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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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ABSTRACT

A newly proposed technique has been utilized to improve surface properties of gas barriering DLC films deposited on PET bottle. The discharge in the bottle is induced by radio-frequency discharge and an external DC system is coupled to the RF power supply to control the potential of discharge electrode. In contrast to conventional discharge configuration, this leads to the capability to optimize the ion bombardment energy and surface properties of deposited films. The effect of negative DC voltage on the adhesion strength, optical transmittance, surface profile, roughness, and permeability of DLC coated PET samples has been investigated using immersion test, UV-visible spectroscopy, optical profilometry, and gas permeability tester, respectively. The results have demonstrated that the DLC coated PET samples with external bias show slight damage during beer immersion tests. Lower light transmittance is induced for the films deposited at high negative bias due to larger ion bombardment effect. There exists a proper bias to give rise to a small surface roughness. The gas permeability of DLC coated PET samples deposited with external bias has been substantially decreased compared to that of untreated one.

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 package market, especial 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 (C_2H_2) 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 top lid and the outer electrode with the gas inlet tube grounded.

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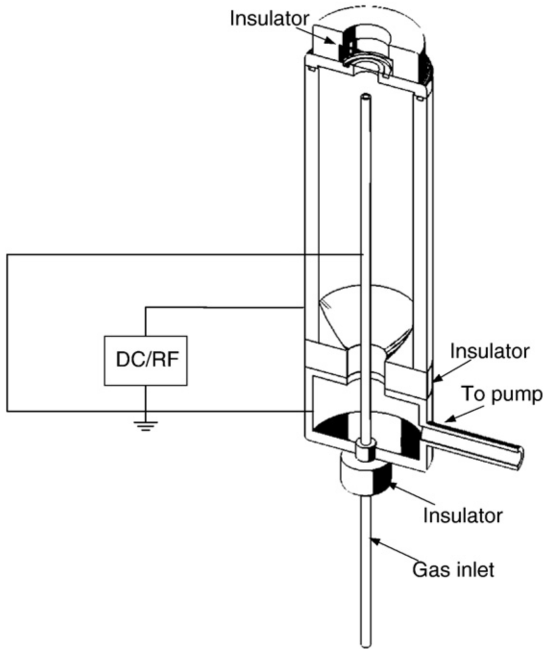


Fig. 1. Experimental setup for film deposition on the inner wall of PET cylindrical barrel.

Cylindrical PET foils with a diameter of Ø63 mm, thickness of 36 um, 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.

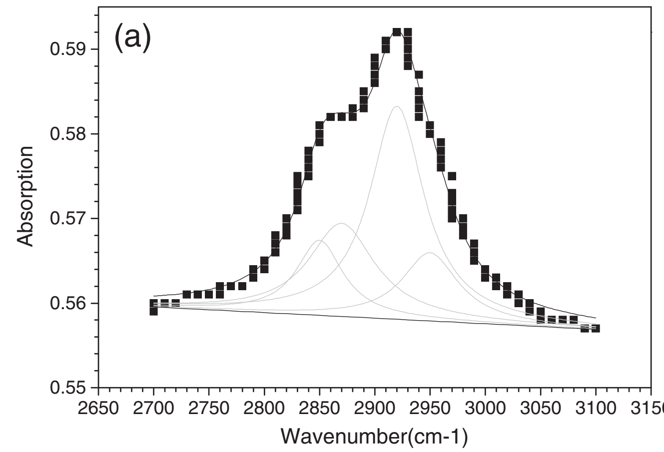
3. Results and discussion

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

Table 1
Instrumental parameters for DLC film deposition.

Sample	C_2H_2 pressure (Pa)	RF power (W)	DC voltage (V)	Time (s)
1	35	200	−100	300
2	35	200	−70	300
3	35	200	−30	300
4	35	200	0	300



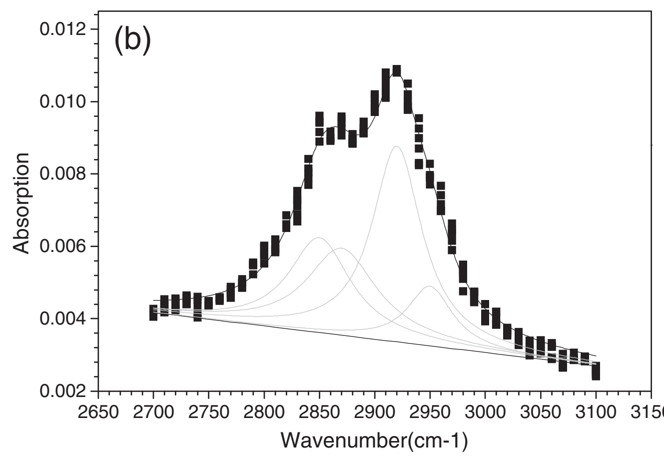


Fig. 2. FTIR absorption spectra with Lorentze fitting for DLC films fabricated at different DC bias (a) 0 V, and (b) −70 V.

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 sp^3 CH_2 mode, while the band at 2870 cm^{-1} is due to symmetric (s) vibrations of the sp^3-CH_3 mode. The band around 2950 cm^{-1} is assigned to the sp^2-CH_2 (olefinic) vibration modes [9,10]. The ratio of sp^3 and sp^2 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 sp^3 CH_2 seems to be lowered, while that of symmetric (s) vibrations of the sp^3-CH_3 is enhanced. Meanwhile, the relative intensity of sp^2-CH_2 (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 sp^2 and sp^3 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 sp^2 and hydrogen content and film thickness. Fig. 3 shows the optical