The Barrier Properties of PET Coated DLC Film Deposited by Microwave Surface-Wave PECVD

Lianhua Yin¹, Qiang Chen²

¹Shanghai Publishing and Printing College, Shanghai 200093, China
²Laboratory of Plasma Physics & Materials, Beijing Institute of Graphic Communication, Beijing 102600, China

Abstract. In this paper we report the investigation of diamond-like carbon (DLC) deposited by microwave surface-wave plasma enhanced chemical vapor deposition (PECVD) on the polyethylene terephthalate (PET) web for the purpose of the barrier property improvement. In order to characterize the properties of DLC coatings, we used several substrates, silicon wafer, glass, and PET web and KBr tablet. The deposition rate was obtained by surface profiler based on the DLC deposited on glass substrates; Fourier transform infrared spectroscope (FTIR) was carried out on KBr tablets to investigate chemical composition and bonding structure; the morphology of the DLC coating was analyzed by atomic force microscope (AFM) on Si substrates. For the barrier properties of PET webs, we measured the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) after coated with DLC films. We addressed the film barrier property related to process parameters, such as microwave power and pulse parameter in this work. The results show that the DLC coatings can greatly improve the barrier properties of PET webs.

1. Introduction

Plastic webs are very widely used in the field of packaging for advantages of qualitative light, environmental friendly, easy to transfer and so on. Polyethylene terephthalate (PET) is one of these plastic materials, which is very commonly used in our life for fruit juice packaging, water and beer bottles [1]. But the high gas transmission rate of plastics limits their applications. In order to improve the barrier properties, therefore, an organic/inorganic layer was coated on the PET surface. In view of the unique properties of DLC, such as the good chemical stability, environmental protection, thermal stability, non-toxic, in particular, the biocompatibility which makes it very suitable in food packaging [2], we selected DLC as the barrier layer of gas transmission in our work. There are many methods for preparation of DLC films, such as electron cyclotron resonance (ECR) [3-5], filtered cathodic vacuum arc (FCVA) [6], plasma source ion implantation (PSII) [7], plasma enhanced chemical vapor deposition (PECVD) [8-10]. However, for the purposes of a quick film deposition, a high density plasma is particularly essential, which can greatly improve films deposition rate.

Previous works reported that surface wave plasma source, which is sustained by electromagnetic waves traveling along the surface boundaries of plasma and dielectric, can provide a high-density (1011~1013cm-3) [11]. It also demonstrates many other advantages, like simple structure, relatively homogeneous spatial distribution [12-14]. In this paper, therefore, we deposited DLC films by using
this microwave surface-wave PECVD. We measured the coating thickness by surface profiler, and analyzed the composition and morphology by Fourier transform infrared spectroscope (FTIR) and atomic force microscope (AFM). We focused on the role microwave power and pulse period in the gas barrier property of the coated webs.

2. Experimental part

2.1. Discharge Structure

Figure 1 is the schematic diagram of the experimental setup, the 2450MHz microwave emitted from magnetron tube and transferred in the rectangular waveguide is coupled to the resonator through the antenna after mode converses. As shown in Figure 1, the antenna is composed of quartz tubes and a copper tube, and plasma is around quartz tube wall [15]. Besides, the experimental apparatus includes a gas system, vacuum system, and circulating cooling system, which are respectively in order to meet the requirements of working pressure, gas flow rate control and microwave power protection.

![Diagram of experimental setup](image)

**Figure 1.** Diagram of experimental setup

2.2. Deposition Process

Before deposition, we cleaned the substrates by alcohol and deionized water ultrasonically, then dried in nitrogen stream. In order to further clean the surface of the substrates and improve the activity of interface, we exposed the substrates to Ar plasma, the process parameters were listed in Table 1. During the DLC deposition, acetylene (C2H2) and Ar were used as monomer and discharge gas, respectively. The plasma was generated in a pulse mode, and the experimental parameters are shown in Table 2. We focused on the influence of process parameters on the DLC films deposition and barrier properties. The objectives to study the effect of pulse parameters are: the ratio of the plasma-on time (t_on) and interpulse period (t_off) (t_on: t_off), and the pulse power. When we studied the effect of pulsed microwave power on the properties, the ratio of t_on: t_off was kept at 4:40 ms; whereas when for the impact of pulse parameters, the pulsed power was maintained at 1500W.
Table 1. Substrates pretreated parameters

| Gas   | Flow rate (sccm) | Pressure (Pa) | Exposure time (s) | Work mode and microwave power (W) |
|-------|------------------|---------------|-------------------|----------------------------------|
| Ar    | 10               | 20            | 10                | Continue, 400                    |

Table 2. Process parameters of DLC deposition

| Sample | C$_2$H$_2$ : Ar (sccm) | Pressure (Pa) | Deposition time (min) | Pulse microwave power (W) | Ratio of t$_{on}$ : t$_{off}$ (ms) |
|--------|-------------------------|---------------|-----------------------|---------------------------|----------------------------------|
| 1      | 4:1                     | 20            | 3                     | 1500                       | 2:40 to 8:40                     |
| 2      | 4:1                     | 20            | 3                     | 1000 to 2500               | 4:40                            |

3. Results and discussion

3.1. Deposition Rate

Figure 2(a) and Figure 2(b) illustrated the deposition rates of DLC film versus the ratio of t$_{on}$ : t$_{off}$ and applied power, respectively, when the substrates were located at 8 cm distance from the bottom of antenna. As seen in Figure 2(a) the deposition rate increases along with the ratio of t$_{on}$ : t$_{off}$ at the beginning, it is maximum at 6:40 ms and then decreases along with the longer ton. This result can be explained by the competitive ablation and growth mechanism [16]. In Figure 2(b) the deposition rate is always increased with the microwave power. The reason is that the W/F value is still smaller to saturate the formation of films.

![Figure 2](image-url)

**Figure 2.** The deposition rate versus a-ratio of ton:toff; b-applied power (substrates were located at 8 cm from the bottom of antenna)

3.2. FTIR spectroscopy

Figure 3 is the FTIR of DLC film. Figure 3(a). is under different t$_{on}$:t$_{off}$ values and Figure 3(b). is in different pulsed powers. The Figures show that the typical group CH$_x$ (0<x<4) peaks locate in the range of 2800-3100 cm$^{-1}$, corresponding to symmetric and asymmetric stretching vibrations of alkanes and olefins, and the stretching vibration of C-C located at 1020–1170 cm$^{-1}$ [17-19].

![Figure 3](image-url)
We analyzed FTIR spectra in detail based on the Gaussian fitting (DLC film was deposited under 1500W and 4:40 ms), and Gaussian fitting results are shown in Figure 4. Figure 4(a). Corresponds to the deconvolution of C-C stretching vibration located at 1020–1170 cm$^{-1}$, including the stretching vibration (1100–1020 cm$^{-1}$), symmetric (1120 $\pm$ 10 cm$^{-1}$) and anti-symmetric stretching vibration (1170 $\pm$ 10 cm$^{-1}$). Figure 4(b). is Gaussian fitting in the range of 2800-3100cm$^{-1}$ for component of carbon-hydrogen bonds in the film; the absorption peaks around 2870, 2925 and 2960 cm$^{-1}$ are corresponded to sp$^3$-CH$_3$ symmetric, sp$^3$-CH$_2$ asymmetric and sp$^3$-CH$_3$ asymmetric stretching; the absorption band ranging from 3000 to 3100 cm$^{-1}$ is sp$^2$-bonded carbon$^{[20-21]}$. The carbon in films is mainly presented in sp$^3$ hybridization, following by sp$^2$ hybridization. We then resulted that the main ingredient of the as-deposited film was hydrogenated amorphous carbon, or polymeric carbon.
3.3. The surface Morphology
In order to analyze the film morphology and microstructure, we employed AFM to scan the surfaces. Figure 5. Shows the AFM images of DLC film deposited on silicon substrate at 1500 W and 4:40 ms, which can unveil the surface uniformity, compactness and smoothness in the scan range of 5 × 5μm. From Figure 5(a). and Figure 5(b). Two-dimensional and three-dimensional images, respectively, we can see there are some pits and small convex protrusions on the surface. The roughness was about 2 nm for 154 nm thickness of DLC, which hints the coating was significantly smooth [2, 22]. Figure 5(c) is a line profile corresponding to the white lines position in Figure 5(a). From it we can examine the topography features and observe the surface smoothness. The variation of 20 nm in the roughness indicates that the film is compact and no obvious flaws in the surface, which is very important for gas barrier properties [23, 24].

![AFM image of DLC film deposited on silicon substrates. A- Two a dimensional image; b- three-dimensional image; c- line profile (1500W of the microwave power and 4:40ms of ton: toff , and coating thickness was 154nm)](image)

3.4. Barrier Properties
The measurement of barrier properties was carried out at 12.5μm PET webs. One can see that after coated DLC film, the barrier properties of PET films OTR and WVTR were greatly improved in all conditions listed in Table 3. Figure 6. (a) shows OTR and WVTR are exponentially decreased with the ratio of $t_{on}: t_{off}$. At the ratio of $t_{on}: t_{off} = 4:40$ms and 6:40ms, the OTR and WVTR reach the minimum values respectively. The OTR was decreased about 48 times from 130 cc/(m²-day) to 4.8 cc/(m²-day), the WVTR was decreased ca.11 times from 32 g/(m²-day) to 2.7 g/(m²-day).

Regarding the influence of applied powers Figure 6 (b) shows that the minimum values of OTR and WVTR are appeared at 1500 W. There are several reasons to explain the applied power role, including the ion sputtering and the film thickness. Basically at a high applied power, the ion
sputtering effect will be more serious, which will damage the film morphology and thinning the coatings, ultimately affect the barrier properties.

**Table 3. WVTR and OTR values of PET coated DLC films under various process conditions**

| Sample | Pulse power (W) | Ratio of t_{on} : t_{off} (ms) | Thickness of DLC films (nm) | OTR (cc/m^2-day) | WVTR (g/m^2-day) |
|--------|----------------|-------------------------------|-----------------------------|-----------------|-----------------|
| 1      | 1500           | 2:40                          | 67                          | 39              | 22              |
| 2      | 1500           | 4:40                          | 154                         | 4               | 5               |
| 3      | 1500           | 6:40                          | 216                         | 12              | 2.7             |
| 4      | 1500           | 8:40                          | 117                         | 11.3            | 4.9             |
| 5      | 1000           | 4:40                          | 45                          | 47.9            | 30              |
| 6      | 2000           | 4:40                          | 208                         | 14              | 10.9            |
| 7      | 2500           | 4:40                          | 228                         | 11.9            | 14              |
| Blank PET | --     | --                            | --                          | 130             | 32              |

**Figure 6.** Relationship of barrier properties of the PET coated DLC films versus a-ratio of ton : toff (1500W); b-microwave power (ton: toff=4:40ms)

4. Conclusion

In this paper, DLC films were deposited on PET web surface by the microwave surface-wave PECVD. In optimal conditions the deposition rate was over 70 nm / min, which means the microwave surface-wave is high efficient source for coating deposition by PECVD. The barrier property of PET film can be greatly improved after coated DLC film on surface: the OTR of PET web can be decreased about 48 times and the WVTR was down ca. 11 times, which will be very usable for the food packaging in a long shelf life. We believe that the microwave surface-wave is a very proper plasma source to deposit film in high speed and good uniformly, and it can be used in the industrial scale in future.

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