A novel technique to enhance surface properties of DLC films deposited on the inner wall of cylindrical PET barrel by DC-RF hybrid discharge

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1. Introduction

Diamond like carbon films have widely been investigated due to its high mechanical hardness, chemical inertness, optical transparency, and wide band gap [1]. Recently the excellent gas barrier property of DLC films has been paid more attention due to the increasing requirement in food and beverage packaging market, especially for plastic beer bottle to prolong the shelf life [2,3]. The inner gas-barrier DLC films on PET bottle could be produced by radio frequency plasma enhanced chemical vapor deposition (RF PECVD) and commercial system can be available [4].

For traditional inner DLC deposition using RF PECVD technique, the PET bottle is placed in a vacuum chamber that functions as the outer electrode. A metal tube is inserted into the bottle acting as the gas inlet and grounded electrode. RF power is then applied to the outer electrode to ignite the discharge between the outer electrode and the grounded metal gas inlet tube and subsidiary chamber [3]. However, there are problems arising from this type of discharge configuration. First, it is difficult to generate the plasma inside the PET bottle due to its special geometry. Second, the self bias of radio-frequency electrode is relatively small leading to weak tailoring effect of the deposited films due to small area ratio of the grounded electrode to RF electrode [5,6]. Consequently the composition and structure of the DLC films may be compromised by the weak ion bombardment as a result of the small self-biasing effect [7]. The surface properties including the adhesion and barrier properties may be hardly optimized.

In this work, we have developed a new system coupling external negative DC bias to RF unit to optimize the surface properties of DLC films. The effect of DC bias on micro structure, composition, and surface properties of DLC films is focused on.

2. Experimental

Fig. 1 shows the schematic of the RF-PECVD system with external DC bias designed for inner deposition for PET bottles. The bottle vessel is made of stainless steel with an inner diameter of 64 mm and wall thickness of 8 mm. The cavity of the main chamber resembling that of the PET bottle is composed of a cylinder and cone. In our system, the gas inlet tube can be grounded or floated. The main chamber has a PMMA window used to observe the discharge behavior.

Before processing, the chamber was evacuated to the base pressure of ~2 Pa. The working gas (C2H2) was then introduced into the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa. The RF and DC voltages were coupled to the chamber through the inlet tube, and the pressure in the chamber was maintained at 35 Pa.
Cylindrical PET foils with a diameter of Ø63 mm, thickness of 36 μm, and length of 180 mm were deposited with DLC films. The experimental parameters were described in Table 1 in details.

The microstructure of the films deposited on wafers (at the central site of the samples) was characterized by a Jobin-Yvon HR800 Raman spectrometer with 20 mW Ar ion laser beam at 458 nm. The FTIR measurement was carried out using a Fourier transform infrared spectrometer with a wave-number resolution of 2 cm⁻¹. A double beam Perkin-Elmer UV visible spectrometer was applied to measure the optical transmission of the DLC films coated PET samples. To obtain the base line, the PET foils were scanned. And the base line was subtracted for DLC film coated samples. The wyko NT9300 optical profilometry was used to analyze the roughness of the films. Beer immersion tests were utilized to evaluate the adhesion strength of DLC film, and the failure behavior of the film was examined by scanning electron microscopy (SEM). Oxygen permeability of PET samples was studied by constant volume/variable pressure method at room temperature.

3. Results and discussion

3.1. FTIR spectra

Fig. 2 indicates that the FTIR spectra between 2700–3100 cm⁻¹. This corresponds to the C–H local vibrations and stretching modes tend to be less pronounced with an increased DC bias. This means that the films lose hydrogen with increasing DC bias, which might contribute to the enhancement of film hardness [8]. The broad band consisting of a superposition of various stretching vibrations of C–H bond can be deconvoluted into different individual peaks. The bands around 2850 and 2920 cm⁻¹ are due to symmetric (s) and asymmetric (a) vibrations of the sp³ CH₂ mode, while the band at 2870 cm⁻¹ is due to symmetric (s) vibrations of the sp³-CH₃ mode. The band around 2950 cm⁻¹ is assigned to the sp²-CH₂ (olefinic) vibration modes [9,10]. The ratio of sp³ and sp² carbon networks can be considered from the relative intensity of the peaks. With an addition of DC bias (−70 V), the relative intensity of symmetric (s) vibrations of the sp³ CH₂ seems to be lowered, while that of symmetric (s) vibrations of the sp³-CH₃ is enhanced. Meanwhile, the relative intensity of sp²-CH₂ (olefinic) vibration seems to be varied slightly by coupling with a DC bias. However, quantitative analysis of the ratio could not be performed due to the difficulty of accurate deconvolution of the FTIR spectra [11]. But the FTIR results still suggest that the films contain a mixture of sp² and sp³ coordinated carbon atoms in a disordered network [12].

3.2. Optical transmittance

The light transmittance is associated with the structure and thickness of films. For DLC films deposited at different DC bias, the transmittance change may be mainly caused by the variation of sp² and hydrogen content and film thickness. Fig. 3 shows the optical
transmission of DLC films deposited at different negative DC bias. The external bias may lower the optical transmission of DLC coated PET samples. Hydrogen removal and carbon accumulation happen on top surface of PET while transformation of sp$^3$ bonds into sp$^2$ bonds allows more cross-linking. These result in higher refractive indices, [13] leading to reduction of the optical transmittance [14]. It is also reported that the deposition rate would decrease as the DC bias increases, [15] which improves the light transmittance as shown in Fig. 4. Therefore, proper DC bias should be optimized to obtain DLC films with lower optical transmittance to prolong the shelf life of light sensitive food and beverage.

3.3. Surface morphology

The surface morphology of DLC coated PET samples has been examined by optical profilometry and the average roughness of treated surface has also been calculated. Fig. 4 shows the morphology of PET samples without DLC film and with DLC films deposited at different DC bias. Small hill-like structure has been observed on PET substrate as shown in Fig. 5(b). The height of the micro-structure ranges from tens to hundreds of nanometers, and valley regions has also been observed. After DLC deposition, the valley regions seem to be filled and flattened. With increasing negative DC bias, the number and height of these small "hills" increased. The relationship between the average roughness (Ra) and negative DC bias of treated samples is demonstrated in Fig. 5. There exists a proper bias leading to the smallest roughness due to coverage effect. A higher bias may induce the preferential growth at local sites.

3.4. Immersion test

The chemical inertness of DLC films makes them very attractive for corrosion prevention applications [16]. However, DLC films are known to have some weakness in the presence of moisture unless carefully structured for exposure to that environment [17]. Therefore, immersion test in beer is performed to evaluate the film adhesion on the PET substrate at room temperature for 3 months. Fig. 6 shows the effect of external DC bias on surface morphology of the samples after immersion test.

Fig. 6(a) shows the PET sample treated without DC bias after immersed in beer. The significant surface damage of DLC film occurs. In contrast, the sample treated with $-30 \text{ V}$ and $-70 \text{ V}$ demonstrated no evident fracture in the film after exposed to beer liquid. As the external DC bias increased to $-100 \text{ V}$, the immersion result shows that film fracture occurred and the debris appeared in the crack. This might be related to the pin-like structure on the sample surface. These micro structures might become the source of crack due to stress concentration.

3.5. Oxygen permeability

Fig. 7 demonstrates the oxygen transmission rate (OTR) through DLC coated PET samples evaluated using constant volume/variation pressure method [4]. The OTR for PET sample without external bias is as much as 58 cm$^3$/day/atm/m$^2$. After depositing DLC film, the OTR of
samples has significantly been decreased to 13.1 cm³/day/atm/m². With an external bias of −70 V, the DLC coated PET samples possess a slightly higher resistance against oxygen penetration.

4. Conclusion

Diamond like carbon films have been fabricated on PET barrel using the novel technique based RF PECVD with an external DC bias. The results demonstrate the enhanced adhesion strength between DLC film and PET substrate. By coupling with an external negative DC bias, the films tend to be more resistant to damage during immersion test in the beer at room temperature. The depressed optical transmittance and oxygen transmission rate have also been achieved for DLC coated PET sample treated at suitable DC bias. These results have clearly indicated that our novel technique is very effective and may be more suitable for DLC deposition in bottle and bottle-like components.

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