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Hydrocarbon Plasma of a Low-Pressure Arc Discharge for Deposition of Highly-Adhesive Hydrogenated DLC Films

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ABSTRACT

Plasma generator based on non-self-sustained low-pressure arc discharge has been examined as a tool for deposition of highly-adhesive hydrogenated amorphous diamond-like carbon(DLC) films. Since the discharge is stable in wide range of gas pressures and currents, this plasma source makes possible to realize both plasma-immersion ion implantation(PIII) and plasma-immersion ion deposition(PIID) in a unified vacuum cycle. The plasma parameters were measured as functions of discharge current. Discharge and substrate bias voltage parameters have been determined for the PIII and PIID modes. For PIID it has been demonstrated that hard and well-adherent DLC coating are produced at 200-500 eV energies per deposited carbon atom. The growth rates of DLC films in this case are about 200-300 nm/h. It was also shown that short(~60 μs) high-voltage(>1 kV) substrate bias pulses are the most favorable for achieving high hardness and good adhesion of DLC, as well as for reducing of residual intrinsic stress are.

Key Words : Diamond-like carbon(DLC), Plasma-immersion ion implantation (PIII), Plasma-immersion ion deposition (PIID)

1. Introduction

Hydrogenated diamond-like amorphous carbon(DLC) films have been widely deposited by plasma-based technologies[1]. This interest is due to the unique properties of these films and the possibility to vary these properties easily depending on the deposition conditions. In particular, it is very effective to employ plasma-immersion ion implantation(PIII) followed by plasma-immersion ion deposition(PIID) for producing of highly-adhesive and hard DLC coatings at different substrates[2]. To create large volumes of hydrocarbon plasma fro PIII and PIID, different types of a glow discharge are mainly used: DC, pulsed, and capacitive RF [3]. They are characterized by moderate power(up to 1 kW), low operating pressures(0.01-0.1 Pa) and, hence, low plasma density (10^8-10^9cm^{-3}) and low growth rate of DLC films (<0.1 μm/hour). In order to increase the productivity of the PIID process, it is necessary to use denser hydrocarbon plasma. In this paper, we studied a possibility to use non-self-sustained arc discharge plasma source for PIID DLC films and preliminary PIII of substrates. In spite of reliability and simplicity of construction and operation, this device is intended for generation of relatively dense(n_i~10^9-10^{11} cm^{-3}), uniform(($\Delta n_i/n_i$) = ±10-20%), and large-volume(~1 m^3) plas-ma, which parameters can be varied in wide range both for realization of large-scale PIII and PIID. The purpose of the paper is preliminary choice of the discharge and substrate bias voltage parameters both for PIII and PIID regimes.

2. Experimental

A schematic diagram of the experimental setup for DLC deposition is presented in Fig. 1. The vacuum chamber(1)600×600×600 mm in size was evacuated with a diffusion pump(2). The plasma generator was mounted on the vacuum chamber wall at a distance of about 20 cm from a water-cooled substrate holder(7) that is immersed

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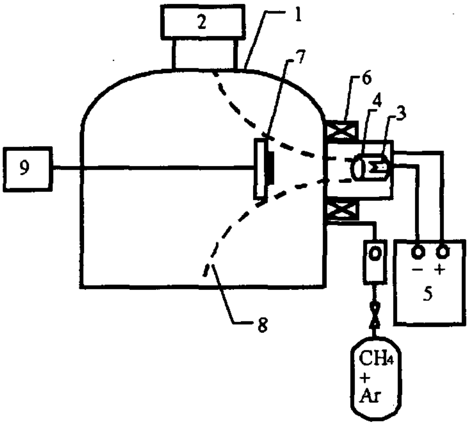

Fig. 1. Schematic of the experimental set-up. 1-vacuum chamber, 2-diffusion pump, 3-tungsten filament, 4-cylinder cathode, 5-DC power supply, 6-magnetic coils, 7-substrate holder, 8-plasma stream, 9-substrate bias generator.

in the plasma stream(8). We used polished silicon, stainless steel, and titanium substrates for the experiments. The combined cathode of the plasma generator consists of a heated tungsten filament(3) surrounded with a metal cylinder(4). The chamber body serves as an anode. The magnetic field increasing ionization degree and stabilizing the arc discharge is created by a set of magnetic coils(6). To ignite the non-self-sustained arc discharge two DC power supplies are used: one is for heating of the filament cathode(it is not shown at the diagram), another(5) is for supplying the discharge between the cathode and the anode. Detailed description of the plasma generator is given elsewhere[4]. Besides, the generator of high-voltage negative substrate bias pulses(9) with the width of 40-60 μs, amplitude of up to 15 kV, and frequency of up to 1 kHz was used in the experiments.

$$s = \sqrt{\frac{4}{9}\varepsilon_0\left(\frac{2e}{M_i}\right)^{1/2}\frac{U_{sub}^{3/2}}{j_i}}, \qquad (1)$$

$$j_i = 0.4en_i\sqrt{2kT_e/M_i}, \qquad (2)$$

where ε_0 is the electrical permittivity of vacuum, e is elementary charge, M_i is ion mass, T_e is electron temperature, U_{sub} is the bias voltage at the substrate, n_i is plasma density.Energy per deposited carbon atom E_C was calculated from balance of ion Φ_i and neutral Φ_C fluxes on the substrate:

$$E_C \approx e \cdot U_{sub} \cdot \frac{\Phi_i}{\Phi_C} \cdot \qquad (3)$$

Neutral flux was estimated after measurements of growth rate v of polymer-like films deposited without applying bias to the substrate (we assumed their density ρ=1 g/cm^3 that is typical for polymers):

$$\Phi_C \approx \frac{v \cdot \rho}{m_C}, \qquad (4)$$

where m_C is carbon atom mass. At last, ion flux to the substrate can be calculated as:

$$\Phi_i = \frac{j_i \cdot \tau_{sub} \cdot f}{e}, \qquad (5)$$

where τ_{sub} and f are width and repetition rate of substrate bias pulses. In addition to the plasma characteristics, the properties of DLC films depending on the deposition conditions were studied. The main tool for analysis of the coating quality was Raman spectroscopy. Amorphous carbon films Raman spectra consist of well-defined *G*-peak(at~1600 cm^{-1}) and less intensive shoulder-like *D*-peak(at~1400 cm^{-1}) (see Fig.4). Both of the peaks are originated from graphite-like component of the DLC film. The former can be assigned to in-plane atomic vibrations in six-fold rings and it is characteristic of graphite crystal structure, while the latter can be found only in polycrystalline and amorphous graphite and can be attributed to grains disorder[5]. The main criterion of films quality was the ratio of the integral intensities of *D*- and *G*-peaks in its spectra the less this ratio, the more diamond-like component contains the coating[5]. The coating thickness was measured after deposition with the use of an optical interferometer. The adhesion and hardness of the coatings were determined qualitatively by the scratch test. In this case a rubber with abrasive SiO_2 particles at a 1 kg load applied perpendicular to the sample surface was moved 10 times alternatively along it. After that, results of the treatment (scratches or film delamination) were observed by optical microscope with 300×magnification.

3. Results and Discussion

3.1 Preliminary plasma-immersion ion implantation

Table 1. Parameters of methane plasma

P(Pa)	I_d(A)	Te(eV)	ni(cm^{-3})	ji(mA/cm^2)
0.5	10	1.5	$3.4 \cdot 10^{10}$	0.92
0.2	5	1.5	$1.7 \cdot 10^{10}$	0.46
0.2	1	1.5	$3.4 \cdot 10^{9}$	0.09

where P-pressure in the chamber, I_d discharge current, T_e electron temperature, n_i-ion concentration, j_i-ion current density.

The probe measurement results of the non-self-sustained low-pressure arc discharge source plasma for different operation regimes are presented in Table 1. The plasma concentration of the non-self-sustained arc discharge is likely to depend linearly on the discharge current I_d. It is necessary to note that in all cases plasma filled the chamber almost uniformly, therefore in the substrate region any spatial non-uniformities of the plasma parameters in the limits of measurement accuracy-(±20%)were not observed. Experiments on the deposition of DLC films from methane with no bias at the substrate have shown that film growth rate v decreased together with discharge current I_d and pressure p(from v=3 μm/h at $I_d = 10$ A and $p = 0.5$ Pa to $v = 500$ nm/h at $I_d = 5$ A and $p = 0.2$ Pa). The plas- ma density in this case only halved from 3.4×10^{16} to 1.7×10^{16} m^{-3} as shown in Table 1. In our opinion, the mode with a lower discharge current(5 A) is the best to realize pure ion implantation since the film deposition rate is too low and the film is completely etched off when a high voltage bias is applied to the substrate. For 12-kV negative bias voltage the thickness of the cathode sheath is 5 cm(Fig.2), which is approximately equal to the mean free path of methane ions at a pressure of 0.2 Pa. Hence the ions bombard the substrate surface with their total energies. As the discharge current is further decreased to 1 A, the plasma density falls noticeably(to 3.4×10^{15} m^{-3}), resulting in a widening of the plasma sheath to 11 cm. This makes the given implantation mode inefficient because of collisions of ions with gas atoms. The experiments on plasma-immersion ion implantation have shown that the integrated dose necessary to attain adhesion of the coatings to stainless steel and titanium substrates should be of the order of 5×10^{17} cm^{-2}. This dose was attained in 30 min with negative bias pulses of 10-12 kV voltage, 0.5 A current, 45 ms duration and 660 Hz repetition rate. Typical waveforms of the bias voltage and current are presented in Fig. 3. Any attempt to further increase the voltage pulse duration or magnitude failed because of the occurrence of breakdowns between the chamber walls and the substrate holder.

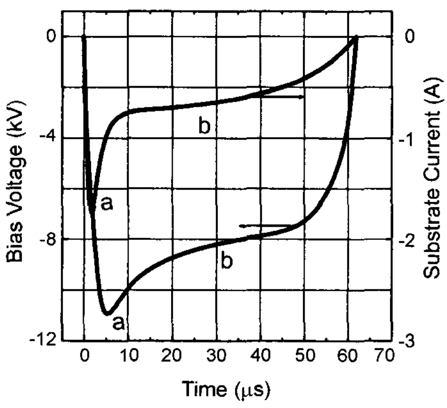

Fig. 2. Cathode sheath thickness versus bias voltage for various discharge current: 1-1A, 2-5A, 3-10A

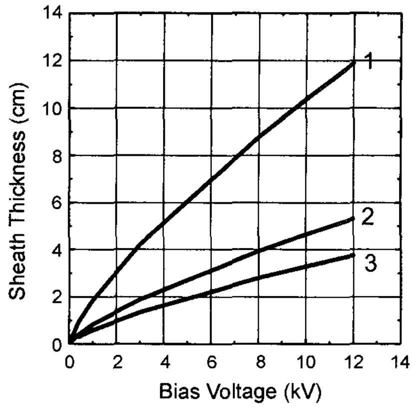

Fig. 3. Susstrate bias noltage and current characteristic oscillograms. a-region of plasma sheath formation, b-region of stable bias parameters.

3.2 Plasma-immersion ion deposition of DLC coatings

An increase in E_C(Table 2) changes the Raman scattering spectra of the films. For $E_C = 40$ eV, there is Another interesting effect also was observed in our case. As it can be seen from Table 2, coatings obtained at higher $E_C \geq 240$ eV have G-peak positioned at lower wave numbers compared to those obtained at lower E_C. As it follows from [8], it can be connected with reduction of residual intrinsic stress in the DLC films occurred at more intensive ion

Table 2. PIID conditions and films properties

#	Gas	U_{sub}(kV)	v(nm/s)	E_C(eV/atom)	*G-shift*(cm^{-1})	I_D/I_G
1	CH_4	0	0.78	0	-	-
2	CH_4	1.2	0.55	40	-	-
3	CH_4	2	0.48	70	-	-
4	CH_4	4	0.18	110	1548	1.1
5	CH_4/Ar (2:1)	2.5	0.06	150	1542	0.8
6	CH_4	6	0.09	180	1544	0.8
7	CH_4/Ar (1:4)	0.5	0.07	240	1538	0.8
8	CH_4/Ar (1:4)	1	0.06	420	1541	0.9

where U_{sub}-amplitude of substrate bias pulses, v-film growth rate, E_C-energy per a deposited carbon atom, *G-shift* position of G-peak in Raman spectra, I_D/I_G-Raman spectra *D*-H *G*-peak integral intensity ratio

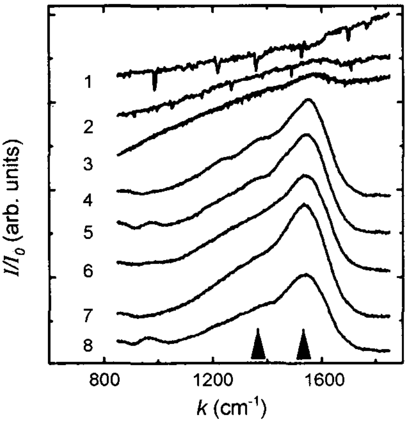

Fig. 4. Raman spectra for carbon films obtained by PIID accordiing to experimental conditions presented in Table 2. Approximate positions of G-and D-peaks are indicated by arrows.

bombardment. Moreover, for the coating obtained at the highest substrate bias voltage(Fig. 4, curve 7) this effect is the most noticeable. At the same time I_D/I_G ratio increases insignificantly, indicating that the films still contain more than 50% of sp^3-sites. The adherence of the films to substrates at higher bias voltages may also be improved due to the mixing between the film and a substrate. Thus, the most favorable for achieving high energies per deposited carbon atom and for reducing of residual intrinsic stress are short(~60 μs)high-voltage(>1 kV)substrate bias pulses. The input parameters optimal for the plasma-immersion deposition of DLC films from the plasma of a low-pressure arc discharge from the viewpoint of the best quality of the films and the highest rate of their growth correspond to the energies per carbon atom ranging between 150 and 420 eV. The resulting rates of film growth are 200-300 nm/h.

4. Conclusions

1. The use of the plasma of a non-self-sustained low-pressure arc discharge in combination with application of a negative pulsed bias voltage to the substrate makes it possible to produce high-quality DLC films showing strong adherence to carbide-forming materials on large-area surfaces. Controlling the discharge parameters over wide limits makes it possible to realize both the mode of preliminary plasma-immersion implantation of the substrate and the mode of deposition of a hard DLC coating in a unified vacuum cycle.

2. Probe measurements have shown that the plasma density may vary with the discharge current of the plasma generator by almost an order of magnitude (from $3.4\times10^{15}\,m^{-3}$ at 1 A to $3.4\times10^{16}\,m^{-3}$ at 10 A). The PIII mode differs from the PIID mode by the lower discharge current (5 and 10 A, respectively), resulting in a decrease in the rate of film growth by more than an order of magnitude, while the plasma density only halves. As a consequence, the coating formed is completely etched off the surface in the process of PIII, and the required dose ($\sim5\times10^{17}\,cm^{-2}$) is built up in 30 min.

3. For PIID it has been demonstrated that the quality and adherence of the DLC coating produced depend on the energy per carbon atom built into the coating. The most favorable for achieving high energies per deposited carbon atom and for reducing of residual intrinsic stress are short(~60 μs) high-voltage substrate bias pulses. The

estimated values of E_C in this case lie in the range 150-420 eV. This agrees with the data for films produced in similar conditions, available in the literature. The growth rate of DLC films is 200-300 nm/h. In our case, the adherence of coatings to the substrate at higher bias voltages is supposed to be better due to the relaxation of internal stresses and the mixing between the film and the substrate.

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