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# Gas barrier properties of carbon films synthesized by atmospheric pressure glow plasma

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**Abstract**

High gas barrier carbon films were successfully synthesized on top of polymer substrates using an atmospheric-pressure glow (APG) plasma CVD equipment by reducing the discharge area and by changing the size of the electrodes of the equipment. Homogeneous and highly stable plasma was constantly generated under an atmosphere of acetylene gas ($C_2H_2$) without using any other dilution gases such as He, Ar and $N_2$ that are generally used in order to stabilize the plasma. The absence of the dilution gases led to form rigid carbon-to-carbon bonds. The rigid C bonds constructed dense carbon films at the very surface of the coated films with high gas barrier properties. The oxygen transmission rates of the polyethylene terephthalate (PET) film coated with this amorphous carbon (a-C:H) material was therefore dramatically improved (23 times less in transmission rate) compared with that of an uncoated PET film. The microstructures of the films were investigated by Fourier transform infrared spectroscopy (FT-IR) and the surface morphology was observed by a scanning electron microscope (SEM).


*Keywords:* Carbon films; APG plasma; Gas barrier; PET

## 1. Introduction

Recently amorphous carbon (a-C:H) films have been used for the food packaging purposes due to their attractive gas barrier properties. Some of them have already been widely commercialized [1,2]. PET bottles for example, when coated inside with the a-C:H films of 10–100 nm thickness, improve the gas barrier properties dramatically by 20~30 times compared with those of uncoated PET bottles [3]. Consequently the shelf life of bottles becomes longer since the newly coated bottles can preserve the taste and the freshness of the stored drink/food in a better condition for even much longer time than uncoated bottles. Although $Al_2O_3$ and $SiO_2$ films were also reported as high gas barrier materials as the amorphous carbon (a-C : H) films [4], the carbon films are considered better materials for the food packaging purposes, due to their flexibility, recyclability and biocompatibility [5].

The low-pressure plasma-enhanced chemical vapor deposition (CVD) method was introduced to synthesize a-C:H films. For this purpose, it is necessary to study how to control the vacuum condition of the equipment to obtain suitable plasma species. Such a vacuum technique, however, proved to be too costly to produce low priced products such as plastic bottles and packages, due to the expensive pumping equipment and the time-consuming vacuum process. Our major target is to overcome these problems, developing a new technique to generate a cost-effective atmospheric pressure glow (APG) plasma system.

According to the studies previously reported by Okazaki et al. related to this field, they stabilized the glow plasma under atmospheric pressure in 1988 by preventing the undesired transition from glow to arc discharge [6–8]. To maintain homogeneous and stable glow plasma, they suggested following three treatments in operating the atmospheric-pressure glow plasma: 1) using helium gas for dilution gas; 2) using a high frequency power source (~kilohertz) and 3) inserting an insulating dielectric plate on the electrodes (Fig. 1). The surface modification [9], the fluorination [10,11] and the film synthesis [12–15] are discussed in several papers. There have been several reports regarding the synthesis of carbon films [16], but the studies based on the practical use of these films are still very few. In this work, we will introduce our strategies on how we

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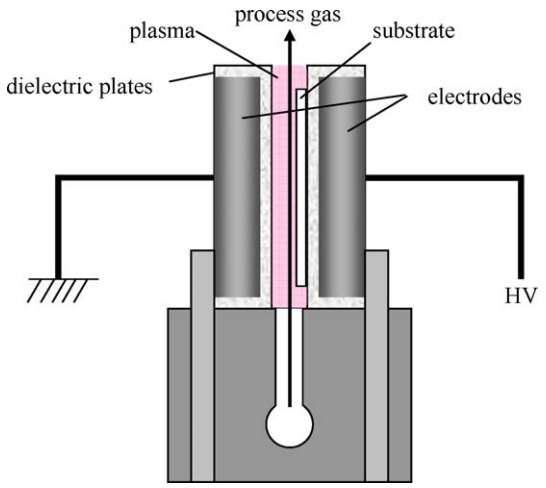


Fig. 1. Schematic diagram of APG plasma CVD equipment.

designed and set up our APG plasma CVD equipment based on the Okazaki's method, but with some improvements that will be presented in detail in the following sections. With this new designed equipment, we synthesized carbon films under the atmosphere of acetylene gas without using any other dilution gases. We also investigated the gas barrier properties of the synthesized films, introducing a novel PET films coated by a-C:H films with high gas barrier properties.

## 2. Experimental

Fig. 2 shows a schematic view of the APG plasma CVD equipment where the plasma is evenly produced and sustained between the parallel-plate electrodes of 60×70 mm in length and width. PET substrates were set between the two electrodes. The distance between electrodes was 1 mm. Acetylene gas ($C_2H_2$) was supplied between the parallel electrodes, during which the flow rate of the acetylene gas was kept constant at 5 l/min. The frequency of the electric power was 9 kHz and the voltage of 15 kV was applied. Polyethylene terephthalate (PET) films with the thickness of 13 μm were used for the oxygen transmission test and single crystal Si wafers were used to analyze the chemical binding characters of the coated carbon films. The temperature of the substrates was kept constant at ~80 °C during the whole synthesis. The thickness of the coated carbon films was measured with Dektak contact-type surface profiler. The oxygen transmission rate was measured under 100% of oxygen atmosphere using MOCON, OX-TRAN permeability testing technique. The detail of the oxygen transmission test is described in Fig. 2. To determine the chemical binding characters, Fourier transform infrared spectroscopy (FT-IR) was employed and the scanning electron microscope (SEM) was used to observe the morphology of the synthesized amorphous carbon (a-C:H) surface.

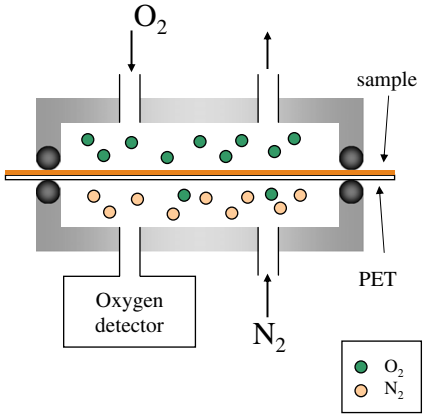


Fig. 2. Schematic diagram of oxygen permeability testing equipment.

## 3. Results and discussion

Previous studies have shown that it was difficult to generate stable acetylene plasma under atmospheric pressure. Okazaki et al. reported that a large amount of dilution gas is necessary to synthesize thin films using the APG plasma technique in order to stabilize the plasma [6–8]. We therefore at first tried to deposit carbon films under various conditions using acetylene gas diluted by Ar and $N_2$ for process gas. Table 1 shows the results of the oxygen transmission test of the synthesized carbon films coated on PET films under the atmosphere of Ar and $N_2$. It was found in our case that these films did not improve the gas barrier property of the PET substrates. The poor gas barrier properties may be due to the presence of the dilution gases of Ar and $N_2$. As for the $N_2$ dilution gas, it was found from XPS analysis that the nitrogen was chemically dispersed in the coated film shown in Fig. 3, constructing C–N (carbon–nitrogen) straight chains. These C–N structures are highly possible to prevent carbon atoms from forming three-dimensional carbon structures, resulting in a reduction of the film density. In the case of the Ar dilution gas, the coated films had powder-like structures showing poor mechanical properties and very low carbon density. The powder-like carbon films were formed even at lower pressure of ~10 Pa when the applied electric power is extremely low at ~10 W. It was also reported by Beshokov et al. that some micro-particles were formed in a-C:H films at low electric power [17]. The voltage to sustain stable Ar plasma under atmospheric pressure was extremely low (~4 kV) while voltage to sustain $N_2$ plasma was relatively higher (15 kV). For example, once a voltage of over 4 kV was applied, Ar plasma was transformed to ark discharge from which it is hard to make

Table 1
Results of oxygen transmission test of the carbon films synthesized by $N_2$ and Ar mixture gas

| Process gas (l/min) | Pressure (PA) | Oxygen (cc/m$^2$/24 h/atm) | Gas barrier property |
|---|---|---|---|
| $C_2H_2+N_2$ | | | |
| 0.03+3.0 | 100 k | 126.2 | 1.00 |
| 0.01+1.0 | 100 k | 127.8 | 0.99 |
| $C_2H_2$+Ar | | | |
| 0.03+3.0 | 100 k | 127.1 | 1.00 |
| 0.01+1.0 | 100 k | 126.8 | 1.00 |
| $C_2H_2$ | | | |
| 0.04 | 13 | 5.7 | 22.26 |

Oxygen transmission of uncoated PET was 126.9 cc/m$^2$/24 h/atm.