



Diamond-like carbon films synthesized under atmospheric pressure synthesized on PET substrates

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ABSTRACT

Diamond-like carbon films were synthesized under atmospheric pressure (AP-DLC) and their gas barrier properties and hardness were measured. The AP-DLC films were uniformly obtained by RF-plasma CVD method at room temperature with a size of 450 mm². The growth rate increased as a function of C₂H₂ concentration and the average growth rate was around 12 μm/min. The maximum deposition rate was ~1 μm/s, which is approximately 2000 times larger than that by low-pressure plasma CVD of 1–2 μm/h. The gas barrier properties of AP-DLC films, ~1 μm thick, were 5–10 times larger than those of uncoated PET substrates. The microhardness of AP-DLC films was around 3 GPa, measured by the nano-indentation method. The issue lies in the removal of macro-particles of the films to improve the microhardness and the surface roughness.

In this paper, we report the physical properties of DLC films synthesized under atmospheric pressure by the radio-frequency CVD method. We also summarize a brief history of PET bottle coating by vacuum-DLC films, as well as that of the development of atmospheric pressure technology and related DLC films, focused on gas barrier properties and micro-hardness.

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1. Introduction

Since the advent of a diamond-like carbon film in the 1970s by Aisenberg and Chabot [1], researches on DLC were conducted all over the world in many fields. At that time, most researchers tried to synthesize diamond from the gas phases by the CVD method, so DLC films did not attract much attention. DLC films have good mechanical, electrical, optical and chemical properties and have propelled the use of DLC coating in mechanical and electrical fields [2]. Ferrari and Robertson reported the relationships of carbon compositions and proposed a ternary phase diagram of carbon films [3]. In fact, this idea is now widespread and useful in developing various DLC films with and without hydrogen. It is now accepted that the lower hydrogen concentration leads to making the DLC film harder.

Around 1990, DLC products gradually appeared in industrial fields and many researchers are now trying to apply them to a variety of fields. In particular, DLC has been found useful in food/beverage and biomedical fields due to the excellent properties of DLC such as acting as a gas barrier, biocompatibility and safety [4]. We have been developing a technique for coating the inside of PET bottles with DLC films as a gas barrier to protect their contents for 10 years. The technique has been commercialized for several years mainly for soft drinks in

Japan. By coating the insides of PET bottles with DLC films of ~20 nm thick, the gas barrier properties improve by ~20 times compared with

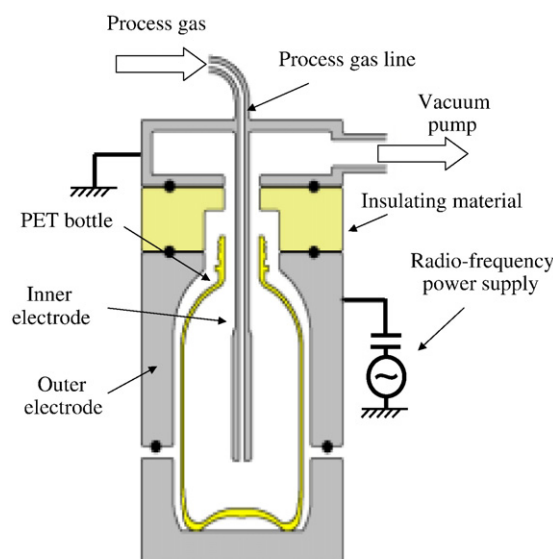


Fig. 1. Around 2000, the coating system by the RF-plasma method was commercialized, which enabled the insides of PET bottles to be coated by DLC films.

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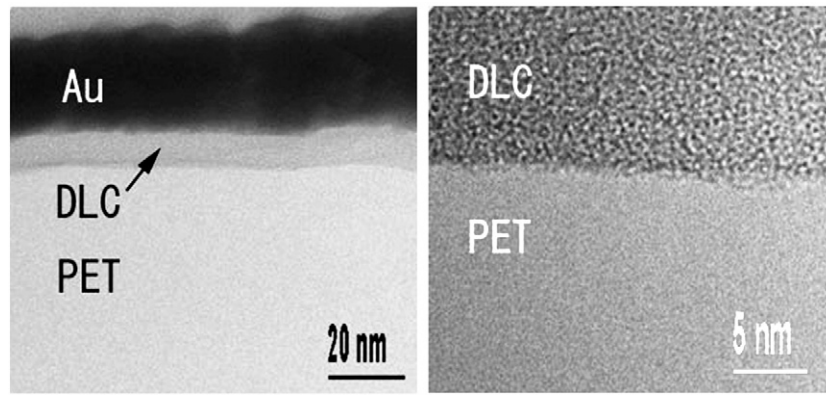


Fig. 2. Cross-sectional TEM photographs between DLC films and PET substrates. DLC films are uniformly coated 20 nm thick. There are no impurities and the second phase is at the interface.

uncoated bottles [5,6]. The films have gas barrier properties but are thought to lack sufficient strength. Around 2002, we started to design new CVD reactors operated under atmospheric pressure for coating DLC films onto PET films based on advances in plasma science and the availability of low cost technology. The high cost of vacuum-DLC attributes to equipment that contains a chamber, several vacuum pumps and other vacuum parts. In particular, there is a huge market for application in low-friction automobile parts that would be coated by DLC if the cost is sufficiently low. As for atmospheric pressure technology other than DLC films, Thomas et al. suggest plasma printing techniques for biomedical and electronics [7].

DLC films are synthesized at a pressure of less than 1 Pa where the carbon radicals reach substrates and gradually form chemical bonds. On the other hand, in the case of atmospheric pressure, there are approximately 10,000 times more radicals in plasma compared to those in vacuum. Therefore, in plasma, radicals react each other in space and coagulate into large particles and fall onto substrates, which leads to the formation of poor density films. Janca et al. first tried to deposit a carbon-based polymer under atmospheric pressure based on the idea of the economic advantages of operating a plasma system without various vacuum equipment [8]. In 1997, Bugaev et al. deposited amorphous carbon films by atmospheric plasma and obtained films at room temperature with a density of 1.3 g/cm^3 and a hardness of 10 GPa by the Vickers microhardness method [9]. Liu et al. also synthesized amorphous carbon films at elevated temperatures and obtained a hardness of 10 GPa by the Knoop method [10]. The problems lie in measuring the hardness of thin films accurately and in particular, the surface of AP-DLC films should have a rough surface. Aguilar et al. summarize atmospheric pressure technology focusing on the microstructure of carbon films [11]. To the best of our knowledge, Klages et al. synthesized DLC films under

atmospheric pressure at an early stage and designed several CVD reactors [12], and they have been developing SiO_2 films and applying them to microfabrication [13]. Kondo et al. used a plasma-jet method to synthesize diamond with a high speed to DLC and achieved AP-DLC with a diameter of 30 mm [14]. Kodama et al. report that a gas barrier with several times that of an uncoated one was obtained by coating AP-DLC onto PET films by dielectric barrier discharge method [15].

In this paper, we first summarize the history of PET bottle coating by conventional DLC synthesized under vacuum. Second, the atmospheric CVD reactor, which we designed and set up is introduced in Section 2. Finally, the physical properties of AP-DLC films based on microstructures and related gas barrier properties and hardness are introduced in Section 3.

2. Coating DLC films inside PET bottles at low pressure

Coating technology for gas barrier enhancement is relatively new and it realizes an industrially favorable situation where extreme performance can be achieved with a thin material. Blocking the passage of gas molecules through the PET wall using ultrathin gas barrier films minimizes the negative impact on the recycling process due to little contamination from different materials. Many coating materials have been subjected to practical trials and as a result, DLC and silicon oxide have become the major materials used in this industry. Silicon oxide coating has a longer history than DLC coating for the gas barrier improvement of transparent plastics film, and has been studied since the early 1980s. However, the intrinsic brittleness of silicon oxide films requires rather complicated conversion processes to withstand mechanical stress and stretching on the PET bottle surface.

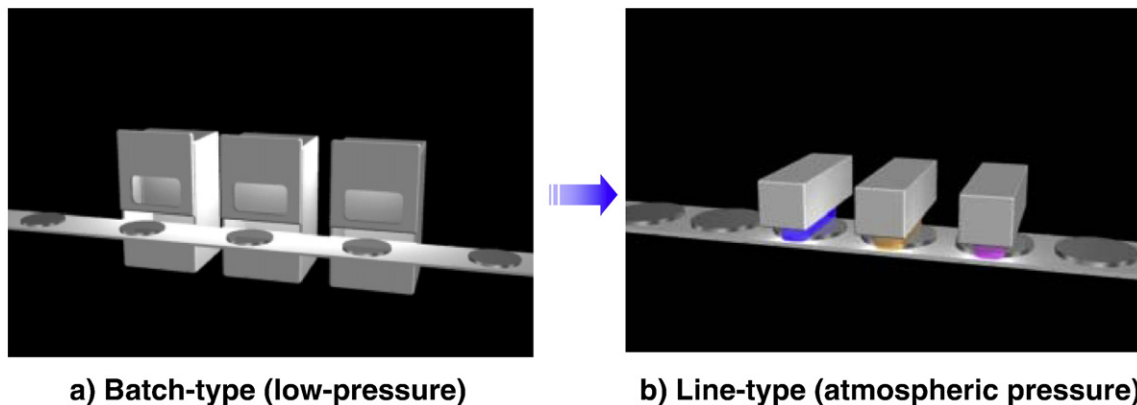


Fig. 3. New mass production system for multilayer coating: By the APG plasma technique, an ideal, low-cost production system may be possible in the future.

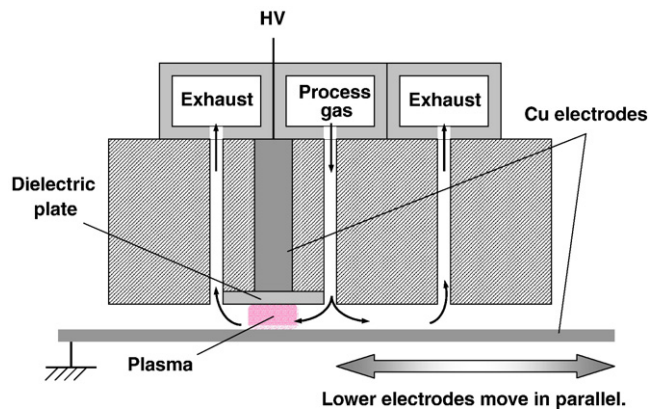


Fig. 4. Schematic diagram of APG plasma CVD equipment. Plasma is sustained between parallel-plate electrodes covered with a dielectric plate.

Kirin Brewery Co., Ltd. developed a unique technology using DLC coating for high gas barrier PET bottles in ~1988, and succeeded in making the first high barrier DLC-coated PET bottles [16]. The advantages of the use of DLC film for PET bottles are primarily derived from its flexible nature along with its high gas barrier property and chemical inertness. Around 2000, the coating system by the RF-plasma method was commercialized as schematically shown in Fig. 1, which enabled the insides of PET bottles to be coated by DLC films [17]. Outer electrodes that enclose the PET bottle are connected to a radio-frequency generator, and a bar-shaped inner electrode inserted into the center of the bottle is grounded. The first step of this coating process is to place a PET bottle into a chamber. After vacuuming down to a pressure of ~10 Pa, the process gas is introduced into the chamber and a radio-frequency of 13.56 MHz is applied between the inner and outer electrodes. Sidel Inc. has developed other types of DLC coating technology, Actis (Amorphous Carbon Treatment on Internal Surface) [18,19]. It also uses acetylene gas as a source of carbon coating. A microwave-assisted process excites the gas into plasma, which deposits a layer of carbon about 0.15 μm thick on the inside of the bottle. The permeation of gas molecules through a polymeric membrane is a result of a combined process of sorption, diffusion and desorption. The permeant passes through thermally fluctuated micro voids existing among tangled polymer chains. The permeability coefficient refers to the amount of molecules passing through the film, per unit of time, area, thickness and pressure difference.

$$P = QL / tAp$$

Where: P = permeability coefficient ($\text{cc cm} / \text{cm}^2 \text{ s mPa}$), Q = amount of gas permeated (cc at standard condition), L = averaged

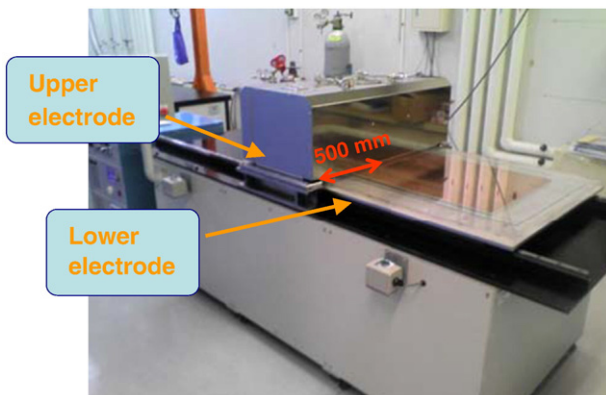


Fig. 5. Flat-panel type CVD equipment: The lower electrode with substrates moves in parallel to the upper one.

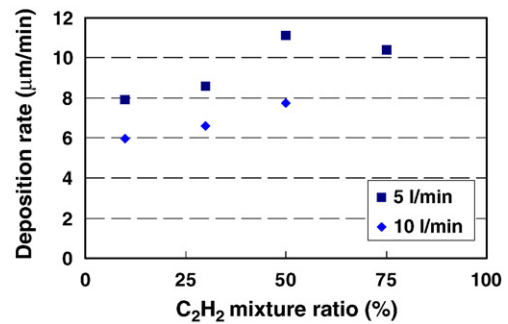


Fig. 6. Deposition rate against C_2H_2 concentration: As the C_2H_2 concentration increases, the deposition rate increases up to ~12 mm/min.

thickness of film (cm), t = time (s), A = permeation area (cm^2), and p = pressure difference (mPa).

The gas barrier property of polymer films is usually expressed as the permeability coefficient, while the gas transmission property of PET bottles such as for oxygen and carbon dioxide is often simply indicated as the gas transmission rate of the whole bottle, for example, in the unit of cc/day bottle.

Fig. 2 shows cross-sectional transmission electron micrographs between DLC films and PET substrates. The film was synthesized by the RF-CVD method under vacuum condition and they were uniformly coated all over PET substrates 20 nm thick. There were no impurities and the second phase at the interface. From the transmission electron microscopy (TEM) observation, it was found that the coated films were completely amorphous [20].

3. CVD apparatus for synthesizing AP-DLC

In 1985, Goldman summarized researches on the corona and dielectric barrier discharge (DBD), which were maintained at atmospheric pressure [21]. Around 1990, Okazaki et al. reported on the stabilization mechanism of glow plasma at atmospheric pressure and succeeded in preventing transformation from glow to arc discharge [22–24]. They suggest the following three conditions in order to stabilize glow plasma at atmospheric pressure:

- (i) using a power source frequency over 1 kHz,
- (ii) inserting dielectric plates between metal electrodes,
- (iii) using helium as the dilution gas.

First, it was necessary to reduce the dilution gases of He in order to lower the cost for industrial purposes. By changing the shape of the upper electrode as well as the material of the dielectric plate, glow plasma was stabilized in air, argon, oxygen and nitrogen. An atmospheric-pressure glow (APG) plasma technique thus became more

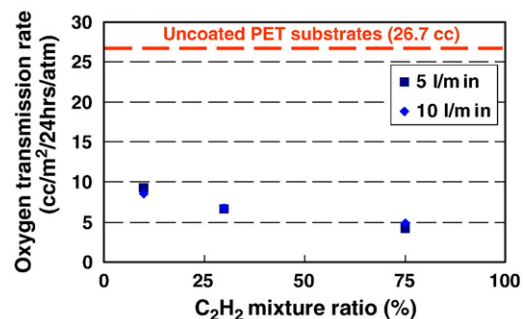


Fig. 7. Oxygen transmission rate against C_2H_2 concentration showing that the gas barrier properties improve with it. The gas barrier properties improve 3–5 times compared with that of uncoated PET films.

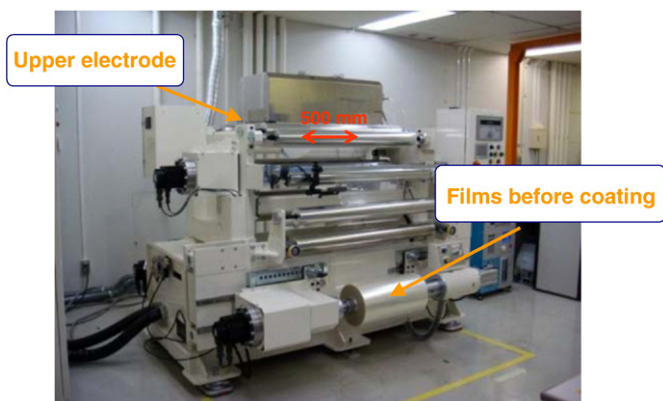


Fig. 8. Roll-type CVD equipment: The lower electrode with substrates move in parallel to the upper one.

practical and studies on surface modification [25], fluorination [26,27] and thin-film deposition have considerably developed. In the beginning, atmospheric pressure technology was used for etching semiconductors such as Si. Second, oxide materials such as SiO₂, were synthesized for protection [28].

Around 2002, we started to design and set up CVD reactors in order to synthesize AP-DLC films with high gas properties, in collaboration with Kirin Beer Co. and Sekisui Chemical Co. Ltd. Fig. 3 indicates the new mass production system for multilayer coating. The APG plasma technique enables development of an ideal, low cost production system.

In 2006, we designed large CVD reactors with the support of Kanagawa Prefecture and Japan Science and Technology as schematically shown in Fig. 4 indicating that the plasma was sustained between parallel-plate electrodes covered with a dielectric plate. Fig. 5 shows flat-panel type CVD equipment where the lower electrode with substrates moves in parallel to the upper one. Both electrodes are covered with dielectric plates. PET substrates were placed between the electrodes. A pulsed power supply operating at 9 kHz in frequency was used for the plasma source.

Fig. 6 shows the deposition rate against C₂H₂ concentration. As the C₂H₂ concentration increases, the deposition rate increases up to ~12 mm/min. Under certain experimental conditions, the maximum deposition rate was ~1 μm/s, which is approximately 2000 times larger than that by low-pressure plasma CVD at 1–2 μm/h. Fig. 7 shows the oxygen transmission rate against C₂H₂ concentration showing that the gas barrier properties improved with it. The gas barrier properties of AP-DLC films ~1 μm thick were 5–10 times those of uncoated PET substrates.



Fig. 9. The flat-type CVD equipment uniformly coats AP-DLC films with a size of 450 mm × 450 mm.

Fig. 8 shows roll-type CVD equipment where the lower electrode with substrates moves in parallel to the upper one. This equipment was originally designed and built in 2006 and used for the R & D of many companies in Kanagawa Prefecture. The film rolls pass through the electrodes of 500 mm in width where DLC films are coated. It was confirmed that these films had gas barrier properties ~5 times that of uncoated PET films, but still have problems in film uniformity.

4. AP-DLC films with high-gas-barrier

At the early stage of our study, we first tried to deposit carbon films under various conditions using acetylene gas diluted by Ar and N₂ for the process gas. However, the films did not improve the gas barrier property of the PET substrates. The poor gas barrier properties would be due to the pore structures of the films caused by the dilution gases of Ar and N₂. As for the N₂ dilution gas, the C–N structures are likely 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 a lower pressure of ~10 Pa when the applied electric power is extremely low at ~10 W. It was also reported by Beshkov et al. that some micro-particles were formed in a-C:H films at low electric power [29]. The voltage to sustain stable Ar plasma under atmospheric pressure was extremely low (~4 kV) while the voltage to sustain N₂ plasma was relatively higher (15 kV). For example, once a voltage over 4 kV was applied, Ar plasma was transformed to arc discharge from which it is difficult to synthesize homogeneous films. The power was considered too low to dissociate a sufficient amount of acetylene molecules to construct homogeneous films, resulting in the formation of a powder-like structure. After changing the experimental conditions, we finally obtained the improvement of gas barrier properties of AP-DLC films by up to ~25 times using C₂H₂ gas [30]. The microhardness of AP-DLC films was around 3 GPa, measured by the nanoindentation method. The removal of particles would improve the microhardness and the surface roughness should be smooth. Fig. 9 shows an optical micrograph of AP-DLC films with the size of 450 mm × 450 mm, synthesized by the flat-type CVD equipment, as is shown in Fig. 5. Table 1 shows the gas barrier properties of AP-DLC films, compared with those of conventional DLC and uncoated PET films. It is natural that the gas barrier properties depend on the film thickness, but the AP-DLC films have sufficient gas barrier properties. Fig. 10 shows cross-sectional TEM photographs of DLC films, synthesized under atmospheric pressure (AP-DLC). The surface of the films is flat, similar to that by the conventional vacuum technique. The enlarged photograph shows that the film does not contain graphitic and polymer contrast, either. Fig. 10 shows the flat-type CVD equipment uniformly coats AP-DLC films with a size of 450 mm × 450 mm.

Furthermore, the deposition rate remarkably increased up to 54 μm/min (~1 μm/s) at an input voltage of 24 kV using a pulsed power supply operated at higher frequency of 35 kHz. This deposition rate is very high, and has not been reached by low-pressure plasma CVD. Thus, it was found that DLC films can be synthesized even at atmospheric pressure while the gas barrier properties of the films are comparable to those of the films synthesized at low pressure,

Table 1

Gas barrier properties of uncoated PET and DLC-coated PET synthesized under vacuum and atmospheric pressure, respectively.

	Uncoated PET	LP-CVD	AP-CVD
Hardness (GPa)	0.1–0.2	10–30	0.5–3
Hydrogen content	–	<30	<50
O ₂ transmittance	50	<5	<10
Film thickness for	–	0.1–0.5	1–2

Hyper barrier: O₂ transmittance < 0.1 cc.

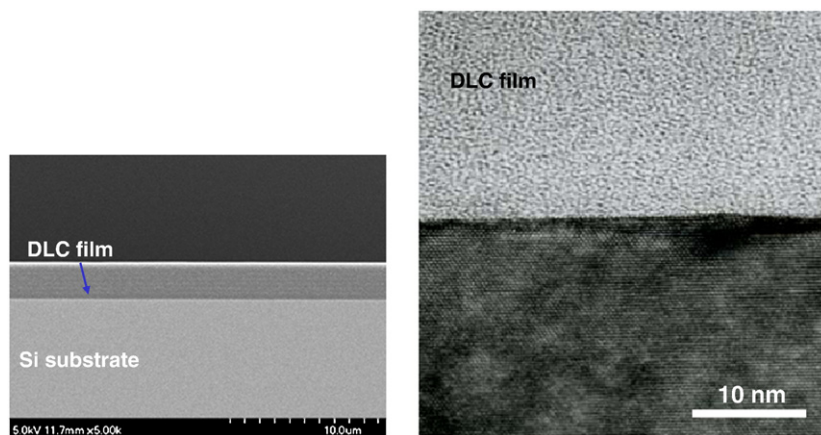


Fig. 10. Cross-sectional TEM photographs of DLC films, synthesized under atmospheric pressure (AP-DLC). The surface of the films is flat, similar to that by the conventional vacuum technique. The enlarged photograph shows that the film does not contain graphitic or polymer contrast, either.

indicating that the APG plasma technique is applicable as a substitute for the low-pressure plasma technique.

5. Concluding remarks

In this paper, DLC films were synthesized under atmospheric pressure and the gas barrier properties and hardness were introduced for practical purposes. The following results were obtained by a series of experiments.

- 1) AP-DLC films were uniformly obtained with a size of 450 mm² at room temperature.
- 2) The growth rate increased as a function of C₂H₂ concentration and the average rate was around 12 μm/min. The maximum deposition rate was ~1 μm/s which is approximately 2000 times larger than that by low-pressure plasma CVD with 1–2 μm/h.
- 3) The gas barrier properties of AP-DLC films ~1 μm thick were 5–10 times those of uncoated PET substrates.
- 4) The microhardness of AP-DLC films was around 3 GPa, measured by the nanoindentation method. Removal of particles would improve the microhardness and the surface roughness should be smooth.

Acknowledgement

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