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Coating diamond-like carbon films on polymer substrates by inductively coupled plasma assisted sputtering

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ABSTRACT

In this paper, a new sputtering technique for coating hydrogen-free diamond-like carbon (DLC) films on polytetrafluoroethylene (PTFE) substrates in an inductively coupled plasma (ICP) will be reported. The ICP has the advantages of producing high-density plasma (HDP) for DLC deposition at low substrate temperatures (<50 °C). The method developed in this work is particularly advantageous for coating on substrates with low melting points such as polymers. Various characterization techniques have been used to investigate the chemical, tribological, and electronic features of the deposited films. Raman spectroscopy revealed two broad peaks at 1386 cm^{-1} and 1573 cm^{-1} corresponding to the D and G peaks respectively. The DLC films produced by this method have less than 20% sp^3 carbon bonds. The average grain size of the hydrogen-free DLC was ~57 nm. The roughness of the uncoated PTFE substrate surfaces decreased dramatically (from 662 to 179 nm) with DLC coating.

1. Introduction

Diamond-like carbon (DLC) is an amorphous carbon with varying fractions of sp^2 and sp^3 carbon atoms. DLC can have low friction, high wear resistance, high hardness, chemical inertness, smoothness, low coefficient of friction, and good optical transparency. Due to these exceptional properties, DLC have many applications in the fields of tribology and industries such as biomedical implants, optical windows, magnetic storage disks, and electronics.

DLC has been deposited on different substrates by many techniques [1]. The films deposited by different methods reveal different mechanical and tribological features. Common DLC coating methods include sputtering [2–4], plasma enhanced chemical vapor deposition (PECVD) [5], direct ion beam deposition (direct IBD) [6], pulsed laser deposition (PLD) [7] and vacuum arc [8]. Choice of plasma source would depend on the intended applications. Each method is considered for a specific application and can have certain advantages and disadvantages. For example sputtering is an inexpensive technique but with the disadvantage of low deposition rate. Moreover, the sp^3/sp^2 ratio is different in each technique with the highest ratio achieved in direct ion beam deposition and the lowest in RF sputtering [9]. Graphite sputtering is commonly used in industrial applications [10]. Sputtering in the absence of hydrocarbon gases is the preferred method for hydrogen-free DLC coatings. Hot filament and magnetron sputtering are used in order to increase the deposition rate of the sputtered graphite [2–4,11]. Low-pressure high-density plasma technology has been improved over the last two decades for industrial applications of DLC, in thin film depositions for semiconductors and electronic devices. Inductively coupled plasmas (ICP) as the high-density plasma (HDP) sources are commonly used in plasma processing and its related manufacturing process. Several attempts have been made to study inductively coupled plasma (ICP) over the last century. ICP is one of the most effective electrode-less plasma sources for many applications, not only in material science and the electronic chip industries, but also in atomic emission spectroscopy and mass spectrometric analysis. Relatively high-density plasma and the tunable ion energy are the advantages of ICP. Moreover, it is simpler than other high-density plasma sources such as electron cyclotron resonance (ECR) plasma, which needs an external magnetic field.

In this paper, a new technique for coating hydrogen-free DLC thin films using the DC sputtering in the ICP plasma chamber will be described. Using ICP as a plasma source has some benefits including the high ion density (10^{10}–10^{12} cm^{-3}) and low pressure (typically < 50 mTorr). The higher ion density leads to more uniform plasma, which is required for plasma processing. Moreover, there is no electrode contamination of plasma in the ICP. We expect a higher deposition rate than a similar experiment in a hot filament glow discharge plasma [11] because of higher plasma densities in ICP. In addition, it is possible to independently control the ion energy and plasma density through an extra biasing in the ICP. This additional biasing can be connected to the substrate or an extra sputtering target.

2. Experiment

DLC thin films were deposited on polytetrafluoroethylene (PTFE) substrates using a DC sputtering in an inductively coupled plasma (ICP) chamber. The ICP reactor used in this work has a cylindrical

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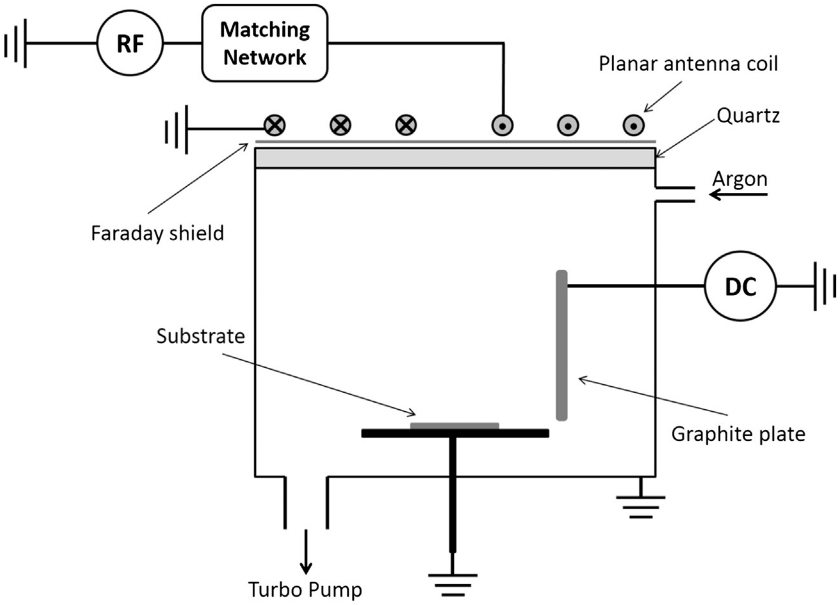

Fig. 1. Schematic of the deposition setup.

stainless steel chamber with an inner diameter of 20.8 cm and a height of 37.5 cm. A 2.5 cm thick quartz plate seals the top of the chamber and isolates the discharge chamber from the RF coil. A planar spiral coil, which is placed on the top of the quartz plate, effectively couples the RF power of 13.56 MHz into the plasma discharge through an automatic impedance matching network. Usually, capacitive coupling is inevitable. To minimize the capacitive coupling in the system, a Faraday shield is installed between the coil and the quartz plate. An RF current is passed through the coils (antennas), which generate a time-varying magnetic field and azimuthal electric field through Faraday's law. The induced electric field accelerates electrons and produces plasma. Argon gas, injected to the chamber at the gas flow rate of 100 SCCM, was used as a working gas in the current project. A roughing and a turbo pump are used to achieve an ultimate pressure on the order of 10^{-8} Torr. The desired working pressure can be adjusted by opening and closing a throttle valve as well as tuning the gas flow rate. A graphite plate, which is the source of carbon, is the target to be sputtered and it is negatively biased with respect to the chamber wall using a DC power supply. So the system is a combination of inductively coupled and DC discharges. The graphite plate is 8 cm long, 6 cm wide and 2 mm thick and is placed perpendicular to the substrate holder surface. There is a grounded circular substrate holder that is made of stainless steel and adjustable in height. Its height is normally adjusted to the level of the graphite target. The temperature of the substrate is carefully monitored by a thermocouple placed under the substrate holder. After forming inductively coupled discharge in the chamber, the negative bias voltage of the sputtering target causes acceleration of the ions to the graphite plate. High-energy ions bombard the graphite plate and sputter atoms off the target plate. Graphite atoms or clusters, through a ballistic movement, can be deposited on the substrate. All experimental parameters were carefully chosen to keep the substrate temperatures below 50 °C and the working pressure of 100 mTorr. The RF power was set to 300 W and the bias current of 70 mA by setting the bias voltage to −1250 V. The deposition time was normally 20 min and the estimated thickness of the films deposited is about 100 nm. The schematic of the experimental setup is illustrated in Fig. 1.

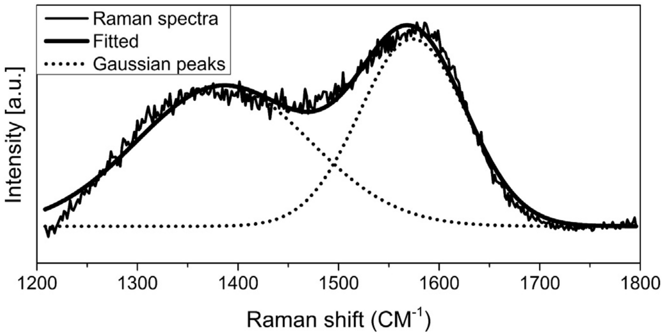

Fig. 2. The Raman spectra of DLC films coated on the PTFE substrate.

2.1. Characterizations

The properties of the coated DLC films were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

Raman spectra were obtained using a Renishaw model 2000 spectroscope equipped with 514 nm Ar ion laser with a spot size of approximately 2 μm. The incident laser power on the sample is 0.3–1.2 mW. Visible Raman spectra of the PTFE coated with DLC confirm that a-C is deposited since two wide D and G peaks can be seen at 1386 cm^{-1} and 1573 cm^{-1} respectively [12] as shown in Fig. 2. The spectra information such as the position, width, and the intensity of the peaks can be extracted by deconvoluting the spectra in terms of two Gaussian peaks or two Lorentzian peaks or a combination of these two [13,14].

XPS measurements were performed in the Omicron Multiprobe system of the REIXS surface science facility at the Canadian Light Source (CLS) using a monochromatized Al K(alpha) X-ray source and a Sphera EA 125 hemispherical electron energy analyzer with the kinetic energies from 250 to 1000 eV.

The AFM images and roughness measurements were carried out on an Agilent 4500 AFM (Agilent Technologies, Chandler, Ariz USA) using

Table 1
Raman parameters extracted from the Raman spectra of the DLC films coated on the PTFE substrate.

Raman parameters	D position	G position	FWHM (G)	I_D/I_G
	1386 [cm^{-1}]	1573 [cm^{-1}]	130 [cm^{-1}]	0.51

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