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**ФИЗИКА РАДИАЦИОННЫХ И ИОННО-ПЛАЗМЕННЫХ
ТЕХНОЛОГИЙ**

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**GROWTH RATE OF DIAMOND-LIKE COATINGS SYNTHESIZED
IN RF DISCHARGE AT VARIOUS RATIOS OF THE CONCENTRATIONS
OF Ar AND C₆H₆**

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Diamond-like coatings (DLC) synthesized by plasma-chemical deposition from a vapor mixture of C₆H₆ and Ar have been investigated. The growth rate of the coating was measured, which showed a nonlinear dependence on the partial pressure of Ar. The mathematical model of the deposition has been developed, which qualitatively and quantitatively describes the dependence of the ion flux density and deposition rate on the partial pressure of argon.

INTRODUCTION

Due to the unique combination of properties, amorphous carbon coatings are widely used for surface modification of parts and tools used in metalworking, mechanical engineering, aerospace, medicine, micromechanics and other industries. Such coatings are characterized by high hardness, low coefficient of friction, chemical inertness, biocompatibility, and high radiation resistance [1, 2]. The development of equipment and processes for the synthesis of high-quality diamond-like coatings (DLC) over a large area is the urgent and important task, the solution of which will increase the productivity of the process, as well as expand the list of processed products. In addition, there is a great need for the deposition of diamond-like carbon to the surface of products with complex shapes (cylindrical, spherical and others, for example, frictional joints of endoprostheses). Improving the characteristics and functional properties of DLC is impossible without knowledge of the physical mechanisms that determine the deposition rate and the processes of formation of the structure and phase composition of the coating material. Therefore, it is important to theoretically study the mechanisms of DLC synthesis, to reveal the role of the bombardment of the growth surface with low-energy ions (from 0.1 to ~1 keV) in the sputtering and activation of radiation-stimulated processes, as well as the effect of the deposition temperature.

One of the types of DLCs are hydrogenated DLC (a-C:H) synthesized by plasma enhanced chemical vapor deposition (PECVD) from the mixture of a hydrocarbon (in this case, benzol C₆H₆) and argon Ar. By changing such parameters as the pressure of the gas mixture in the vacuum chamber, the potential and temperature of the substrate, it is possible to obtain DLC

with different properties.

In this work, carbon coatings were deposited in RF discharge in the mixture of Ar and C₆H₆ with different ratios of Ar and C₆H₆. The aim of the work was to study the deposition rate of the coating material. Also, the theoretical study of the effect of the ratio of Ar and C₆H₆ on the indicated characteristics was carried out. A comparison with the experimental data of the results of calculating the deposition rate of the synthesized carbon coatings on the concentration of Ar in the mixture is carried out.

EXPERIMENTAL TECHNIQUE

Carbon coatings were deposited in the RF discharge at the substrate potential of 1.3 kV in the mixture of Ar and benzol with different ratios of partial pressures of gases while maintaining the total pressure of the mixture $p = 6 \cdot 10^{-3}$ Torr. The thickness of the investigated coatings was in the range of 0.5...1.1 μm . The list of samples and the parameters of their deposition are given in Table. In the experiments, the ratio of the partial pressures of gases $P_{\text{Ar}}/P_{\text{benz}}$ varied in the wide range from 0.2/5.8 to 5.8/0.2. It can be seen from Table that the deposition rate of coatings changes nonlinearly with increase of the argon content in the gas mixture: first, it increases from 1.9 $\mu\text{m}/\text{h}$ at $x = 0.0333$ to 2.15 $\mu\text{m}/\text{h}$ at $x = 0.5$, and with further growth of x , it rapidly decreases to 0.57 $\mu\text{m}/\text{h}$ at $x = 0.967$. Here the designation $x = P_{\text{Ar}}/(P_{\text{benzol}} + P_{\text{Ar}})$ is introduced. The Table also shows the results of nanoindentation of the samples. It can be seen that the coatings obtained at the argon pressure of $(1...4) \cdot 10^{-3}$ Torr have fairly close hardness values in the range of 19...23 GPa. With increase in the argon content, the hardness decreases to 10 GPa at $x = 0.967$.

Deposition parameters and characteristics of DLC synthesized at various ratios of the concentrations of Ar and C₆H₆

No of sample	$P_{\text{Ar}}, 10^{-3}$ Torr	$P_{\text{benzol}}, 10^{-3}$ Torr	x	$v, \mu\text{m}/\text{h}$	H, GPa	E, GPa	H/E
1	1	5	0.167	2.0	18.9	182	0.10
2	2	4	0.333	2.1	22.8	244	0.09
3	3	3	0.5	2.15	19.3	184	0.10
4	4	2	0.667	2.0	18.8	199	0.09
5	5	1	0.833	1.6	–	–	–
6	5.8	0.2	0.967	0.55	10.1	112	0.09
7	0.2	5.8	0.033	1.9	–	–	–

MATHEMATICAL MODEL

The derivation of a formula for the growth rate of the DLC coating obtained by the PECVD from the mixture of C_6H_6 and Ar is given below. The formula links the growth rate with the partial pressure of argon.

We will assume that the carbon film is deposited from the mixed flux of $C_6H_6^+$ and Ar^+ ions when the average bias potential $U = 1.3$ kV is applied to the substrate. The ions $C_6H_6^+$ are formed both as a result of ionization of C_6H_6 molecules by electron impact, and in the process of charge exchange upon collision of the neutral C_6H_6 molecule with the Ar^+ ion. In contrast, Ar^+ ions are formed only as a result of ionization of Ar atoms by electron impact. Charge exchange upon collision of the Ar atom with the $C_6H_6^+$ ion is suppressed, since the ionization potential of argon $\varepsilon_{Ar} = 15.76$ eV exceeds those of benzol $\varepsilon_{C_6H_6} = 9.24$ eV. Because of this, the equilibrium density of Ar^+ ions decreases due to charge exchange when they collide with neutral benzol molecules, in which the Ar^+ ion takes an electron from the C_6H_6 molecule and is neutralized. Considering the above, we can write the following stationary relationships between the densities of ions and neutral components in the mixture of Ar and C_6H_6 :

$$n_A^+ = \gamma_A n_A - \gamma_{AB} n_A^+ n_B, \quad (1)$$

$$n_B^+ = \gamma_B n_B + \gamma_{AB} n_A^+ n_B, \quad (2)$$

where n_A and n_B are the densities of argon and benzol components, respectively, and n_A^+ and n_B^+ are the densities of argon and benzol ions in the gas mixture Ar + C_6H_6 , respectively, γ_A and γ_B are the ionization coefficients of argon and benzol due to electron impact, respectively, γ_{AB} – is the ionization coefficient of benzol as a result of charge exchange upon collision with the argon ion. We will assume that the densities of the components are proportional to their partial pressures: $n_A = \alpha p x$ and $n_B = \alpha p (1-x)$. It is taken into account here that the partial pressures in the gas mixture of Ar and C_6H_6 are $p x$ and $p(1-x)$, respectively. The total pressure of the mixture is constant and equal to p . Note that in the approximation of the Boltzmann ideal gas we have $\alpha = 1/(k_B T)$, where k_B is the Boltzmann constant, T is the absolute temperature of a gas.

Equations (1) and (2) make it possible to determine the equilibrium concentrations of $C_6H_6^+$ and Ar^+ ions:

$$n_A^+ = \frac{\gamma_A \alpha p x}{1 + Y(1-x)}, \quad (3)$$

$$n_B^+ = \gamma_A \gamma_{AB} \alpha^2 p^2 (1-x) \left[X + \frac{x}{1 + Y(1-x)} \right]. \quad (4)$$

Here we used the notation $X = \gamma_B / (\gamma_A \gamma_{AB} \alpha p)$, $Y = \gamma_{AB} \alpha p$.

For the flux densities of Ar^+ and $C_6H_6^+$ ions incident on the substrate, we obtain, respectively, the following expressions:

$$j_A = \gamma_A \alpha p \sqrt{\frac{2eU}{M_A}} \frac{x}{1 + Y(1-x)}, \quad (5)$$

$$j_B = \gamma_A \gamma_{AB} \alpha^2 p^2 \sqrt{\frac{2eU}{M_B}} (1-x) \left[X + \frac{x}{1 + Y(1-x)} \right]. \quad (6)$$

Here $v_A = \sqrt{2eU/M_A}$ and $v_B = \sqrt{2eU/M_B}$ are the velocities of Ar^+ and $C_6H_6^+$ ions, respectively, acquired under the action of the potential U , $M_A \approx 40m_p$ и $M_B \approx 78m_p$ are masses of argon and benzol ions, respectively, e и m_p are the charge and mass of the proton, respectively.

The total density of the ion flux onto the substrate can be represented as:

$$j(x) = \frac{j_0}{X} \left\{ (1-x) \left[X + \frac{x}{1 + Y(1-x)} \right] + \sqrt{\frac{M_B}{M_A}} \frac{1}{Y} \frac{x}{1 + Y(1-x)} \right\}, \quad (7)$$

where $j_0 = \gamma_B \alpha p \sqrt{2eU/M_B}$ is the flux density of incident ions at $x = 0$, that is, the flux density of purely hydrocarbon ions. The energy flux density J_E incident on the substrate can be determined from the expression:

$$J_E(x) \approx eU j(x). \quad (8)$$

Here we have neglected the energy of the sputtered atoms. As shown by the estimates made with the SRIM2000 [3], this energy is small compared to the energy of the incident ions. Knowledge of the incident energy flux density is necessary when assessing the heating of the deposition surface, which can affect the characteristics of the deposited coating.

Note that the growth of the coating is provided only by the flux of $C_6H_6^+$ ions, while the Ar^+ ions, on the contrary, retard the growth due to sputtering. The knowledge of the flux densities j_A and j_B , as well as the sputtering coefficients k_A and k_C of the carbon target by argon and carbon ions, makes it possible to calculate the growth rate of the coating v :

$$\begin{aligned} v(x) &= 6j_B(1-k_C) - j_A k_A = \\ &= v_0 \frac{1}{X} \left\{ (1-x) \left[X + \frac{x}{1 + Y(1-x)} \right] - \right. \\ &\quad \left. - \frac{1}{6} \frac{k_A}{1-k_C} \sqrt{\frac{M_B}{M_A}} \frac{1}{Y} \frac{x}{1 + Y(1-x)} \right\}, \quad (9) \end{aligned}$$

where the designation $v_0 = 6(1-k_C)j_0$ is introduced for the deposition rate at $x = 0$.

It is assumed here that all ions are singly charged,

therefore the energy of the Ar^+ and C_6H_6^+ ions is eU , and the energy of each of the C atoms falling on the coating is calculated by the formula:

$$E_C = eU \frac{M_C}{6M_C + 6M_H}, \quad (10)$$

where $M_C \approx 12m_p$ and $M_H \approx m_p$ are the masses of carbon and hydrogen atoms, respectively, m_p is the proton mass. If we take the energy of C_6H_6^+ and Ar^+ ions equal to $E = 1.3$ keV, then we get $E_C = 200$ eV for the energy of C atoms. Using SRIM2000, we get for $U = 1.3$ V [3]:

$$k_A \equiv k_A(1.3 \text{ keV}) = 0.2,$$

$$k_C \equiv k_C(0.2 \text{ keV}) = 0.09.$$

Hydrogen ions arising from the decay of benzol molecules have a low energy $E_H = 17$ eV. Such ions do not sputter the coating atoms and make the insignificant contribution to the heating of the substance in the peaks of benzol ions [4].

In Fig. 1 shows the calculated dependence of the growth rate of the carbon coating on the fraction x of argon in the $\text{C}_6\text{H}_6 + \text{Ar}$ mixture, as well as the experimental points taken from Table. The calculation was carried out for the values of the model parameters: $X = 0.135$, $Y = 3.5$, $\nu_0 = 1.9$ $\mu\text{m/h}$ at which the best agreement with the experimental data is achieved.

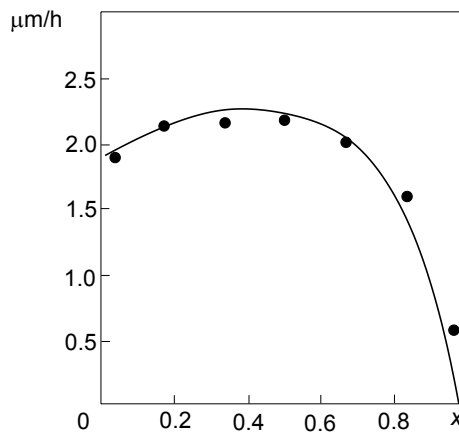


Fig. 1. Dependence of the growth rate of the carbon coating on the fraction x of argon in the $\text{C}_6\text{H}_6 + \text{Ar}$ mixture. Black symbols are experimental points taken from Table [5]

As can be seen from the figure, the rate of growth of the coating varies nonmonotonically with the increase of the fraction of argon in the mixture [5]. The increase in the growth rate of the coating with the increase in the argon content in the range $0 < x < 0.5$ is associated with the charge exchange process, as a result of which the concentration of C_6H_6^+ ions increases due to the transfer of the positive charge from Ar^+ ions to neutral C_6H_6 molecules. The decrease in the growth rate of the coating at $x > 0.5$ is associated with both the decrease in the benzol concentration and the increase of the sputtering of the growth surface due to the increase in

the intensity of bombardment by Ar^+ ions. Note that knowledge of the parameter ν_0 makes it possible to estimate the value of the ionization coefficient of benzol under the action of electrons. In the ideal gas approximation, we obtain $\gamma_B = 10^{-5}$.

Thus, the proposed model qualitatively correctly describes the rate of deposition of a carbon coating from a mixture of benzol with argon. The model can be used to describe the deposition rate of the carbon coating from arbitrary mixture of a hydrocarbon with an inert gas.

In Fig. 2 shows the dependence of the flux density of incident ions on the argon fraction x (solid curve), calculated for the selected values of the parameters X , Y , and ν_0 . Taking into account the value ν_0 chosen above, it was assumed in the calculations that $j_0 = 0.35$ $\mu\text{m/h}$, which is equivalent to the current density of singly charged ions ~ 0.19 mA/cm^2 . The figure also shows the current densities of benzol and argon ions (dashed curves 1 and 2, respectively).

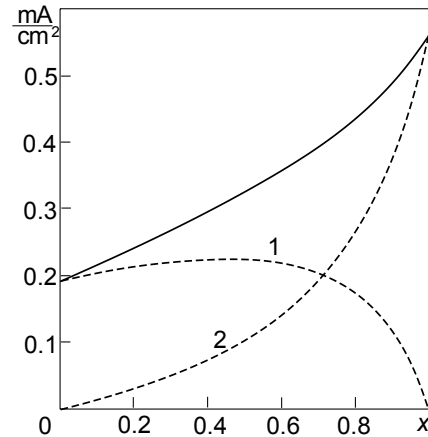


Fig. 2. Dependence of the flux density of incident ions on the argon fraction x during the deposition of the carbon coating from the mixture of $\text{C}_6\text{H}_6 + \text{Ar}$ (solid curve). Dashed curves 1 and 2 are the current densities of benzol and argon ions, respectively

The maximum energy flux density on the deposited surface calculated according to expression (8) is $J_E(1) = 0.71$ W/cm^2 . It is easy to verify that such an energy flux does not lead to significant heating of the coating. Indeed, according to the classical Fourier equation, the overheating temperature ΔT of the irradiated surface of the substrate, which is cooled from the reverse side, is determined by the expression $\Delta T = J_E h / \lambda$, where λ is the specific thermal conductivity of the plate material. Taking $\lambda = 15$ W/m/deg (stainless steel), $h = 10^{-3}$ m (substrate thickness), we get: $\Delta T = 0.47$ K. Such overheating is small compared to the overheating in the ion peaks [4] and does not affect structure formation.

CONCLUSIONS

1. The growth rate of hydrogenated DLC, synthesized by plasma-chemical vapor deposition from the mixture of benzol and argon, was studied at different ratios of components. In the experiments, the ratio of the partial pressures of gases $p_{\text{Ar}}/p_{\text{benzol}}$ varied over a

wide range from 0.2/5.8 to 5.8/0.2 while maintaining the total pressure of the mixture $p = 6 \cdot 10^{-3}$ Torr.

2. It has been shown that, the growth rate changes nonlinearly with the argon content in the gas mixture. It increases from 1.9 $\mu\text{m/h}$ at $p_{\text{Ar}}/p_{\text{benzol}} = 0.2/5.8 = 0.033$ to 2.15 $\mu\text{m/h}$ at $p_{\text{Ar}}/p_{\text{benzol}} = 1$, with further rapid decrease to 0.57 $\mu\text{m/h}$ at $p_{\text{Ar}}/p_{\text{benzol}} = 5.8/0.2 = 0.967$.

3. The mathematical model is proposed for describing the growth rate ν of the coating, based on taking into account both the processes of ion formation during electron impact and recharge, and the processes of sputtering. The expression obtained in the framework of the model for the growth rate of the coating correctly describes the dependence of ν on the argon concentration and, with an appropriate choice of model parameters, agrees with the experimental data.

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СКОРОСТЬ РОСТА АЛМАЗОПОДОБНЫХ ПОКРЫТИЙ, СИНТЕЗИРОВАННЫХ В ВЧ-РАЗРЯДЕ, ПРИ РАЗЛИЧНЫХ СООТНОШЕНИЯХ КОНЦЕНТРАЦИЙ Ar И C_6H_6

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Исследованы алмазоподобные покрытия, полученные плазмохимическим осаждением из паровой смеси C_6H_6 и Ar. Измерена скорость роста покрытия, которая показала нелинейную зависимость от парциального давления Ar. Разработана математическая модель осаждения, качественно и количественно описывающая зависимость плотности потока ионов и скорости осаждения от парциального давления аргона.

ШВИДКІСТЬ РОСТУ АЛМАЗОПОДІБНИХ ПОКРИТТІВ, СИНТЕЗОВАНИХ У ВЧ-РОЗРЯДІ, ПРИ РІЗНИХ СПІВВІДНОШЕННЯХ КОНЦЕНТРАЦІЙ Ar І C_6H_6

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Досліджено алмазоподібні покриття, які отримані плазмохімічним осадженням з парової суміші C_6H_6 і Ar. Виміряна швидкість росту покриття, яка показала нелінійну залежність від парціального тиску Ar. Розроблено математичну модель осадження, що якісно і кількісно описує залежність густини потоку іонів та швидкості осадження від парціального тиску аргону.