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Plasma-immersion Ion Deposition of Hydrogenated Diamond-like Carbon Films on Dielectric Substrates

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Abstract

Method of plasma-immersion ion deposition of hydrogenated DLC films on relatively thick flat dielectric substrates from plasma of not-self-sustained low-pressure gas arc discharge is suggested. Coating properties have been investigated experimentally, average energy per a deposited carbon atom depending on discharge current has been calculated. Optimum deposition parameters for obtaining sufficiently hard and transparent high-adhesive a-C:H films on a 4-mm thick glass substrates have been determined. Possibility to use these coatings for photo-tools protection from abrasion wear at low operating loads is shown in general.

1. Introduction

Essential efforts are applied in the recent years to the development of methods of amorphous diamond-like coating (DLC) deposition. This is explained by excellent tribological properties of DLC characterized by high hardness and low friction coefficient. Combination of these properties allows increasing the wear resistance of machine parts subjected to low loads even if the diamond-like coating thickness is several tens of nanometers (e.g., DLC on rigid magnetic computer discs). DLC transparency in the visible and IR ranges allows using them as protective coatings at photo-tools and other optical articles as well.

It is well known that for DLC deposition it is necessary to create thermodynamically non-equilibrium conditions at a substrate. It can be attained by means of high energy ion bombardment [1]. In case of PIID it can be realized most simply by applying to a substrate pulsed or constant negative bias. In case of thick dielectric substrates this approach is restricted by fast charging the surface by the ion flux. That's why for deposition of high-quality DLC on dielectrics, it is necessary to choose the pulsed bias and plasma parameters taking into account the capacity of a dielectric substrate in order to provide a necessary ion bombardment regime. So, to show general possibility of high-voltage pulsed bias use and to determine proper deposition regime for PIID of DLC films was the aim of this work.

2. Experimental

Both plane photo-tools consisting of a soft 100-㎛ thick emulsion layer on a 4-mm thick glass and 4-mm thick glass have been used as the substrates for the DLC films deposition. Fig. 1 presents an experimental setup for the PIID process. A vacuum chamber (1) of $600 \times 600 \times 600$ mm^3 with plasma source mounted on it is evacuated by a diffusion pump (2). A combined cathode of this plasma generator consists of a heated tungsten filament (3) surrounded by a hollow metal cylinder (4). The chamber walls are used as an anode.

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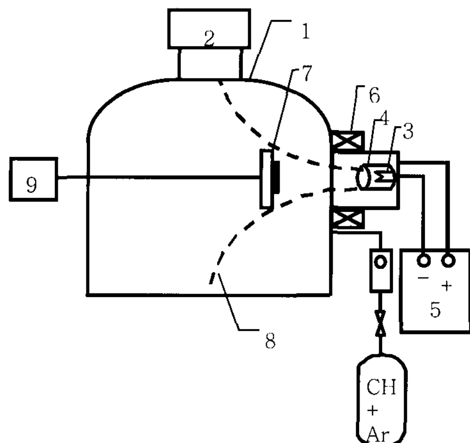

Fig. 1. Schematic of the experimental set-up: 1- vacuum chamber, 2- diffusion pump, 3- hot filament cathode, 4- cylindrical cathode, 5- DC power supply, 6- magnetic coils, 7- substrate holder with dielectric substrate, 8- plasma flow, 9- pulsed high-voltage substrate bias generator.

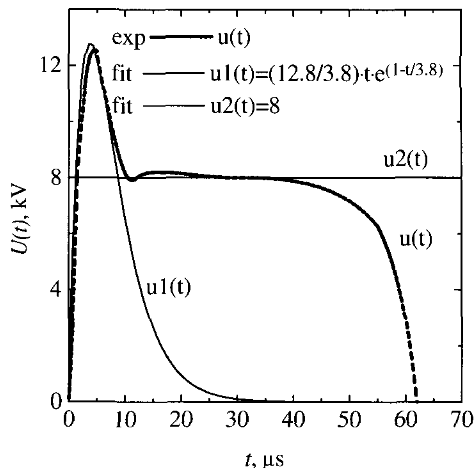

Fig. 2. Bias voltage pulse waveform and corresponding fitting functions.

When constant 60~70 V voltage is applied to the cathode from DC power supply (5), a low-pressure arc discharge appears in the chamber. The discharge current can reach 50 A and is controlled by gas pressure and filament heating current. Magnetic field stabilizing the discharge is created by means of the magnetic coil system (6). More detailed description of the plasma generator can be found in [2]. A plane water-cooled metal substrate holder of 175-cm^2 (7) was installed at a 40-cm distance from the plasma source with heated cathode(PSHC). At this disposition the substrates are immersed into the plasma flowing from the plasma source (8). Pulsed bias voltage was applied to the holder by means of a high-voltage pulsed generator (9).

During the previous experiments on PIID of hydrogenated DLC films on conductive substrates using the same technique [3] we have found that high-voltage pulsed substrate bias is preferable compared to the low-voltage one. Bombardment of the film and substrate surface by high-energy ions (>1000 eV) makes active the processes of mixing and relaxation of internal stresses at a film-substrate boundary. This allows to obtain DLC films with good adhesion to different materials. In case of relatively thick dielectric substrates the use of low negative bias voltage becomes practically impossible due to fast charging of the substrate surface by the ion current from plasma. Therefore, exclusively high-voltage pulsed bias was used in these experiments. Fig. 2 presents the oscillogram of the bias voltage pulse that characterized by constant amplitude except peak at its front. The latter was caused both by bias power supplly characteristics and transitional processes in a plasma.

During the experiments we examined DLC film characteristics depending on the discharge. The argon-methane mixture with ratio of 2:1 at a 0.2~0.3 Pa pressure was used as an operating gas. Discharge voltage was equal to 60 V and current was controlled in the limits of 1~10 A. Amplitude, width and repetition rate of bias voltage pulses were 8 kV, 60 μm and 660 Hz, respectively and were kept constant. Further increase of amplitude and repetition rate was impossible because of breakdowns in the chamber, and their decrease was also undesirable, as it will be shown below. To exclude the arc breakdowns development in the chamber, the bias potential was applied to the substrate holder through the ballast resistance R=5 kΩ in series. The coating growth rate was determined from their thickness measurements after deposition by means of an interferometer/microscope. The absorption coefficient of the films was determined

from measurements of their transparency at λ =365 nm by means of a spectrophotometer. Scratch and wear resistance as well as adhesion were determined qualitatively by means of a rubber with SiO_2 abrasive particles. The results of the sand-rubber action on the coating were observed by means of an optical microscope. The procedure of defining the average energy E_C per a deposited carbon atom is described below.

3. Results and Discussion

3.1 Calculation of average energy per deposited carbon atom

Bias voltage $U(t)$ supplied from the source drops at 1) a ballast resistance $U_R(t)$; 2) a capacity formed by the surfaces of a plane dielectric substrate $U_C(t)$; and 3) a cathode sheath formed between the external surface of the dielectric substrate and plasma boundary $U_S(t)$. In order to determine E_C, it is necessary to know $U_S(t)$ that can be described as

$$U_S(t)=U(t)-U_R(t)-U_C(t) \tag{1}$$

Ion current density to the substrate j_i is determined exclusively by plasma concentration and doesn't depend on the voltage at the cathode layer, therefore, we'll consider that j_i=const at $U_S(t)\geq 0$ and j_i=0 at $U_S(t)<0$. Besides, it is necessary to take into account the current of the secondary electrons $j_e(t)$ emitted from the surface of DLC film:

$$j_e(t)J_i \cdot k \cdot U_S(t) \tag{2}$$

where $k=10^{-4}$ V^{-1}. We have obtained this dependence for secondary electron emission coefficient earlier during investigation of PIID of DLC films on conductive substrates [3]. Then the density of the total current charging the substrate surface can be described in the form:

$$\frac{d\sigma(t)}{dt} j_i \cdot \left(1+k\cdot\left(U(t)-R\cdot S\cdot\frac{d\sigma(t)}{dt}-\frac{\sigma(t)}{C}\right)\right) \tag{3}$$

where $\sigma(t)$ is the surface charge density of the dielectric substrate, C is the substrate capacitance per unit of area, S is the substrate area.

As it is obvious from Fig. 2, the bias voltage oscillogram $U(t)$ can be approximated by analytical functions of time:

$$U(t)=\begin{cases}\frac{U_{\max}}{t_{\max}}\cdot t\cdot\exp\left(1-\frac{t}{t_{\max}},\right) & t\leq t^* \\ U_{const} & t>t^*\end{cases} \tag{4}$$

For the considered regime, U_{max}=12.8 kV, t_{max}=3.8 μs, U_{const}=8 kV and t^*=8.8 μs. The Eq. (3) has the analytical solution that is not presented here because of its complexity. The dependence $U_S(t)$ can also be obtained from the equation (3).

Assuming that the DLC coating is formed from radicals CH_x (x=1~3) and energetic bombardment of the surface is realized by the Ar^+ ions we can determine the average energy per a deposited carbon atom E_C from the ratio of ion and radical fluxes:

$$E_C=\frac{e\cdot\langle U_S(t)\cdot\Phi_i\rangle\cdot\Phi_i}{\Phi_{CH}} \approx\frac{f\cdot m_C\cdot j_i\cdot\int U_S(t)dt}{\rho\cdot\nu} \tag{5}$$

where e is the elementary charge, Φ_i and Φ_{CH} are the fluxes of argon ions and hydrocarbon radicals to the surface, m_C is the carbon atom mass, f is the repetition rate of the bias voltage pulses, ρ and ν are the density and growth rate of the film correspondingly and integral is taken in the region of $U_S(t)\geq 0$. Obviously, radical flux to the substrate depends only on the plasma concentration and therefore can be preliminary determined in the absence of the bias potential at the substrate. As in these conditions a polymer-like film is formed, then for evaluations it is sufficient to know only the growth rate supposing ρ =1 g/cm^3.

3.2 DLC films characteristics

Growth rate of the DLC films in the absence of a

bias potential at a substrate was proportional to the discharge current I_d and varied from 120 nm/h at I_d=1 A to 1.2 μm/h at I_d=10 A. So, the flux of methane decomposition products Φ_{CH} to the substrate increases from 1.7×10^{14} to 1.7×10^{15} $cm^{-2}c^{-1}$ with the discharge current rise from 1 to 10 A (Table 1).

More complicated dependence on the discharge current is observed for the ion flux to the surface. On the one hand, ion current density to the dielectric substrate surface j_i growths proportional to the plasma density. On the other hand, the ion current exists only limited time (at $U_S(t)\geq0$) because of the dielectric surface charging. Obviously, the higher is the density of the current charging the substrate, the shorter is this time interval. Fig. 3 presents the curves of $U_S(t)$ calculated by the Eq. (1)-(4) for the bias voltage pulse $U(t)$ depicted in Fig. 2 and for different discharge currents I_d. It can be seen that the time of a 4-mm thick glass surface charging decreases from 53 μs at I_d=1 A to 7 μs at I_d=10 A (Table 1). The ion flux to the substrate Φ_i remains practically constant up to I_d=10 A as the surface charging time decrease is compensated by the increase of the ion current density. Thus, the effect of secondary electron emission on Φ_i is not sufficient in our case. Table 1 presents as well the mean voltage values at the cathode layer $<U_S(t)>$ during the pulse time. It is seen from Fig. 3 that the $U(t)$ behavior at the pulse front is very important in case of high discharge currents (I_d > 4 A)

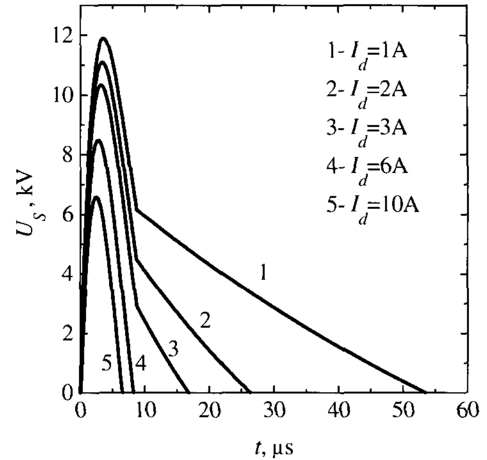

Fig. 3. Calculated voltage drop within cathode sheath vs. time for various discharge currents:1- I_d=1A, 2- I_dd=2A, 3- I_dd=3A, 4- I_d=6A, 5- I_d=10A.

while for low currents (I_d < 3 A) an essential role plays a constant part of the bias voltage pulse. Thus, resulting from Table 1, the flux and the mean energy of the ions bombarding the substrate have no essential changes in the interval of I_d=1 A~10 A. Average energy per a carbon atom calculated by the Eq. (5) rises from 64 eV at I_d=10 A up to 476 eV at I_d=1 A only due to the decrease of the flux of CH_X radicals to the substrate surface.

Fig. 4 presents the dependences of the DLC film growth rate and its absorption coefficient for λ=565 nm on the discharge current. The growth rate changes

Table 1. Calculated deposition parameters vs. discharge current.

I_d, A	$\Phi_{CH}\cdot10^{-14}$, $cm^{-2}\cdot s^{-1}$	τ, μs	$<U_S>$, kV	$\Phi_i\cdot10^{-13}$, $cm^{-2}\cdot s^{-1}$	E_C, eV
1	1.7	53	3.9	2.1	476
2	3.3	26	4.0	2.0	245
3	5.0	17	4.4	2.0	174
4	6.7	12	4.8	1.9	137
5	8.4	9	5.4	1.8	116
6	10	8.3	5.0	2.0	101
10	17	6.5	4.2	2.6	64

where I_d is discharge current, Φ_{CH} is neutral flux to the substrate surface, τ is duration of ion current to the substrate surface, $<U_S>$ is mean voltage drop on the cathode sheath during voltage pulse, Φ_i is ion flux to the substrate surface, E_C is average energy per deposited carbon atom

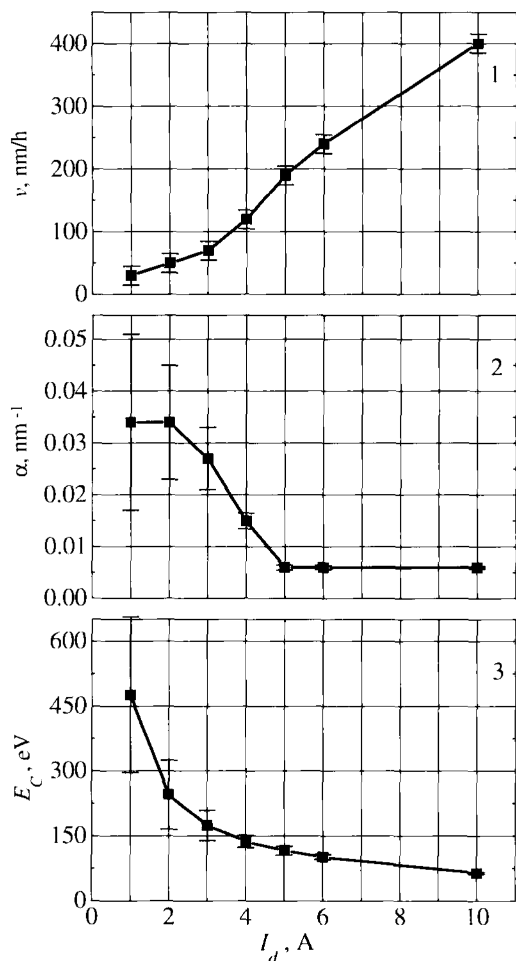

Fig. 4. Experimental dependences of growth rate (1), absorption coefficient at λ=365 nm (2), and average energy per deposited carbon atom (3) of DLC films on discharge current.

from 30 nm/h at I_d=1 A up to 400 nm/h at I_d=10 A. This is approximately three-four times lower than in the same conditions but without substrate bias because of the processes of the coating densification and re-sputtering by the high-energetic ions (Fig. 3). The absorption coefficient changes from (=0.006 nm^{-1} for Id=10 A to α=0.034 nm^{-1} for I_d=1~2 A. According to the published data [4], soft polymer-like films typically have α < 0.01 nm^{-1}, while for graphite-like films α > 0.02 nm^{-1}. Furthermore, hard but still sufficiently transparent DLC films have α in the limits of 0.012~0.015 nm^{-1}. Thus, according to the measurements of α, in our case the transition from polymer-like to diamond-like and, further, to graphite-like films occurs in the narrow interval of the discharge current values I_d=3~5 A. Calculated values of E_C agree with these changes as well. As it is known from [1], the amorphous diamond-like film formation becomes possible at E_C~30~150 eV depending on the conditions and technique of deposition. A portion of sp^2-bonded carbon is enlarged at the further increase of EC in the DLC coating. This practically has no effect on mechanical properties of the coating but essentially affects its optical characteristics. Thus, optimum value of E_C in our case is approximately 140 eV that corresponds to a 4 A discharge current.

Qualitative measurements of hardness and adhesion of the films on glass have shown that the coating deposited at high discharge currents (I_d=5~10 A) is scratched and delaminated after sand-rubber test, i.e., has low hardness and insufficient adhesion. The coating deposited at I_d=4 A is not scratched already but its adhesion is still low. The coating deposited at low discharge currents I_d=1~3 A is not scratched and delaminated from the substrate. The absence of hardness at high discharge currents is explained by insufficient E_C and the adhesion improvement at low currents occurs due to the ion mixing that becomes possible at U_S~10 kV. In order to use the DLC films as the protective coatings on the photo-tools, high hardness, good adhesion, and the sufficient transparency (~80% at λ=365 nm) are required. In the suggested method this is achieved by deposition of a thin (~1 nm) intermediate layer at low discharge current I_d=1 A and a functional ~15 nm-thick layer at the current I_d=4 A. In this case, the intermediate layer is sufficiently thin in order to provide the required transparency and adhesion of the whole coating and the functional layer is sufficiently hard and thick in order to provide the photo-tool wear resistance.

4. Conclusions

1. For plasma-immersion ion deposition of hydrogenated

DLC films on thick dielectric substrates it is necessary to use a high-voltage (~10 kV) pulsed bias. This allows not only to attain the required average energy per a deposited carbon atom (>100 eV) but also to improve the coating adhesion due to the ion mixing at a film-substrate boundary.

2. It has been found that at the high discharge currents of 6~10 A, the soft transparent polymer-like films are produced on a 4-mm thick glass due to low energy per deposited carbon atom E_C=60~100 eV. As the current decrease to 4 A, E_C increases up to 140 eV. As a result, the films become hard but still have the sufficient transparency (α=0.015 nm^{-1} at α=365 nm), however, their adhesion is rather low. At small currents of 1~2 A, the films are characterized by high hardness and adhesion due to efficient ion mixing but have high absorption coefficient (α=0.034 nm^{-1} at α=365 nm^{-1}) caused by excessive ion bombardment.
3. In order to obtain a sufficiently hard and transparent coating with good adhesion, it is necessary to deposit an intermediate adhesive layer at the low discharge current I_d=1 A preliminary and then a functional layer at the higher I_d=4 A. At the 1- nm thick intermediate and 15-nm thick functional layer, the a-C:H coating has high transparency (80% at λ=365 nm) and can be used for protection of photo-tools from abrasive wear at low operating loads.

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