.0 kW. Figure 6 shows Oxygen transmission rate as a function of the thickness. Thickness was correlated with oxygen transmission rate at the microwave of 1.0-3.0 kW. The correlation coefficients (r) were calculated to be -0.90, -0.98 and -0.98 at 1.0, 2.0 and 3.0 kW, respectively. There was no correlation at 4.0 kW (r=-0.23). Increase of thickness led to a decrease of oxygen transmission rate.

Figure 7 shows surface roughness of DLC films as a function of the C$_2$H$_2$ flow rate at various microwave power. Surface roughness decreased with increasing C$_2$H$_2$ flow rate. Figure 8 shows Oxygen transmission rate as a function of the surface roughness. Surface roughness was correlated with oxygen transmission rate at the microwave of 1.0-3.0 kW (r=0.97, 0.85 and 0.93 at 1.0, 2.0 and 3.0 kW, respectively). There was no correlation at 4.0 kW (r=0.06). Decrease of surface roughness led to decrease of oxygen transmission rate. It was suggested that surface roughness was associated with an internal structure of the DLC films.

The DLC film synthesized at lower microwave power showed nearly the same level of oxygen transmission rate at low thickness. This result suggests low microwave power plasma reduced damage to the PE substrates. The DLC film synthesized at C$_2$H$_2$ flow rate of 0.50 l/min and microwave power of 4.0 kW showed abnormality, and requires further investigation.

![Figure 5](image1.png)  
**Figure 5.** Thickness of DLC films as a function of the C$_2$H$_2$ flow rate.

![Figure 6](image2.png)  
**Figure 6.** Oxygen transmission rate as a function of the thickness.
4. Conclusions
The DLC films were synthesized at the condition of 10 kPa, 70 ºC using MPCVD equipment. In terms of carrier gases, Ar was found to be a better candidate for synthesizing DLC films on plastics like PE. By using Ar carrier, lower synthesizing temperatures were obtained. Oxygen transmission rate decreased as thickness increased and surface roughness decreased with increasing C$_2$H$_2$ flow rate. The DLC films synthesized at low microwave power have a higher ratio of gas barrier to thickness compared to those at higher microwave power.

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