

## Characteristics of DLC Coating Prepared by Pulse Biasing: Analysis in Model of Thermoelastic Peak of Ion

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A mode of pulse biasing of DLC coating deposition is theoretically investigated. In this mode a deposited ion flow of plasma with energy of  $E_0 \sim (20 \div 200)$  eV is modified by superimposing of pulse potential  $\sim 1000$  V. It was shown that intrinsic stress in a DLC coating can be decreased in several times without of essential decrease of  $sp^3$ -bonded carbon concentration compared with DLC made in stationary mode deposition at  $E_0$  ion energy. A method of optimization of pulse mode parameters is proposed which is based on analysis of location of thermoelastic peaks of ions on phase  $P, T$ -diagram of carbon.

**Keywords:** DLC coating, Plasma-based ion deposition, Pulse mode deposition, Intrinsic stress, Phase  $P, T$ -diagram of carbon, Non-local thermoelastic peak of ion.

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### 1. INTRODUCTION

Tetrahedral amorphous carbon (ta-C) formation at deposition of low-energy  $C^+$  ions is directly connected with subsurface phenomena occurring near the ion trajectory in carbon target [1]. Different aspects of ta-C formation at ion implantation were explained with concept of a thermal spike of ion that is a small nanometer-sized region where implanted ion energy contains [2-5]. Particularly, a model of ta-C formation at implantation of ions with energy from 25 to 1000 eV in carbon target was proposed in [4, 5]. According to this model, ta-C forms as a result of short-time coaction of high temperature and pressure in non-local thermoelastic peak (NTP) containing thermalized phonon loss of ion energy. The pressure in the peak consists of a thermoelastic component, a deformational one due to additional introduced volume and an intrinsic stress appearing in the coating at the ion bombardment. As it was shown experimentally and theoretically [1, 2, 5], intrinsic stress value varies depending on energy of deposited ions and substrate temperature in the range from  $\sim 10$  GPa to 0.5 GPa when the ion energy  $E$  varies from 25 eV to 1000 eV. The compression stresses stimulate a dense phase formation but on the other hand they can lead to splitting of coating and its detachment from substrate [2].

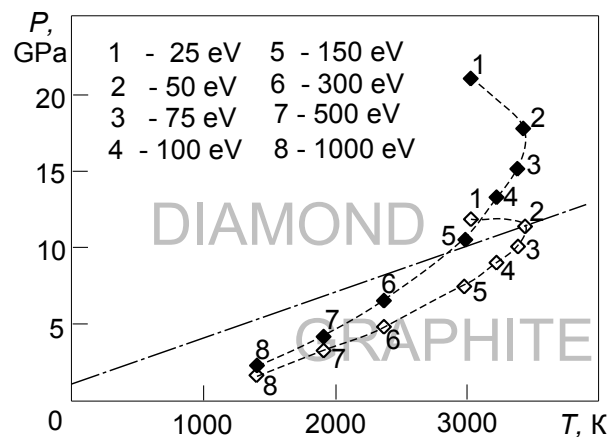
Therefore, elaboration of deposition methods to decrease intrinsic stress without appreciable degradation of physical and mechanical properties of coatings is the highly actual problem. One of working methods ensuring intrinsic stress decrease is the plasma immersion ion implantation in a pulse biasing mode [6,7]. In this case stationary deposition of ions with energy  $E_0 = (20-200)$  eV alternates with pulse bombardment by ions with considerably high energies  $E \sim 1000$  eV.

The goal of this work is the analysis of thermodynamic conditions of carbon coating formation in pulse biasing mode to determine influence of ion deposition parameters, i.e. duration and frequency of pulses as well as ion energy in pulses, on carbon coating characteristics.

### 2. METHOD OF ANALYSIS AND CALCULATION

Calculations of radius  $R(t, E)$ , temperature  $T(t, E)$  and pressure in NTP of  $C^+$  ion in ta-C depending on ion energy  $E$  and time  $t$  from moment of origination gave an opportunity to build NTP trajectories of  $C^+$  ions of different energies on phase  $P, T$ - diagram of carbon [4, 5]. Location of  $P, T$ - trajectory relatively to boundary "diamond - graphite" was accepted as the main test of possibility of ta-C production in the ion NTP.

Fig. 1 displays the initial locations of NTPs of  $C^+$  ions with different energies in an unstressed ta-C matrix (symbols  $\diamond$ ). As can be seen in Fig. 1, only the ion peaks with minimal energies  $E \leq 25$  eV lie in the area of diamond stability. According to accepted supposition only ions with these energies produce  $sp^3$ -bond carbon effectively.



**Fig. 1** – Initial localization of  $C^+$  NTPs of different energies in carbon matrix on phase  $P, T$ -diagram of carbon. The symbols  $\diamond$  correspond to case of unstressed target; symbols  $\blacklozenge$  show peak locations subject to intrinsic stress appearing at deposition of ions of different energies in stationary mode

As it was noted in INTRODUCTION, a compressive stress  $\sigma(E)$  appears in coating at deposition of ions with energy  $E$ . The expression for  $\sigma(E)$  was obtained in [5] using NTP model of implanted ion:

$$\sigma(E) = B \frac{M}{\rho} \cdot \frac{E_Y}{1 - \Pi} \cdot \frac{E^{1/2}}{(R/j) + w(E)}, \quad (1)$$

where  $R$  is the flux density of deposited atoms,  $j$  is the flux density of bombarding ions,  $M$  is the atom mass,  $\rho$  is the mass density of a coating material, and  $B$  is the numerical constant. The number of thermoactivated transitions  $w(E)$  in NTP with migration energy of defects  $U = 0,3$  eV depends on temperature and is determined subject to decrease of defects due to migration:

$$w(E, T_0) = n_0 \nu \int_0^{t_c} V(t, E) e^{-\frac{U}{k_B T(t, E, T_0)}} \nu \int_0^t e^{-\frac{U}{k_B T(\tau, E, T_0)}} d\tau dt,$$

Here  $n_0$  is the bulk concentration of atoms,  $\nu$  is the Debye's frequency for carbon,  $t_c = -R^2/4\kappa$  - is the effective time of cooling,  $\kappa$  - is the thermal diffusivity of a target material,  $k_B$  is the Boltzmann constant. Temperature in NTP is determined from Debye's formula for energy of solid as a root of equation [4]:

$$\frac{\eta(E)E}{\rho C V(t)} = TD\left(\frac{\theta}{T}\right) - T_0 D\left(\frac{\theta}{T_0}\right),$$

where  $C$  is the high-temperature limit of heat capacity,  $\eta(E)$  is the fraction of phonon energy loss of  $C^+$  ion with energy  $E$  in carbon target, and

$$D(x) = \frac{3}{x^3} \int_0^x \frac{z^3 dz}{e^z - 1}.$$

Eq. (1) is a modification of known Davis'es formula [2]. It takes into account nonlocality of ion energy loss, substrate temperature  $T_0$  and dependence of thermal capacity on temperature. NTP volume is determined by expression [4]:

$$V(E, t) = \pi \left[ \frac{2}{3} R(E, t)^3 + \frac{L(E)}{2} R(E, t)^2 - \frac{1}{3} \frac{L(E)^3}{8} \right],$$

where  $L(E)$  is the average projective range of  $C^+$  ion. Functions  $L(E)$  and  $\eta(E)$  are calculated by TRIM2000 [8].

Fig. 2 displays dependence of compressive stress in deposited ta-C coating on energy of  $C^+$  ions calculated by Eq. (1) (stationary mode of deposition) [5]. Substrate temperature  $T_0$  is equal to 300°K. Analogous dependence was obtained in [2] assuming that  $U = 3$  eV.

Subject to these stresses, NTPs of  $C^+$  ions on phase diagram occupy places shown by symbols  $\blacklozenge$  in Fig. 1. The initial locations of peaks shifted in the direction of diamond stability area, the ion energy range producing  $sp^3$ -bond carbon increases considerably (from 25 eV up to ~250 eV) [5].

In pulse biasing mode a coating is produced by ions of two different energies. It is known that in stationary mode  $C^+$  ions of low energies  $E_0 \leq 100$  eV produce ta-C coating with maximal concentration of  $sp^3$ -bonds [1, 2]. However low-energy ions generate maximal compressive stresses  $\sigma_0 = (8 - 10)$  GPa. The purpose of "high-energy" pulses is to reduce intrinsic stresses in coating. Deposition of  $C^+$  ions with energies  $E \sim 1000$  eV leads to generation of considerably lower stresses  $\sigma \leq 1$  GPa

[1,2]. However, it forms mainly  $sp^2$ -bond carbon because thermodynamic conditions appearing in NTPs of  $C^+$  ions with such energy are favourable for its production [5].

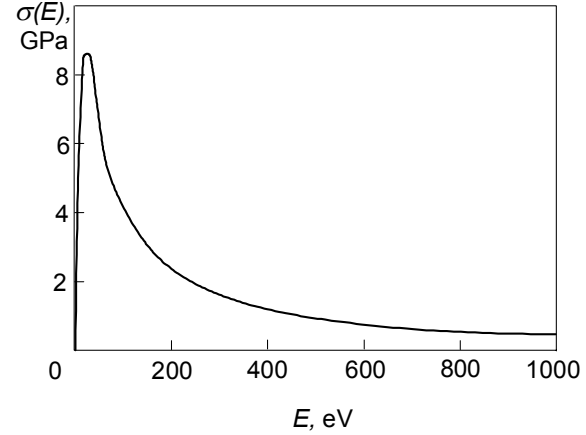


Fig. 2 – Compressive stress in ta-C coating vs. energy of  $C^+$  ion (stationary mode of deposition)

Intrinsic stress  $\sigma_p(f, E)$  which generates in the coating in pulse biasing mode is determined by additive effect of ions of two different energies:

$$\sigma_p(f, E) = ft_p \sigma(E) + (1 - ft_p) \sigma(E_0), \quad (2)$$

Expression (2) is true when the following conditions are satisfied: 1) applicability of NTP model; 2) establishing of stationary intrinsic stress during pulse time; 3) independence of activation energy of defect migration on pressure.

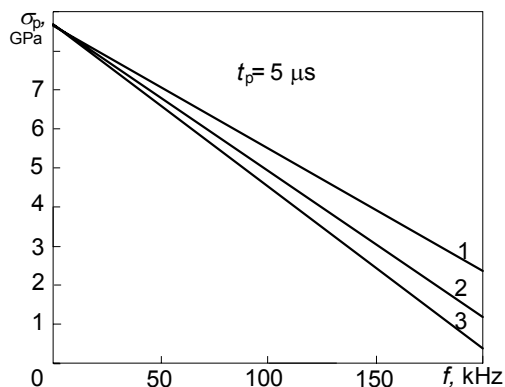
Fulfilment of these conditions permits to use function  $\sigma(E)$  shown in Fig. 2 [5, 9].

It is obviously that intrinsic stress value lies in the range  $\sigma(E) < \sigma_p < \sigma_0$ . Dependence of intrinsic stress  $\sigma_p$  in carbon coating deposited in pulse mode on pulse-repetition frequency  $f$  is shown in Fig. 3. Calculation data adduce for three different energies of ions in the "high-energy" pulse at  $E_0 = 25$  eV.

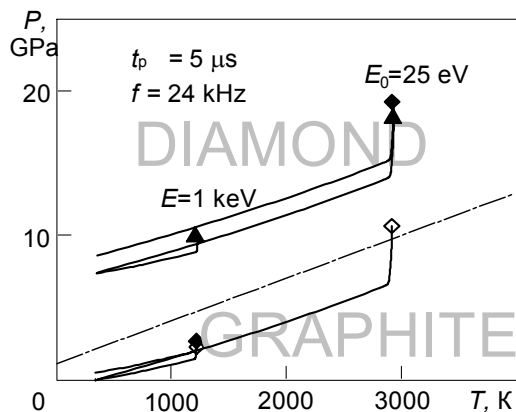
Assuming  $E_0 = 25$  eV,  $E = 1000$  eV, we find that intrinsic stress changes in rather wide range  $0.5 \text{ GPa} < \sigma_p < 8.6 \text{ GPa}$  depending on pulse-repetition frequency  $f$ . Arising intrinsic stress leads to 'rising' of NTP of 'high-energy' ion and to 'lowering' of NTP of 'low-energy' ion on phase  $P, T$ - diagram of carbon at arbitrary frequency  $f$  from allowed range  $0 \leq f \leq 1/t_p$ . So, Fig. 4 shows location of NTPs of ions with energies 25 eV and 1000 eV in unstressed matrix (symbols  $\diamond$ ), in stressed matrix at deposition of ions of specified energies in stationary mode (symbols  $\blacklozenge$ ), in stressed matrix at deposition of ions in pulse mode (symbols  $\blacktriangle$ ). Characteristics of the pulse mode are the following  $t_p = 5 \mu\text{s}$ ;  $E_0 = 25$  eV;  $f = 24$  kHz;  $E = 1000$  eV.

Fig. 4 shows that NTP location of 'low-energy' ion of 25 eV changed insignificantly as compared with stationary mode and it stays in the area of diamond stability. On the contrary, NTP of 'high-energy' ion has considerably risen in the area of higher pressures passing from the area of graphite stability to the one of diamond stability. For this reason, deposited ions of high-energy fraction have to produce  $sp^3$ -bond carbon as 'low-energy' ions. In this case, the use of pulse mode

decreases insignificantly effectiveness of generation of  $sp^3$ -bond carbon coating as compared with deposition of ions of 'low' energy  $E_0 = 25$  eV.



**Fig. 3** – Dependence of intrinsic stress  $\sigma_p$  on pulse-repetition frequency  $f$ . Energy of ions in pulse is equal to 200 eV, 400 eV and 1000 eV (curves 1, 2, 3, correspondingly)



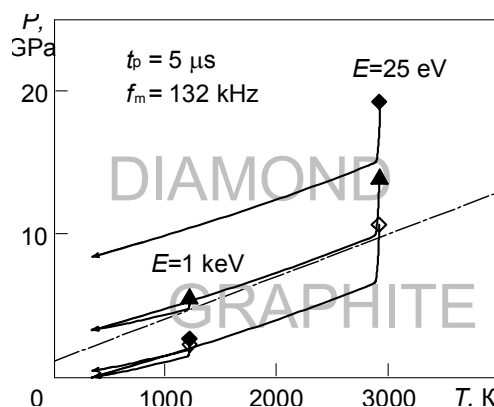
**Fig. 4** – Initial points and trajectories of NTPs of  $C^+$  ions with energies 25 eV and 1000 eV in carbon matrix on phase  $P,T$ -diagram of carbon in cases of unstressed target ( $\diamond$ ); in stationary mode of deposition ( $\blacklozenge$ ); in pulse mode with repetition frequency  $f = 24$  kHz ( $\blacktriangle$ )

Intrinsic stress in deposited coating decreases when repetition frequency  $f$  of 'high-energy' pulses increases (see Fig. 3). Due to this regularity we can reduce residual stress in the coating at insignificant decrease of effectiveness of generation of  $sp^3$ -bond carbon. At that a necessary condition is that initial locations of the ion NTPs and their trajectories in phase  $P,T$  – diagram of carbon do not go beyond area of diamond stability. The extreme case that corresponds to minimal residual

stress  $\sigma_{pmin} = 3,2$  GPa is reached at  $f_m = 132$  kHz (see Fig. 5).

Further increase of repetition frequency of 'high-energy' pulses leads to shift of NTP trajectory down into the area of graphite stability. It causes decrease of effectiveness of generation of  $sp^3$ -bond carbon that leads to considerable decrease of hardness and modulus of elasticity of coating.

The use of pulse mode of DLC coatings deposition permits to reduce residual stress in coating more than in 2.5 times as compared with deposition of ions with energy  $E_0 = (20 \div 200)$  eV in stationary mode when high residual stress  $\sigma$  occurs (up to  $\sim 10$  GPa). At that effectiveness of  $sp^3$ -bond carbon formation does not decrease considerably.



**Fig. 5** – Initial points and trajectories of NTPs of  $C^+$  ions with energies 25 eV and 1000 eV in carbon matrix on phase  $P,T$ -diagram of carbon in cases of unstressed target ( $\diamond$ ); in stationary mode of deposition ( $\blacklozenge$ ); in pulse mode with repetition frequency  $f = 132$  kHz ( $\blacktriangle$ )

### 3. CONCLUSIONS

1. The use of pulse biasing mode of DLC coating deposition permits to reduce considerably (in several times) residual stress and to maintain effectiveness of  $sp^3$ -bond carbon formation as compared with deposition of ions with energies  $E_0 = (20 \div 200)$  eV in stationary mode.

2. Analysis of location of  $C^+$  ion NTPs on phase  $P,T$ -diagram of carbon permits to chose optimal characteristics of pulse mode deposition ensuring  $sp^3$ -bond carbon generation in NTPs of both 'low-energy' and 'high-energy' ions.

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