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Fabrication and characterization of adherent diamond-like carbon based thin films on polyethylene terephthalate by end hall ion beam deposition

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ABSTRACT

This work aims to develop novel techniques, including low energy end-hall ion (EDH) source, nitrogen and silicon doping, to enhance the adhesion strength of Diamond-like carbon (DLC) on Polyethylene Terephthalate (PET) to address their major application issues. For this purpose, Nitrogen doped DLC (N-DLC) and Silicon doped DLC (Si-DLC) thin films with different compositions were prepared on PET substrates using EDHI beam deposition. The composition and bonding states of the films were characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and near edge X-ray absorption fine structure (NEXAFS). The results show that sp^3 carbon bonding concentration in Si-DLC is higher than in N-DLC and the doped Si forms sp^3 Si—C bonds and N forms sp^3 C—N and sp^2 C═N bonds in films. Nano-indentation tests were used to measure the hardness and Young's modulus while pin-on-disk sliding tests and scratching tests were used to evaluate the tribological and adhesion behavior of the samples, respectively. The results illustrate hardness reduction and adhesion enhancement in N-DLC and hardness enhancement of Si-DLC. In addition, the coefficient of friction (COF) of N-DLC is lower than pure DLC and Si-DLC, while it has been observed that formation of silicon oxide can reduce COF of Si-DLC. The coating roughness measured by an optical profiler decreases by increasing nitrogen concentration in N-DLC. This is probably because N doping reduces residual stress and thus makes film dense and smooth. By optimizing deposition condition, highly adherent DLC based thin films on PET have been achieved.

1. Introduction

Due to the unique properties of polymers such as low density, low cost, chemical inertness, high specific strength, good formability, high flexibility, and variety of compositions, forms, and structures, they have been used extensively and the applications continue to increase in the past decades. For example, they have been widely used in packaging, furniture, toys, automobiles, food and beverage containers, biomedical implants, and solar power devices. Among polymers, Polyethylene terephthalate (PET) holds diverse applications as cardiovascular implants (artificial heart valves and blood vessels), food and beverage containers, and components in solar cells [1–3]. PET is a semicrystalline polymer with a simple long chain belong to polyester family and possesses outstanding properties like chemical inertness, high mechanical strength, toughness, and fatigue resistance. In PET structure, aromatic ring is coupled with a short aliphatic chain of a total length of 1.09 nm and a molecular weight of approximately 200 [4]. PET film was developed by injection molding and extrusion in late 1950s and was mostly utilized in videos, photographic and X-ray films as well as in flexible packaging. The first oriented three-dimensional PET was produced in the early 1970s by blow molding [5]. Since then, PET applications in industry have been increased rapidly. Nevertheless, PET surface suffers drawbacks of low hardness, lack of biocompatibility, and low gas retention, significantly limiting its applications.

Surface coating is a prominent way to enhance surface characteristics with no sacrifice of bulk properties. SiO_2 and Si_3N_4 thin films were applied to PET surface to improve its gas barrier properties [6–8]. However, it is hard to coat ultra-thin dense films of oxides or nitrides or carbides on PET because of its low thermal stability. It is good that diamond-like carbon (DLC) based materials can be coated on substrates at temperatures as low as 20C°. In addition, DLC is hard, transparent, chemical inert, highly biocompatible, a good gas barrier, and of low friction coefficient, high wear and corrosion resistance [8,9], which makes DLC an ideal coating material for modifying the surfaces of PET for applications as food and beverage containers [10], and biomedical implants. However, DLC usually has high internal stress due to the ion bombardment during the deposition and has low adhesion strength to polymers because of the large difference in mechanical properties, leading to the delamination of DLC from polymers. Therefore, it is very important to develop techniques to lower the stress of DLC and to enhance the adhesion strength of DLC to polymers. Different approaches have been used

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to improve DLC adhesion on polymers. Plasma surface treatment on polymers is one of the most common techniques to modify the polymer surface and increase the film adhesion by rising the number of free radical on the surface before deposition [11–13]. It has been reported that alloying and doping can reduce the DLC internal stress and consequently improve the film adhesion [14,15]. The effect of nitrogen doping on internal compressive stress reduction in DLC coating deposited on different substrates has been investigated [16,17] and the results show that it is effective in releasing internal stress. The influence of silicon incorporation into DLC deposited on PET has been studied using plasma enhanced chemical vapor deposition in a mixture of acetylene (C_2H_2) and tetramethylsilane (TMS) and improvement of gas barrier properties was reported accordingly [18]. Another potential way to reduce the stress is to use low energy ion beams for deposition. This technique has not been fully studied for DLC deposition.

Gridless end-Hall (EH) ion sources [19], a broad beam source, can supply large ion current (up to 5 A) with the average ion beam energy of 40–210 eV that covers the ion energy range for DLC deposition. Low ion energy is beneficial for DLC deposition on PET because lower ion energy results in lower sp^3 concentration with lower intrinsic stress for improved adhesion. Therefore, EH ion beam deposition would be the most suitable technique for large area DLC deposition on polymers for industrial applications [20,21]. Although progress has been made on EH ion beam deposited carbon thin films, investigations of the microstructure and mechanical properties of a-C:H thin films deposited on PET with EH ion beam are still scarcely reported. Furthermore, no report has been found on the effect of nitrogen and silicon doping on the structure and properties of DLC on PET using EH ion beam deposition.

In this paper, we report on the deposition and characterization of highly adherent DLC based thin films on PET and the investigation of the effect of doping (N and Si) and substrate pretreatment on the structure and properties of DLC on PET.

2. Materials and methods

2.1. Film deposition

PET thin sheet purchased from Goodfellow Co. with the thickness of 0.1 mm was used as substrate for DLC deposition. The sheets were cut into small pieces, cleaned with alcohol bath, washed with distilled water, and then dried at room temperature. Pieces of cleaned silicon wafer with the size of 1 cm × 1 cm were used as a reference sample. Cleaned and dried Si and PET sheets were put into the substrate stage in the dual ion beam deposition system manufactured by 4 wave Inc. described in a previous publication [20]. One EH ion source feeding with a mixture of Ar at flow rate of 12 sccm and CH_4 at a flow rate of 8 sccm was used to deposit hydrogenated DLC. Si-DLC was achieved with simultaneously running another EH ion beam for sputtering of silicon target under different target bias (400 and 800 V). N-DLC was achieved by adding Nitrogen gas with flow rates of 1, 2 and 3 sccm respectively. All the DLC based thin film samples were synthesized in the energy range of 55–65 eV without extra heating of the substrate for a duration of 4 h. The substrate holder was inclined at an angle of 45° to the incident deposition ion beam for all the depositions. The base pressure was 3×10^{-7} Torr and the working pressure was kept at approximately 5×10^{-4} Torr.

2.2. Structural characterization

Raman spectroscopy was carried out using Renishaw Invia Reflex Raman microscope (Renishaw, Gloucestershire, UK) operated under 514 nm Ar ion laser with a spot size of approximately 2 μm. Fourier Transform Infrared (FTIR) spectra were obtained using IlluminatIR II FTIR microscope accessory (Smith's Detection, Danbury, CT) equipped with liquid nitrogen cooled MCT detector. ATR-FTIR measurements were performed in the range of 4000–650 cm^{-1}. XPS measurements were performed at Omicron Multiprobe system of the REIXS surface science facility at the Canadian Light Source (CLS), University of Saskatchewan, using a monochromatized Al K (alpha) X-ray source and a Sphera EA 125 hemispherical electron energy analyzer with the kinetic energies from 600 to 1500 eV. Electron gun was also used to neutralize the charging effect on the polymer surface. Film composition and chemical structure was analyzed with CasaXPS software. Bonding nature of carbon in DLC based samples deposited on silicon reference were studied with Near Edge X-ray Absorption Spectroscopy (NEXAS) carried out at SGM beamline at Canadian Light Source, University of Saskatchewan.

2.3. Mechanical property characterization

The hardness and Young's modules of DLC based films coated on Si substrates were measured using nano-indentation equipped in a Universal Materials Tester (UMT) manufactured by Center for Tribology (CETR) Inc. The indentation was performed on nine different locations for each sample with a Berkovich type indenter. The mechanical properties were calculated from the load-displacement curves based on Oliver and Pharr method [22]. Scratching testing was done using the UMT manufactured by The Center of Tribology Inc. to measure the adhesion of the thin films. Scratch tests were performed in the fully computerized UMT with Tungsten carbide pins as the scratcher. A load was applied via a closed-loop servo-mechanism and was programmed to increase linearly from 0.1 mN to 0.5 mN. The scratch lines at three different locations (beginning, middle and the end) were observed using an optical microscope. Ball-on-disk tribometer equipped in the same system was used to measure the coefficient of friction (COF) of the samples. The balls is made of ultra high molecular weight polyethylene (UHMWPE) with a diameter of 4 mm. Reciprocating mode with a sliding length of 5 mm was used and the tests were performed for 14,400 cycles under a load of 1 N in ambient atmosphere (22 °C and a relative humidity of 40%).

2.4. Contact angle and surface roughness characterization

The water contact angle of PET substrate with and without DLC coatings was measured with a goniometer equipped with a micropipette under precisely controlled droplet size and injection force, a Nikon Cool Pix 8400 camera having 3264 × 2448 resolution, a sample stage and a contact angle analysis software. The measurement was carried out in three points with distilled water at room temperature. The obtained images were characterized with open source multi-platform java image processing program ImageJ using the Low Bond Axisymmetric Drop Shape Analysis Model of Drop Shape Analysis (LB_ADSA) plug in. Young - Dupre equation $[E = \gamma(1 + \cos\theta)]$ was used to calculate surface energy [23], here γ is water surface tension at 20 °C which is equal to 72.8 mN/m and θ is the contact angle (°). New View 8000 optical profilometer manufactured by Zygo was utilized to investigate the surface topography before and after coating.

3. Results and discussion

3.1. Raman spectroscopy

A typical Raman spectrum of DLC films consists of two broad peaks: a disordered D peak centered around 1360 cm^{-1} and a graphitic G peak around 1575 cm^{-1}. Since π states (sp^2 bonds) have lower bond energy than σ states (sp^3 bonds), π states can be easily polarized to have much larger Raman scattering cross section than σ states. Furthermore, G peak is sensitive to the stretching vibration of sp^2 sites in either C=C chain or aromatic ring while D peak is only sensitive to breathing mode of sp^2 sites in the ring [15]. Therefore, visible Raman can give valuable information on the bonding states of DLC by analyzing the position and full width of half maximum (FWHM) of the G peak and the intensity ratio of the D peak to G peak [15]. The Raman spectra of N-DLC and Si-DLC with different concentrations are shown in Fig. 1. For N-DLC, the G

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