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INTRINSIC STRESS IN CARBON COATINGS DEPOSITED FROM HYDROCARBON ION FLOW

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Within the model of the nonlocal thermoelastic peak (NTP) of low-energy ion, the emergence of intrinsic stress in carbon coatings deposited from the flow of ions of hydrocarbon molecules is theoretically studied. The expression is obtained for intrinsic stress depending on species and ion energy. The time dependence of temperature and pressure in the NTP of CH_4^+, $C_2H_2^+$ and $C_6H_6^+$ ions was studied The position of NTP of ions of different species and energies on the *P*,*T* phase diagram of carbon was found and their trajectories were constructed. The position of the NTP trajectories of various ions with respect to the regions of structural stability of carbon was analyzed. The conditions for the predominant formation of sp^3 bonds in the NTP of ion are discussed.

INTRODUCTION

One of the methods for diamond-like coatings producing is the deposition of beams of ions of carbon or hydrocarbon molecules with characteristic energies of 25 to 1000 eV/atom [1–3]. The physical and mechanical characteristics of the resulting coating depend both on the type of implanted particles and on their energy. In [4], the conditions for the formation of tetrahedral amorphous carbon (ta-C) upon bombardment by C^+ or noble gas ions carbon target were theoretically studied. These conditions are realized as a result of the combined action of elevated temperature and pressure in nonlocal thermoelastic peaks (NTPs) – nanometer-sized regions near the trajectories of ions in substance where the thermalized energy of the ion is concentrated. The developed model made it possible to analyze various factors influencing the formation of ta-C and evaluate the efficiency of "sp^2 to sp^3" conversion, depending on the energy of carbon ions. Similar studies of the formation of diamond-like carbon during the deposition of ions of hydrocarbon molecules were presented in [5]. At the same time, these works did not consider such an important factor influencing many processes in the solid under irradiation as the intrinsic stress arising. Irradiation of the solid coating with low-energy ions leads to the appearance of compression stress which plays the significant role in the kinetics of formation and destruction of coatings [1, 2]. In particular, the powerful compressive forces present in the deposited film contribute to the creation of a dense, homogeneous material without microcracks and cavities. In some cases, such stress is the factor that stabilizes the process of preferential formation of the dense phase of the deposited material, as is the case during the deposition of ta-C films [2]. On the other hand, excessive stress can lead to cracking and peeling of the film [2, 6]. Taking these processes into account is extremely important in the manufacture of superhard coatings such as ta-C [1, 2]. Experiments have shown the correlation between intrinsic stress and the proportion of sp^3 bonds during ion deposition of the carbon coating. On the other hand, the connection was discovered between deposited ion energy and the intrinsic stress value [2, 3]. In addition, a rather sharp transition $sp^3 \rightarrow sp^2$ was discovered at deposition temperatures exceeding 150…200 °C [1, 2, 7].

Thus, the structure of the film can be changed by varying the type and energy of ions and the substrate temperature T_0. However, for the controlled effect on the properties of the film, it is necessary to establish the nature of the stress that arise and the relationship between its value and the parameters of the deposition process. The significant numbers of works are devoted to the theoretical study of the occurrence and role of intrinsic stress in coatings during ion deposition [2]. It is worth noting the widespread use of molecular dynamics (MD) simulations, which made it possible to establish many characteristics of growing films depending on the ion energy, substrate temperature, etc. At the same time, there are certain difficulties when including rare microsecond-scale processes in MD calculations. Therefore, the development of analytical models for the formation of intrinsic stress in coatings during ion bombardment continues to be relevant. The most significant work in this direction was the model developed by C. Davis [6]. According to the Davis model, the intrinsic stress is formed as a result of the action of two simultaneous but differently directed processes: 1) stress generation due to the implantation of incident ions and 2) stress relaxation due to thermally activated processes of defect migration in the superheated region that occurs near the ion trajectory. Applying the model of the point thermal peak (PTP) [8] to determine the number of thermally activated processes, Davis obtained the formula

$$\sigma_r(E) \propto \frac{E_Y}{1-\Pi} \cdot \frac{\sqrt{E}}{1+0.016\left(E/\varepsilon\right)^{5/3}}, \qquad (1)$$

connecting the value of the resulting intrinsic stress σ with energy E of the incident ions. Here E_Y is the Young's modulus; Π is the Poisson's ratio of the coating material; ε is the activation energy for defect migration.

Formula (1) gives qualitative agreement with experimental data with the appropriate choice of the

value of ε. However, the use of the PTP model contradicts the non-local nature of energy transfer from the ion to the coating substance. As a result, the agreement with experimental data is achieved at activation energies of ε = 3…11 eV, which are many times greater than the known values for defect migration processes. Thus, the value ε serves as a fitting parameter in the Davis model [6]. In addition, the Davis formula does not explain the experimentally observed dependence of the intrinsic stress on the deposition temperature T_0 [7, 9], which is also due to the use of the PTP model, which does not take into account the finiteness of the temperature of the real thermal peak. In [10, 11], the modification of the Davis formula was proposed

$$\sigma_r(E) = A\frac{E_Y}{1-\Pi}\cdot\frac{\zeta(E)}{1+w(E,T_0)}, \qquad (2)$$

based on the NTP model of the low-energy ion, characterized by the finiteness of the volume and temperature of the NTP. Coefficient A is found by comparing the calculation results with experimental data. Here, to describe the rate of defect formation, the defect formation function $\zeta(E)$ is used, given by calculating using the SRIM2000 software package the fraction of ion energy spent on the formation of Frenkel pairs. Function

$$w(E,T_0) = n_0\nu\int_0^{\tau_c} V(E,t)\, e^{-\frac{\varepsilon}{k_B T(E,T_0,t)}} dt \qquad (3)$$

specifies the number of thermally activated transitions in the NTP. Here n_0 is the concentration of atoms; ν is the vibration frequency of the atom, $\tau_c(E) \sim \left[R(E,0)\right]^2 / 4\kappa$ is the effective lifetime of the NTP; κ – is the thermal diffusivity coefficient of the coating; k_B is Boltzmann's constant; $V(E,t)$ is the volume of the NTP. The NTP is approximated by the spherical segment with the center in the middle of the mean projective range of the ion $L(E)$, with radius $R(E,t) = L(E)/2 + 2\sqrt{\kappa(t+\tau)}$, where τ – is the ion-ion relaxation time [4].

The modified formula made it possible to explain the peculiarities of the behavior of intrinsic stress in ta-C coatings deposited from the flow of C^+ ions, in particular, the decrease in stress with increasing substrate temperature. However, it is not applicable to the case of deposition of coatings from the flow of ions of polyatomic molecules, in particular, hydrocarbon ions.

In this work, we theoretically study the occurrence of intrinsic stress σ_r in a-C:H coating deposited from the flow of ions of hydrocarbon molecules CH^+_4, $C_2H_2^+$, and $C_6H_6^+$. The results of calculations σ_r are used to construct trajectories of NTP ions on the phase P,T-diagram of carbon when analyzing the structural state of the material in the deposited coating.

MATHEMATICAL MODEL

As shown in [5, 12], the nonlocal thermoelastic peak with the radius

$$R(E,t,n) \equiv R_C(E/n) = \frac{L_C(E/n)}{2} + 2\sqrt{\kappa(t+\tau)} \qquad (4)$$

and energy content $E\eta_C(E/n)$ is formed in the target material as a result of implantation of the ion of C_nH_{n1} molecule with energy E. Here $L_C(E)$ and $\eta_C(E)$ are the mean projective range length and the relative phonon losses of the C^+ ion in the carbon coating.

The volume $V(E,t,n)$ of the NTP is given by the expression

$$V(E,t,n) = \pi\left[\frac{2}{3}R_C\left(\frac{E}{n},t\right)^3 + \frac{L_C\left(\frac{E}{n}\right)}{2}R_C\left(\frac{E}{n},t\right)^2 - \frac{1}{3}\frac{L_C\left(\frac{E}{n}\right)^3}{8}\right] \qquad (5)$$

and the temperature in the NTP $T(E,T_0,t,n)$ is found from the equation

$$\frac{\eta_C\left(\frac{E}{n}\right)E}{\rho\, C\, V_C(E/n,t)} = TD\left(\frac{\theta}{T}\right) - T_0 D\left(\frac{\theta}{T_0}\right). \qquad (6)$$

Note that in the chosen approximation, the parameters of the NTPs of ions CH_4^+ and C^+ coincide.

In Fig. 1 shows the dependence of the volumes of the NTPs of C^+, $C_2H_2^+$, and $C_6H_6^+$ on the ion energy E. In Fig. 2 shows the dependence of the temperature in the peaks of the C^+, $C_2H_2^+$, and $C_6H_6^+$ ions on the ion energy. The substrate temperature T_0 was taken equal to 300 K.

The expression for intrinsic stress arising during the deposition of the carbon coating from hydrocarbon ions has the form:

$$\sigma_{hc}(E,T_0,n) = A\frac{E_Y}{1-\Pi}\frac{\zeta_C(E/n)}{1+w_{hc}(E,T_0,n)}, \qquad (7)$$

where

$$w_{hc}(E,T_0,n) = n_0\nu\int_0^{\tau_c(E/n)} V_C(E/n,t)\, e^{-\frac{\varepsilon}{k_B T(E,T_0,t,n)}}\, dt\,. \qquad (8)$$

The functions $L_C(E)$, $\eta_C(E)$ and $\varsigma_C(E)$ used in the calculations were found using the SRIM2000 software package. It is assumed that deposition is carried out in DC mode.

In Fig. 3 shows the functions of defect formation of C^+, $C_2H_2^+$, and $C_6H_6^+$ ions in the carbon target. In the calculations, the density of carbon coating $\rho = 2.4$ g/cm^3 was assumed.

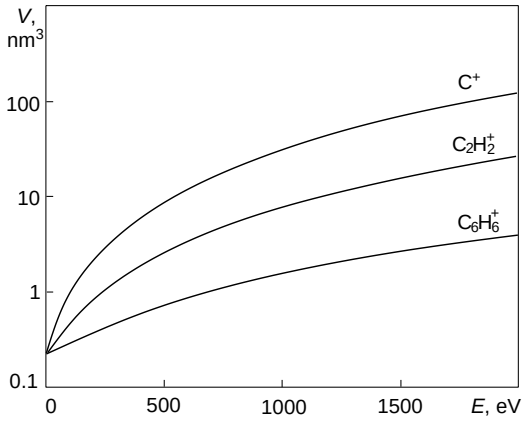

Fig. 1. Dependence of the volumes of NTP of C^+, $C_2H_2^+$, $C_6H_6^+$ ions in the carbon target on ion energy E

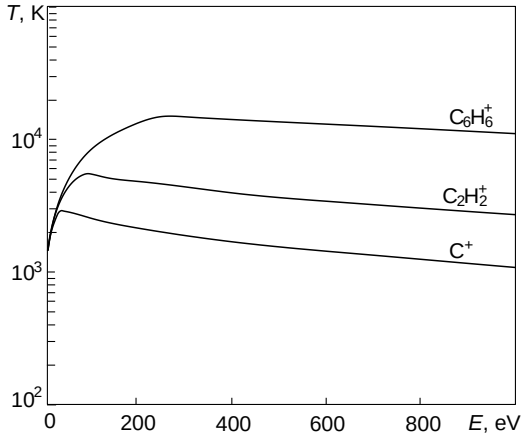

Fig. 2. Dependence of temperature in NTP of C^+, $C_2H_2^+$ and $C_6H_6^+$ ions on ion energy E

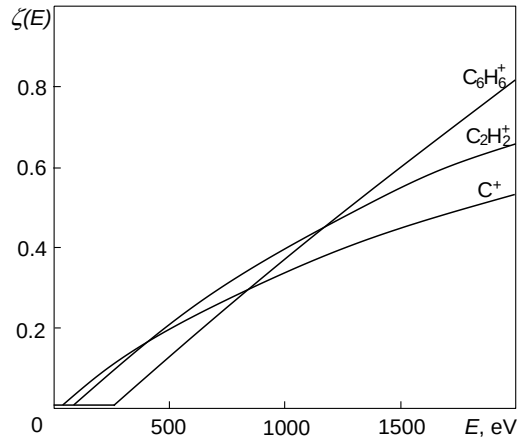

Fig. 3. Functions of defect formation of C^+, $C_2H_2^+$, and $C_6H_6^+$ ions in the carbon target

RESULTS AND DISCUSSION

In Fig. 4 shows the results of calculations using formula (7) of intrinsic stress depending on the potential on the substrate *U* in the carbon coating deposited from beams of C^+, $C_2H_2^+$, and $C_6H_6^+$ ions.

As can be seen from Fig. 4, the more carbon atoms are present in the deposited hydrocarbon ions, the lower the intrinsic stress in the deposited coating. Obviously, this is due to the fact that the thermal peaks of hydrocarbon ions have the high temperature, the more carbon atoms there are in the hydrocarbon molecule (see Fig. 2). This ensures faster migration of defects and their removal to the boundaries of the coating. The sharp dip in the low-energy region in the stress curves for $C_2H_2^+$ and $C_6H_6^+$ is explained by the fact that in this region heavier hydrocarbon ions do not generate point defects at all, and the heavier the ion, the wider the width of this energy region.

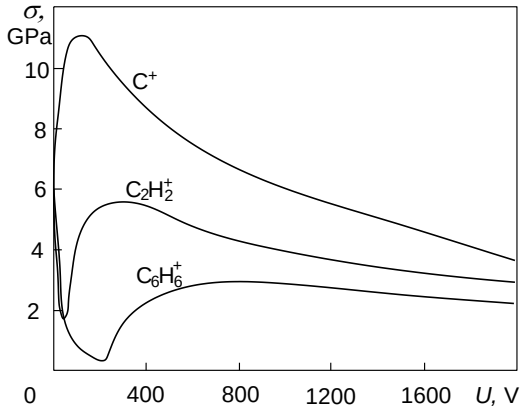

Fig. 4. Intrinsic stress arising in the carbon coating deposited from flows of C^+, $C_2H_2^+$, and $C_6H_6^+$ ions. The case of DC regime of deposition

Let us carry out the qualitative analysis of the structural state of carbon deposited from the flow of ions of hydrocarbon molecules. To do this, we determine the NTP trajectories on the phase *P,T*-diagram of carbon, similar to how it was done in [4, 10]. The pressure *P* in the NTP of the hydrocarbon ion includes:

1) the thermoelastic component generated by the thermal expansion of the substance in the peak. Here Γ and s are the Grüneisen parameter and the sound velocity of the target material;

$$P_T\left(E,t,n\right)\approx\begin{cases}\dfrac{\Gamma\eta_C\left(\dfrac{E}{n}\right)E}{V_C\left(\dfrac{E}{n},t\right)}, & t\le\dfrac{R_C\left(\dfrac{E}{n},0\right)}{s},\\[2ex] \dfrac{2\left(1-2\Pi\right)}{3\left(1-\Pi\right)}\cdot\dfrac{\Gamma\eta_C\left(\dfrac{E}{n}\right)E}{V_C\left(\dfrac{E}{n},t\right)}, & t>\dfrac{R_C\left(\dfrac{E}{n},0\right)}{s};\end{cases}\tag{9}$$

2) the deformation component due to the increase in the volume of the material during ion implantation:

$$P_D\left(E,t,n\right)\approx\begin{cases}\dfrac{KnV_1}{V_C\left(\dfrac{E}{n},t\right)}, & t\le\dfrac{R_C\left(\dfrac{E}{n},0\right)}{s},\\[2ex] \dfrac{2\left(1-2\Pi\right)}{3\left(1-\Pi\right)}\cdot\dfrac{KnV_1}{V_C\left(\dfrac{E}{n},t\right)}, & t>\dfrac{R_C\left(\dfrac{E}{n},0\right)}{s}.\end{cases}\tag{10}$$

Here V_1 is the volume introduced into the target material during implantation of the only one ion; K is the modulus of uniform compression;

3) the intrinsic (residual) stress $\sigma(E,T_0,n)$.

Thus, the pressure in the NTP is given by the expression

$$P(E,T_0,t,n)=P_T(E,t,n)+P_D(E,t,n)+\sigma(E,T_0,n). \quad (11)$$

The NTP trajectories on the phase P,T-diagram of carbon were constructed using the time dependences $T(E,t)$ and $P(E,t)$, which set in parametric form the relationship between pressure and temperature in the peak (Fig. 5, dotted lines).

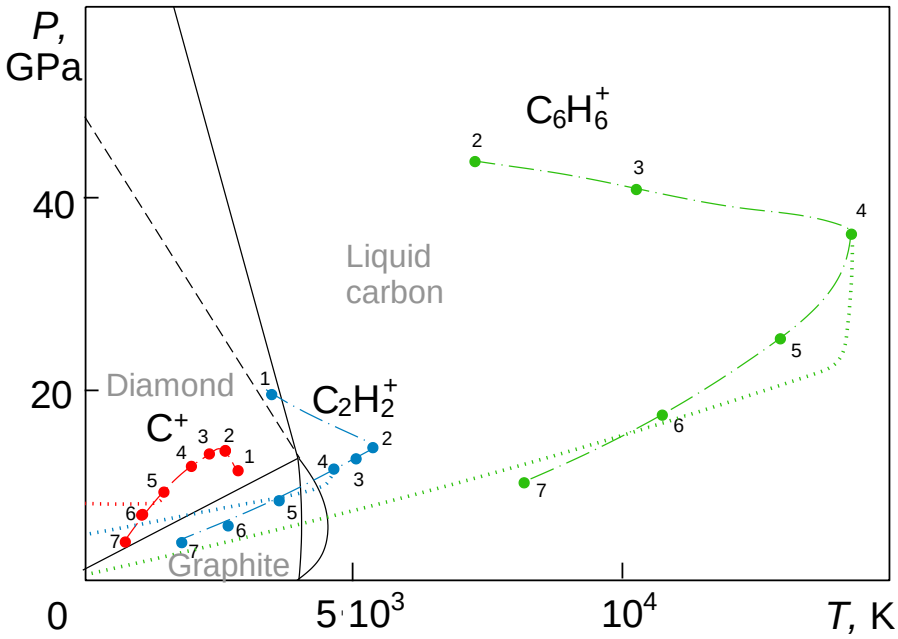

Fig. 5. P,T-trajectories (dotted lines) of the NTP of C^+, $C_2H_2^+$, and $C_6H_6^+$ ions on the phase P,T-diagram of carbon. Dashed-dotted lines are the initial localization of peaks of each species with different energies

Solid lines separate the regions of stability of different structural states of carbon, while the dash-dotted lines show the locus of initial positions of the peaks of specific species. The positions of the ions at certain values of the accelerating potential are also given: 1 – 0, 2 – 50, 3 – 100, 4 – 200, 5 – 500, 6 – 1000, 7 – 2000 V.

The sharp drop in pressure at the initial stage of NTP development corresponds to the departure of the acoustic pulse from the peak volume without significant cooling of the NTP material (see expressions (9), (10)). After this, the pressure reaches a quasi-static level and decreases in accordance with the change in temperature of the NTP as a result of the thermal conduction.

The location of the NTP ion trajectory on the phase P,T-diagram of carbon relative to the diamond-graphite boundary is the main information for the qualitative analysis of the possibility of sp^3 formation by this ion. Fig. 5 shows that some trajectories are completely located in the diamond stability region (for example, the trajectory of thermal peak No. 5 of the C^+ ion with energy of 500 eV). Other trajectories lie completely outside this region (for example, the trajectory of thermal peak No. 4 of the $C_6H_6^+$ ion with energy of 200 eV) .

It can be assumed that in the NTPs of the first group of ions there is the effective restructuring of the structure to sp^3 bonds, while in the peaks of the second group only sp^2 bonds are formed. The third group includes ions whose NTP trajectories pass through the stability regions of both diamond and graphite (for example, the trajectory of thermal peak No. 4 of the $C_2H_2^+$ ion with energy of 200 eV). Therefore, bonds of both types are formed in the peaks of these ions. The necessary condition for the partial formation of sp^3 bonds in the NTP ion is the predominance of intrinsic stress, compared to the boundary pressure at the "diamond-graphite" interface at low temperatures $\sigma_r > 1.8$ GPa. In this case, the NTP trajectory ends in the stability region of the diamond.

Thus, studying the location and movement of NTP of hydrocarbon ions on the phase P,T-diagram of carbon provides a clear picture of the processes of structure formation during ion deposition of the carbon coating.

CONCLUSIONS

Using the model of the nonlocal thermoelastic peak (NTP) of the low-energy ion, the expression for intrinsic stress in the carbon coating deposited from the flow of ions of hydrocarbon molecules is obtained. This made it possible to determine the time dependence of the total pressure in the NTP and, in combination with the time dependence of the temperature in the NTP, made it possible to construct the NTP trajectories of ions of various species on the phase P,T-diagram of carbon. It has been shown that the location of the NTP ion trajectory relative to the diamond-graphite boundary is important information for analyzing the possibility of the formation of diamond-like carbon by this ion.

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ВНУТРІШНІ НАПРУЖЕННЯ У ВУГЛЕЦЕВИХ ПОКРИТТЯХ, ОСАДЖЕНИХ З ПОТОКУ ВУГЛЕВОДНЕВИХ ІОНІВ

О.І. Калініченко, В.Є. Стрельницький

У рамках моделі нелокального термопружного піку (НТП) низькоенергетичного іона теоретично досліджується виникнення внутрішніх напружень у вуглецевому покритті, що осаджується з потоку іонів вуглеводневих молекул. Отримано вираження для внутрішнього напруження залежно від виду та енергії іонів. Досліджено часову залежність температури та тиску в НТП іонів CH_4^+, $C_2H_2^+$ та $C_6H_6^+$. Знайдено положення НТП іонів різних енергій на фазовій *P,T*-діаграмі вуглецю, та побудовано їх траєкторії. Проаналізовано положення траєкторій НТП різних іонів щодо областей структурної стабільності вуглецю. Обговорено критерії переважного формування sp^3-зв'язків у НТП іона.