DLC deposited by dual RF-PECVD and its barrier properties

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Abstract: DLC (diamond-like carbon) films on the inner surface of the PET (polyethylene terephthalate) bottles were deposited by dual RF-PECVD (radio frequency plasma-enhanced chemical vapor deposition) plasmas with C_2H_2 as the carbon source and Ar as the dilution gases. As the barrier layer of gas permeation and humidity in the inner side of the PET bottle, the influence of the DLC film structure, composition and morphology analyzed by FTIR (Fourier transform inferred), AFM (atomic force microscope) and SEM (scanning electron microscope) on the barrier properties were performed. It obtains that the DLC film can be synthesize in the inner side of the PET bottle. The barrier property is depended on the plasma parameters. The DLC film deposited only in CCP (capacitively coupled plasma) source shows a micro-cracks, which is detrimental for barrier performance. In contrast, in dual radio frequency plasma source, i.e. ICP (inductively coupled plasma) source incorporated with CCP source, micro-cracks are disappeared, the OTR (oxygen transmission rate) is significantly improved.

Keywords: DLC, PECVD, barrier property

1. Introduction

With the advantage of their lightweight, designable, physical toughness and economy, the PET bottles occupied more than 80% of the total number of beverage and 4% of beer containers, which is increasing by ca.11.5% annual in the world[1]. However, a vital disadvantage of PET bottles compared with metallic or glass containers is its low gas barrier property, which cause the sensitive contents such as tea and beer tend to deteriorated by permeation of gases, in particular oxygen and carbon dioxide. Therefore, the coated PET polymer to improve the barrier properties was extensively explored. In this campaign the plasma deposition shows a domain role based on its fast, dry, one-step process. The different plasma sources have been developed to deposit DLC and SiOx coatings decreasing the gas and humid permeation through plastic or bottles[2-4]. In here the PET coated with amorphous DLC is a promising route due to high oxygen barrier property, good anti-fragile, easy manipulation and low processing costs as well as excellent recycle without any pollution[5].

Dual radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) was utilized as a new plasma source to deposit DLC coatings on PET surface in this paper. The influences of different plasma source on the film properties, DLC structure, composition and morphology, which were analyzed by FTIR, AFM and SEM were explored. Additionally, the relationship between the surface morphology of the DLC films and the oxygen transmission rate (OTR) were also detected.

2. Experimental

DLC films were deposited in a dual frequency plasma source, i.e. a capacitively coupled plasma source (CCP) and an inductively coupled plasma source (ICP) with the . carbon source acetylene (C_2H_2) and diluted Ar gas. A schematic illustration of the apparatus is shown in Fig.1. During deposition, the discharge parameters, such as the acetylene concentration, the explosion time and total gas pressure were kept constant at 11%, 20min and 20Pa, respectively.

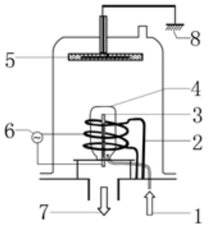

Fig.1. Schematic diagram of dual frequency PECVD reactor (1-mixed gas; 2-ICP coil; 3-CCP electrode; 4-PET bottles; 5-grounded electrode; 6-RF power-1; 7-vacuum; 8-ground)

The OTR was measured as an index of the oxygen barrier property (Model 8001, Illinois instrument). During OTR measurement, both chambers were purged with dry N_2 gas for 5h. All measurements were conducted under ambient conditions (～25°C, 30-50% relative humidity).

The morphology of the film were characterized by SEM and AFM (CSPM 3000, Ben Yuan, China) where AFM measurements are conducted on an area of $5\times5\mu m^2$. The employed tapping mode can ensure a high resolution measurement without causing any damage or alteration of the thin film surfaces.

The structural component of the coatings were determined by FTIR. The measurement in the range of 500-4000cm^{-1} were performed on KBr substrates. The group of CH stretching peak around 2920cm^{-1} is obtained after an interference correction. The shape and amplitude of this peak provide information about the carbon backbonding (carbon hybridization) in the coating. The peak was deconvoluted into individual contributions representing the specific stretching vibrations[6]. For the deconvolution the peak was separated into five Gaussians and used the vibration frequencies according to Dischler[7].

3. Results and discussion

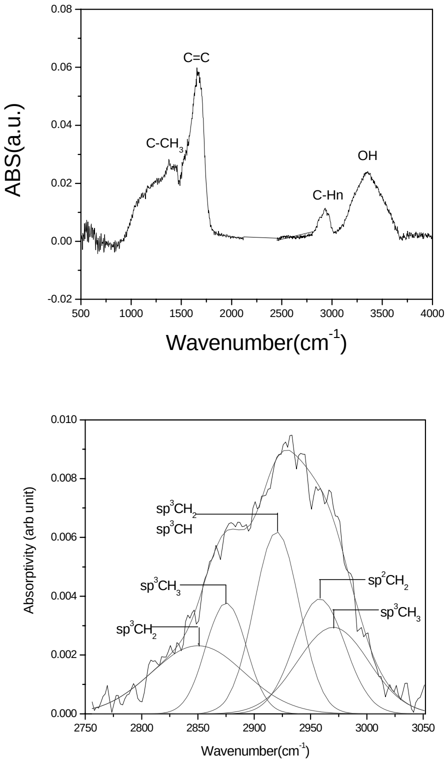

Fig. 2 FTIR of DLC film.(a-The spectrum at 500～4000cm^{-1}; b-The detailed spectrum for group CH at 2750-3050cm^{-1} Ar:C_2H_2=8:1, 150W, 20Pa, 20min)

In the Fig.2a, The obvious absorption peak at around 1400cm^{-1} assigned to the C-CH_3 groups(sp^3) stretching vibration and the absorption peaks in the range of 3000～2800cm^{-1} for C-H_n stretching vibrations clearly demonstrate that the film consists of DLC component. Analysis the spectrum one can obtain that the DLC film was mostly composed of sp^3 hybridized bonding and has high bonded hydrogen content[8]. Otherwise, owing to C-H stretching vibrations under 3000cm^{-1}, it is considered that carbon atoms were at a saturation state in the film. The strong absorption peak at 3410～3300cm^{-1} was O-H vibrational mode following DLC film post-reaction.

Fig.2b displays the results of Gaussian fitting peaks at 2800～3050cm^{-1}. The spectrum reveals the coating was a typical polymer-like structure: the sp^3 CH_3 bone types at 2875cm^{-1} and 2970cm^{-1} strongly dominate the spectrum, but the clear contribution from sp^2 CH_2 at 2958cm^{-1} definitely means it was polymer-like material based on the ascription by Dischler[7].

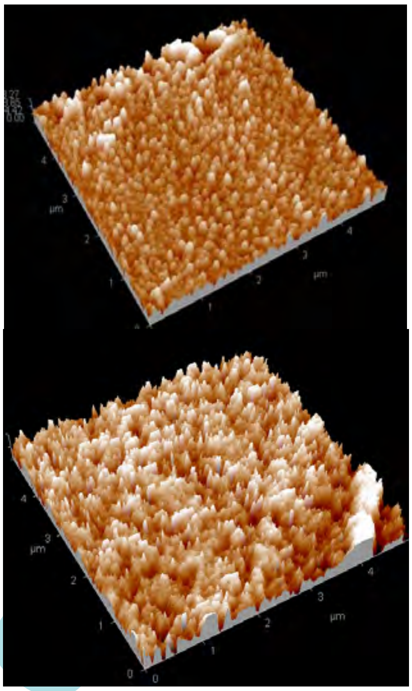

Fig.3 Topographic AFM images of DLC film (a-CCP 150W, b-CCP 150W+ICP 100W)

Fig. 3 shows AFM images of the films deposited at different plasma sources on p-Si (100) substrates. In the Fig. 3a, it can been seen that when only CCP source was employed, the film is composed of uniformly nano spherical particles and following island growth mode. While DLC-film was deposited under dual frequency plasma source, i.e. CCP and ICP sources, however, DLC-film is formed in compact structure (Fig.3b), no distinguished growth mode can be recognized from the image. But the ablation was obviously increased in the dual frequency discharge. The roughness of root mean square (RMS) of film was 4.99nm in this condition of CCP 150W+ICP 100W instead of 2.04nm in film deposited in CCP 150W only. Based on another measurement, such as Kurtosis[9] refered a non-dimensional quantity to evaluate the shape of data about a central mean, and Skewness[10] used the symmetry of surface data about a mean data profile, the dual frequency discharge can improve the film roughness as listed in Table1.

Table 1. The surface topography and roughness affected by the plasma source (nm)

Sample	RMS	Skewness	Kurtosis
a-CCP150W	2.04	0.112	4.13
b-CCP150W+ICP100W	4.99	0.109	3.17

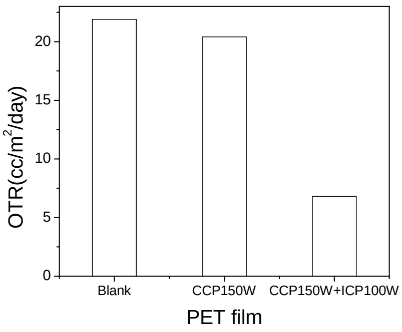

Fig.4 OTR of PET coated by DLC in different plasma sources

Fig.4 shows influence of plasma source on OTR value. It is noticed that for control PET film(24μm) the OTR value is about 22cc/m^2/day. For CCP synthesized DLC coating the OTR show only slight decrease. But in dual frequency discharge, the synthesized DLC coating signficantly decreased the OTR value over four times.

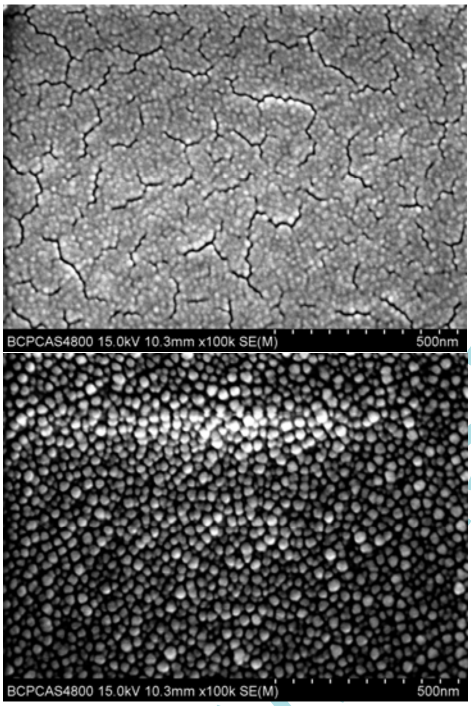

Fig.5 SEM of DLC film (a-CCP 150W; b-CCP 150W+ICP 100W)

Fig.5a clearly shows that a network-cracks were formed and spreading out over the whole surface in CCP deposition DLC coating. In contrast with ICP plasma source addition, the cracks completely disappeared (Fig.5b), but the spherical aggregation was viewed on the surface. The possible explanation for the formation of cracks is due to the strong interface force and intrinsic stress in DLC and PET during DLC growth[11]. The residual stress was released through surface cracks, and the polymeric substrate deformation can also cause the fragile DLC crack in the plastic surface.

SEM images can also be used to explain the different OTR value in CCP and CCP+ICP sources. The obvious crack in CCP deposited DLC film definitely can not block the gas permeation, where the OTR was slightly decreased. In dual frequency plasma source the crack was disappearance, which certainly improve the OTR property. But the film consisted of aggregated spherical particles also can not provide perfect barrier property, the gap between the spheres still was the path for gas permeation, then the OTR was decreased due to the relatively compact surface by the remarkable ablation in dual frequency discharge but the gap between the spheres cause the OTR difficultly reach the zero point scale. Therefore, the future investigations shall be emphasized on decrease of film formation by spherical particles and cracks.

4. Conclusions

The influence of plasma sources on the DLC films can be summarized as follows:

1)The FTIR shows the DLC film in the inner side of the PET-bottle was mostly composed of sp^3 hybridized bonds.

2) The AFM images show the DLC film deposited in CCP source is composed of network of micro-cracks, which was suggested to be a intrinsic property, and correlated to the intrinsic stress in DLC films and the force between the PET and DLC coating.

3) In dual frequency plasma, the cracks in DLC film was solved and gas barrier property was improved. The OTR still decrease in this condition due to the formation of spherical particle of the coatings.

Acknowledgements

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