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

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A R T I C L E I N F O

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A B S T R A C T

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 mm^2. The growth rate increased as a function of C_2H_2 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.

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

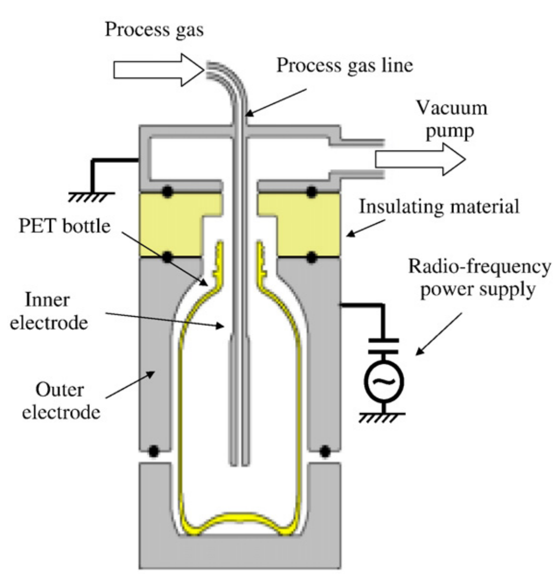

Fig. 1. Around 2000, the coating system by the RF-plasma method was commercialized, which enabled the insides of PET bottles to be coated by DLC films.

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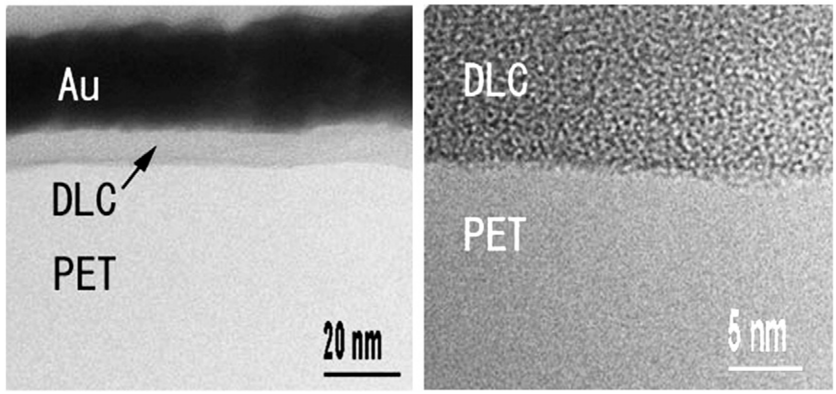

Fig. 2. Cross-sectional TEM photographs between DLC films and PET substrates DLC films are uniformly coated 20 nm thick. There are no impurities and the second phase is at the interface.

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.

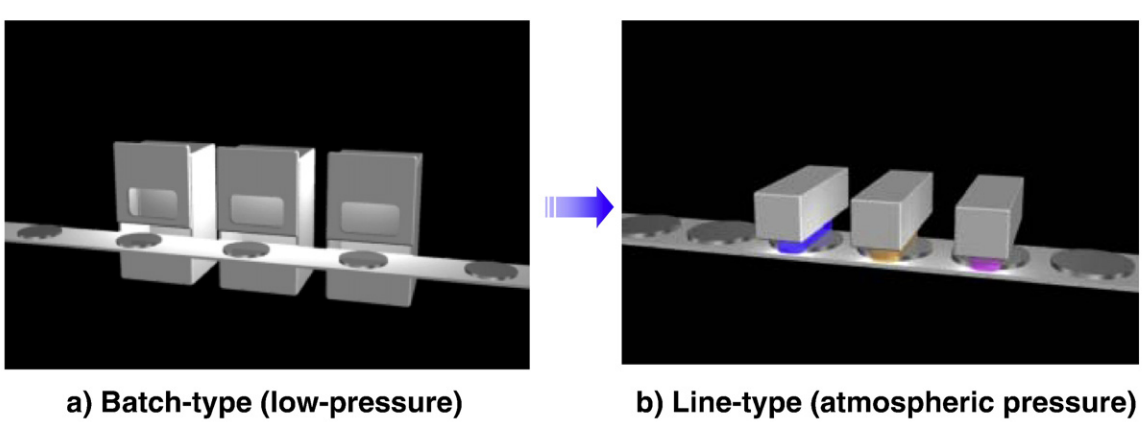

Fig. 3. New mass production system for multilayer coating: By the APG plasma technique, an ideal, low-cost production system may be possible in the future.