INTRINSIC STRESSES IN DLC COATINGS DEPOSITED IN MODES OF DC AND PULSE BIAS POTENTIALS

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Formula for intrinsic stress calculation in coatings deposited from ion flux in the pulse potential mode is derived. The criterion of applicability of derived formula is proposed which permits determining critical parameters of the pulse potential mode. Calculation of stress in DLC coatings at deposition of low-energy ions C^+ from filtered vacuum arc plasma is presented. The qualitative agreement of calculated stresses with experimental data is stated. The important role of deposition temperature for intrinsic stress control in deposited coating is noted.

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INTRODUCTION

The intrinsic stresses σ originating in diamond-like (ta-C) coatings at deposition from C^+ ion flux with energy E substantially determine physical properties and operational characteristics of obtained coatings. In [1] the formula for the calculation of σ, using model of the point thermal peak (PTP) of ion has been obtained. In PTP model the value σ is determined by number of thermoactivated transitions $w_0(E,u)$, depending from energy of implanted ion E and the activation energy of defect migration u. However, the use of the PTP model for description of stress relaxation contradicts to nonlocality of energy transition from ion to matter therefore it is inconsistent. Hereupon analytical curve fits experimental data at values of $u = 3…11$ eV, that multiply exceeds known values of activation energy of defect migration. Therefore, u is adjustable parameter in the Davis model [1] excluding its physical interpretation. Also, one should note inherent inconsistency of the model which was developed only for the case of zero temperature of target and for constant thermal capacity at the same time. The last condition contradicts to the Debye theory and experimental data. Hence, this model can not explain experimentally observed dependence of intrinsic stress on deposition temperature.

In [2] the formula modification for calculation of intrinsic stresses σ was proposed which takes into account the substrate temperature T_0:

$$\sigma\left(E,u,T_0\right) \sim \frac{E_Y}{1-\Pi}\cdot\frac{\sqrt{E}}{\xi+w\left(E,u,T_0\right)}, \qquad (1)$$

where E_Y and Π are the Young's modulus and the Poisson's ratio of a target material, ξ is the ratio of fluxes of deposited atoms R and ions j. The model of nonlocal thermoelastic peak (NTP) was used for calculation of the number of thermoactivated transitions $w(E,u,T_0)$ produced by low-energy ion:

$$w\left(E,u,T_0\right) = n_0\nu\int_0^{\tau_c} V\left(t,E\right)e^{-\frac{u}{k_BT\left(t,E,T_0\right)}}\,dt\,, \qquad (2)$$

where n_0 is the concentration of atoms, ν is the frequency of atomic oscillations, $V(t,E)$ is the NTP volume, T is the temperature in NTP, k_B is the Boltzmann constant, and τ_c is the NTP life time in the target material: $\tau_c \sim R_{NTP}{}^2/\left(4\kappa\right)$, where R_{NTP} is the NTP radius, and κ is the thermal diffusivity.

The modified formula (1) permitted explaining set of regularities observing at deposition of carbon and BN coatings in mode of DC bias potential [2]. But development of new deposition technologies, particularly, the pulse bias potential mode requires generalization of theory of intrinsic stress origination in deposited coating.

The purpose of the work is derivation of the formula for calculation of intrinsic stress in coatings deposited in the pulse potential mode and its application for calculation σ in ta-C coatings at deposition from C^+ ion fluxes in pulse mode.

MATHEMATICAL MODEL

Intrinsic stresses in films and coatings arise as the result of two opposite processes: 1) subsurface ion implantation, leading to the emergence of volumetric strain and compressive stress, and 2) decrease of defect number due to their thermal migration in ion NTPs that result in stress relaxation.

In the pulse potential mode ions of two different energies $E_2(U) = E_0 + ie\left(U+U_0\right)$ and $E_1 = E_0 + ieU_0$ are alternately deposited. Here E_0 is the initial ion energy, U is the potential supplied to the substrate, U_0 is the floating potential, e is the proton charge, and i is the ion charge in e units. If the duration and the repetition frequency of high-energy pulses are equal to t_p and f, respectively, then the duration of the period when the target is irradiated with low-energy ions is equal to $f^{-1} - t_p$ where $f^{-1} > t_p$. In this case, the intrinsic compressive stresses which are established in the coating depend on the type of the originating coating (i.e., it is laminated or homogeneous). If the pulse width is sufficiently large, then material which is deposited during each pulse can be regarded as a solid layer of macroscopic thickness. The intrinsic stress in each layer should be evaluated using the expression (1), where E is the energy of the ions forming the concerned layer. In this case, the coating can be regarded as multi-layer sandwich, and the equilibrium stress can be calculated taking into account the stress and the thickness of each layer [4]. However, if the effective thickness of each layer does not exceed the interatomic distance a, it is senseless to talk about the stress formation in each of these ‘layers’, because the size of the ion NTP is considerably higher than the layer thickness [2]. In this case, we can assume that the coating is formed by a mixture of ions of two different energies (approximation of mixed beam), and the proportion of ions with energies E_2 and E_1 is ft_p and $1-ft_p$, accordingly. Condition for the realization of the last case has the form:

$$f > Ra^2 . \tag{3}$$

Taking for estimations R= 5 mA/cm^2 = 3·10^{20} m^{-2}s^{-1}, a =2.5·10^{-10} m, we get from (3): $f > 20$ Hz. In known experiments on coating deposition this requirement is carried out with great reserve in the pulse potential mode.

The proposed model, as well as the Davis model [1] is based on the hypothesis of a linear relation between volumetric deformation of solid films bombarded by energetic particles, and density of defects formed as a result of scattering of ions on the target atoms. As it was supposed in [5], the rate of formation of defects per unit area $\dot{n}_i$ is associated with the flux density of bombarding ions j and with ion energy E by ratio

$$\dot{n}_i \sim jE^{1/2} . \tag{4}$$

If ions of two different energies E_1 and E_2 are presented in the flux, then equation (4) can be rewritten as:

$$\dot{n}_i \sim j\left[ft_p\sqrt{E_2} + \left(1-ft_p\right)\sqrt{E_1}\right]. \tag{5}$$

Stress relaxation is determined by the number of thermally activated transitions of atoms in the ion NTP according to expression (2). The relaxation rate $\dot{n}_R$ per unit area is proportional to the number of thermally activated transitions of atoms in the ion NTP $w\left(E,u,T_0\right)$, to fraction of atoms which are in meta-stable states n/n_0, and to the flux of implanted ions j:

$$\dot{n}_R = \frac{n}{n_0} jw\left(E,u,T_0\right), \tag{6}$$

where n is the defect concentration.

If the ion flux consists of ions of two different energies they produce NTPs of two different types, bringing in various contributions to forming processes of thermally activated transitions. Then the expression for $\dot{n}_R$ takes the form:

$$\dot{n}_R = \frac{n}{n_0} j\left[ft_p w\left(E_2,u,T_0\right) + \left(1-ft_p\right) w\left(E_1,u,T_0\right)\right]. \tag{7}$$

At plasma-ion deposition intrinsic stress in the coating can be calculated starting from the assumption that there is equilibrium between processes of defects generation by ion implantation and their loss due to migration therefore the density of the implanted atoms does not depend on time.

The rate per unit area at which the defects are implanted into the film, is equal to $R(n/n_0)$ where R is the total rate per unit area of attachment of atoms to a growing film. On the other hand, the resultant rate of defects formation given by the difference between the rate of defect generation due to ion implantation and the rate of their loss due to thermally activated migration. Consequently, the condition of stationarity (i.e., constancy of defect density) leads to the relation [1]:

$$\dot{n}_i - \dot{n}_R = R\frac{n}{n_0} . \tag{8}$$

Substituting $\dot{n}_i$ and $\dot{n}_R$ in (8) and expressing the part of the implanted ions in film n/n_0 from obtained equation, we get:

$$\frac{n}{n_0} \sim \frac{ft_p\sqrt{E_2} + \left(1-ft_p\right)\sqrt{E_1}}{\xi + ft_p w\left(E_2,u,T_0\right) + \left(1-ft_p\right) w\left(E_1,u,T_0\right)} . \tag{9}$$

For thin coating the compressive stress acting in coating plane is related to volumetric strain υ by expression $\sigma = \sigma_Y\upsilon$, where $\sigma_Y = E_Y/1-\Pi$. Considering that volumetric strain is proportional to part of the implanted atoms in film n/n_0, we obtain:

$$\sigma \sim \sigma_Y \frac{ft_p\sqrt{E_2} + \left(1-ft_p\right)\sqrt{E_1}}{\xi + ft_p w\left(E_2,u,T_0\right) + \left(1-ft_p\right) w\left(E_1,u,T_0\right)} . \tag{10}$$

Assuming $ft_p = 1$ we obtain expression (1) for intrinsic stress in the case of the DC mode.

RESULTS AND DISCUSSION

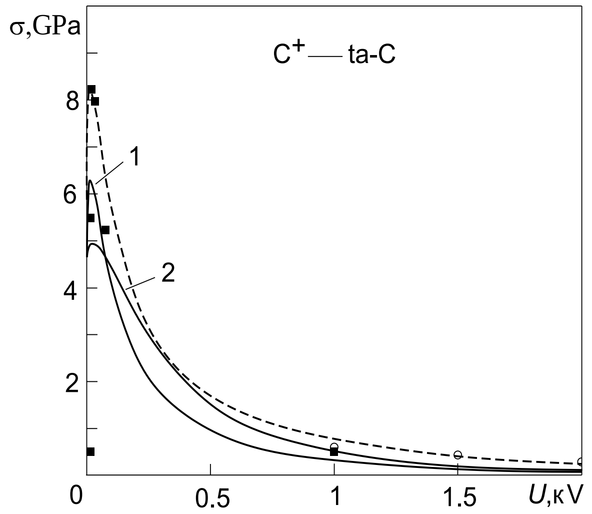
Expression (10) allows to determine the value of intrinsic compressive stress in ta-C coatings deposited from C$^+$ ion flux in modes of DC and pulse potentials at energies of ions E <1 keV. However the statistical analysis which was carried out with use SRIM2000 [6] have shown opportunity of calculation of functions w and σ in the framework of NTP model for energies of ions C$^+$ up to 2 keV [7].

Dependences of stresses in deposited ta-C films on potential U in modes of DC (the curve 1, ft_p =1) and pulse (the curve 2, ft_p =0.12) potentials are shown in Figure. Calculation of stresses was carried out by formula (10) at following values of parameters: E_Y = 500 GPa, Π = 0.07, ξ =1, U_0= 16 V, E_0= 22 eV, u = 0.3 eV, t_p= 5 µs, f = 24 kHz.

It is necessary to consider deposition temperature at intrinsic stress calculation because T_0 can essentially vary with energy of deposited ions (the ion flux heats up the coating surface). One can show that in approximation of the linear heat equation with constant thermal conductivity in steady state deposition temperature T_0 is associated with potential U by linear dependence: $T_0(U)=\lambda\left[\bar{q}(U+U_0)+E_0\right]+T_{00}$, where $\bar{q}=e\sum_i i\chi_i$ is the average ion charge, χ_i is the part of ions with charge ie, T_{00} is the temperature of unexposed substrate.

According to the data presented in [8], C^+ ions at their deposition from vacuum arc filtered plasma have charge i from 1 to 2, and χ_1 = 0.98; χ_2 = 0.02. We accepted in calculations χ_1 = 1, χ_2 = 0 and $\bar{q}=e$.

The value λ depends on technical parameters of the installation for coating deposition. It was chosen from requirement of equality of deposition temperature to its experimental value at known energy of deposited ions. In accordance with data given in [9] it was taken on T_0(0 V) ≈ 300 K and T_0(450 V) ≈ 380 K that gives an estimation of λ ≈ 0.1 K/eV.



Dependence of compressive intrinsic stress in ta-C coating on substrate bias potential in modes of DC (curve 1) and pulse (curve 2) bias potentials at deposition temperature T_0 = 400 K. The dotted curve matches to intrinsic stresses in mode of DC bias potential at T_0 = 300 K; ■ – experimental data [9]; ○ – calculated data [7]

Dependence of intrinsic stress in deposited ta-C film, obtained at deposition temperature T_0 = 300 K in mode of DC bias potential qualitatively agrees with experimental data from [9] (the dotted curve in fig. 1 which is normalized on maximum of experimentally observed stress~8.2 GPa, determines the scale of all other displayed curves). In particular, at zero bias potential calculation yields for stress σ~5 GPa, that in order of magnitude agrees with the experimental data from [9]. At T_0 = 400 K the maximum of intrinsic stress σ_m~6.3 GPa is attained at U~15 V (the curve 1). It is shown, that intrinsic stress sharply decreases at increase of deposition temperature.

In mode of pulse bias potential at the same deposition temperature the maximum of intrinsic stress σ_m~5 GPa is attained at U~25 V (the curve 2 in Figure), i.e. the maximum shifts to higher energies that qualitatively agrees with the experimental data from [9,10]. Also, it is important to note, that at E< 100 eV deposition in mode of pulse bias potential results in smaller stresses, than a deposition in mode of DC potential.

Noted peculiarities remain at other deposition temperatures.

CONCLUSIONS

1. In framework of model of nonlocal thermoelastic peak the expression for intrinsic stress in ta-C coating deposited from flux of vacuum-arc carbon plasma was derived. The expression is true both for DC mode, and for pulse bias potential mode.
2. It was shown that intrinsic stress sharply decreases at increasing of deposition temperature in regimes of DC mode and pulse bias potential mode.
3. Comparison of simulation results of internal stress in ta-C coatings deposited from a beam of C^+ ions with the experimental data has shown their qualitative agreement. Deposition in the mode of pulse potential at low ion energy E <100 eV leads to lower value of intrinsic stress than deposition in the DC mode. The pulse potential mode allows to obtain coatings with low intrinsic stresses at appropriate choice of deposition temperature.

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ВНУТРЕННИЕ НАПРЯЖЕНИЯ В АЛМАЗОПОДОБНЫХ ПОКРЫТИЯХ, ОСАЖДАЕМЫХ В РЕЖИМАХ ПОСТОЯННОГО И ИМПУЛЬСНОГО ПОТЕНЦИАЛОВ СМЕЩЕНИЯ

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Дан вывод формулы для расчета внутренних напряжений в покрытиях, осаждаемых из потока ионов в режиме импульсного потенциала. Предложен критерий применимости полученной формулы, позволяющий определить критические параметры режима импульсного потенциала. Приведены расчеты напряжений в алмазоподобных покрытиях при осаждении низкоэнергетических ионов C^+ из фильтрованной плазмы вакуумной дуги. Констатируется качественное согласие расчетных напряжений с экспериментальными данными. Отмечается важная роль температуры осаждения при контроле внутренних напряжений в осаждаемом покрытии.

ВНУТРІШНІ НАПРУЖЕННЯ В АЛМАЗОПОДІБНИХ ПОКРИТТЯХ, ОСАДЖУВАНИХ У РЕЖИМАХ ПОСТІЙНОГО ТА ІМПУЛЬСНОГО ПОТЕНЦІАЛІВ ЗМІЩЕННЯ

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Наведено виведення формули для розрахунку внутрішньої напруги в покриттях, що осаджуються з потоку іонів у режимі імпульсного потенціалу. Запропоновано критерій застосовності отриманої формули, що дозволяє визначити критичні параметри режиму імпульсного потенціалу. Приведено розрахунки напруги в алмазоподібних покриттях при осадженні низькоенергетичних іонів C^+ з фільтрованої плазми вакуумної дуги. Констатується якісна згода розрахункової напруги з експериментальними даними. Відзначається важлива роль температури осадження при контролі внутрішньої напруги в осаджуваному покритті.