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## Deposition of diamond-like carbon films on interior surface of long and slender quartz glass tube by enhanced glow discharge plasma immersion ion implantation

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#### ABSTRACT

Diamond-like carbon (DLC) films are deposited on the interior surface of 100 mm long quartz glass tubes with inner diameters of 6, 4, and 0.9 mm by enhanced glow discharge plasma immersion ion implantation (EGD-PIII) at 10 kV. The acetylene plasma is generated inside the tube by electrons created in the plasma near the substrate and secondary electrons from ion bombardment. Acetylene gas pressure distribution obtained from finite element method shows that the pressure varies linearly from the inlet to the outlet of the tube. The electron mean free path,  $\lambda_e$ , and collision frequency,  $\nu_e$ , are introduced to qualitatively explain the non-uniform DLC film thickness. Raman scattering indicates that the DLC films at different locations have a similar structure.

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#### 1. Introduction

Diamond-like carbon (DLC) films possessing desirable properties such as high hardness, low friction, good wear resistance, chemical inertness, and smooth finish are used in many applications [1-3] such as dies [4], bearings [5], cutting tools, [6] and artificial joints [7]. However, it is relatively difficult to deposit DLC films on the inner surfaces of a long and slender component with a large length to diameter ratio by traditional methods. Owing to the excellent properties of DLC films, deposition on inner areas has aroused interest for applications to pipes [8]. large aspect ratio dies [9], vascular grafts [10,11], and so on. For instance, Baba et al. [12,13] have developed a plasma-based ion implantation (PSII) method to deposit on the interior surface of steel tubes 200 mm long and 20 mm in inner diameter and Wen et al. [14] have treated the inner surface of 50 mm long and 4 mm diameter PVC tubes using a direct current glow discharge plasma source. Ohgoe et al. [15] have proposed a method to deposit DLC on the inside surface of 100 mm long polycarbonate tubes with an inner diameter of 10 mm using a cylindrical electrode producing a radio frequency glow discharge plasma. In spite of recent progress, it is still difficult to deposit DLC films on the inner surface of insulating tubes with a large length-to-diameter ratio, although a convenient and simple inner surface plasma deposition technique is required for many biomedical and industrial applications of DLC.

In this work, a hybrid deposition method, enhanced glow discharge plasma immersion ion implantation (EGD-PIII) [16], is used to deposit DLC films on the inner surfaces of a quartz glass tube with different length-to-diameter ratios. Our results demonstrate that EGD-PIII is suitable for inner surface film deposition on quartz tubes with an inner diameter as small as 0.9 mm and length-to-diameter ratios of over 100.

#### 2. Experimental details

The schematic diagram of the EGD-PIII system with a base pressure of  $2 \times 10^{-3}$  Pa is depicted in Fig. 1. 100 mm long quartz tubes with inner diameters of 6, 4, and 0.9 mm were used in the experiments. As shown in Fig. 1, one end of the quartz tube was inserted into the top of a glass chamber and the other end was connected to a gas feeding system via an electrically conductive feed conduit. The exit of the feed conduit was grounded and served as the hollow anode. The area of the exit of feed conduit was much smaller than that of the substrate. The glass chamber was located on an aluminum substrate at the end of a conductive rod that extended though the wall of the vacuum chamber and connected to the negative electrode of a high voltage power supply. Negative voltage pulses of 10 kV with a pulse duration of 100 µs and repetition rate of 50 Hz were applied to the aluminum substrate. Acetylene was bled in at flow rates of 60, 50, and 40 ccm for tubes with diameters of 6, 4, and 0.9 mm, respectively. The film deposition time was 15 min.

The acetylene pressure distribution was simulated by the finite element method. The tube was 100 mm long with 4 mm diameter







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Fig. 1. Schematic of the EDG-PIII system for inner surface treatment of quartz tubes.

and the glass chambers had a 170 mm inner diameter with 270 mm height. The pressure at the bottom of glass chamber (Fig. 1) was set as the exit of the model and is ideally fixed at 1.1 Pa. The acetylene was bled in the vertical direction at a rate of 50 sccm. The acetylene density and coefficient of dynamic viscosity at standard temperature and pressure were  $1.17 \text{ kg/m}^3$  and  $10.5 \times 10^{-6} \text{ Pa} \cdot \text{s}$  respectively [17].

DLC films deposited on the inner surface at three locations, 5 mm away from the inlet end, middle, and 5 mm away from the outlet were used for estimation of thickness homogeneity. The films' thickness was determined by scanning electron microscopy (SEM, JEOL, JSM6010) and chemical structure was characterized by Raman scattering using an excitation wavelength of 523 nm and an argon ion laser.

#### 3. Results and discussion

The photos of the DLC films coated quartz glass tubes are displayed in Figs. 2 and 3 and show the films' thickness variation of the DLC films deposited on the inner surface of 100 mm long and 4 mm diameter quartz tube. The film thicknesses at the inlet, middle, and outlet are 19.6, 11.5, and 4.5  $\mu$ m, respectively and the deposition rates vary from 0.3  $\mu$ m/min to 1.3  $\mu$ m/min. A roughly linear relationship is observed and the thickness increases from the outlet to the inlet with the maximum being about 20  $\mu$ m. The deposition rate at the inlet is larger due to the higher density plasma in this region.

In order to explain the different DLC films deposition rates, the effects of the electron mean free path,  $\lambda_{e}$ , and collision frequency,  $\nu_{e}$ , are investigated [18] by using the following formulas:

$$\lambda_e = \frac{KT}{P\sigma} \tag{1}$$

$$\sigma = \phi(E_e) \tag{2}$$

$$\nu_e = \frac{V_e}{\lambda_e} \tag{3}$$

$$V_e = \sqrt{\frac{8KT_e}{\pi m_e}}.$$
(4)

Here, K, T, P,  $\sigma$ ,  $E_e$ ,  $T_e$ ,  $V_e$ , and  $m_e$  are Boltzmann's constant, temperature in the vacuum chamber, gas pressure, total cross section, electron energy, electron temperature, electron speed, and electron mass, respectively. The temperature in vacuum chamber is set at 400 K. The



**Fig. 2.** Photos of the 100 mm long quartz tubes with different inner diameters deposited with DLC films on the interior: (a) 6 mm, (b) 4 mm, (c) 0.9 mm in diameter.

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