Calculation of intrinsic stresses in the diamond-like coatings produced by plasma ion deposition in modes of DC and pulse bias potentials

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Abstract. The formula derivation for calculation of intrinsic stress in diamond-like coatings deposited from the ion flux in modes of continuous and pulsed potentials in view of process of defects formation is given. The criterion of applicability of obtained formula allowing to determine critical parameters of the pulsed potential mode is suggested. Results of calculation of stresses in diamond-like coatings at deposition of low-energy ions C^+ from filtered vacuum arc plasma are adduced. The influence of the bias potential, repetition frequency and pulse duration, on the value of intrinsic stress is discussed. Qualitative agreement of calculated stress and experimental data is stated. The important role of deposition temperature in control of intrinsic stress in deposited coating is noted.

1. Introduction

Intrinsic stresses σ arising in diamond-like (ta-C) coatings at deposition of C^+ ions substantially determine the physical properties and operational characteristics of the obtained coatings. In [1] formula for σ calculation using the point thermal spike (PTS) model of the ion has been suggested. The PTS model was used for determination of the number of thermally activated transitions specifying the relaxation rate of intrinsic stress.

However, the use of the PTS model for description of stress relaxation contradicts to nonlocality of energy transition from ion to target matter. Consequently, the qualitative agreement with experimental data is achieved at values of migration energy $u = 3 - 11$ eV, exceeding in many times known values for processes of defect migration. Therefore, u is the fitting parameter in the Davis formula [1], and its physical interpretation is difficult. Also, one should note the internal contradiction of PTS model which was developed only for the case of zero target temperature and for constant thermal capacity at the same time. The last condition contradicts to the Debye theory as well as to experimental data. Hence, Davis model can not explain experimentally observed dependence of intrinsic stress on deposition temperature T_0.

In [2] modification of Davis formula for calculation of intrinsic stresses σ was proposed, taking into account the deposition temperature T_0:

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

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where E is the ion energy, 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 ion j. The model of nonlocal thermoelastic peak (NTP) was used for calculation of the number of thermoactivated transitions $w(E,u,T_0)$:

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

where n_0 is the concentration of atoms, ν is the frequency of atomic oscillations, $V(t,E)$ is the NTP volume, $\tau_c \sim R_{NTP}{}^2/\left(4\kappa\right)$ is the life time of NTP with radius $R_{NTP}(t, E)$, κ is the thermal diffusivity of target material, T is the temperature in NTP, and k_B is the Boltzmann constant [3].

The modified formula (2) permitted to explain some regularities observing at deposition of carbon and BN coatings in mode of direct current (DC) bias potential [2]. However expressions (1), (2) cannot explain experimental results of paper [4] concerning deposition of diamond-like coatings in the DC bias potential mode. Furthermore the implementation of new deposition technologies, in particular, the pulse bias potential mode requires generalization of theory of intrinsic stress formation in deposited coatings.

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

2. Mathematical model

Deriving formula for intrinsic stress we followed the reasonings used by C.A. Davis [1]. Intrinsic stresses in films and coatings deposited from ion fluxes arise as the result of two opposite processes: 1) subsurface ion implantation, leading to formation of defects and origin of 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 the ions of two different energies $E_2 = E_0 + ie\left(U + U_0\right)$ 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 bombardment of target by low-energy ions is equal to $f^{-1} - t_p$. In this case the intrinsic compressive stress which is established in the coating depends on the type of the formed coating. If the pulse width is sufficiently large, then material deposited during t_p can be regarded as a solid layer of macroscopic thickness. The intrinsic stress in each layer should be evaluated using the expression (1), in which E is the energy of the ions forming the deposited 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 [5].

However, if the effective thickness of each layer does not exceed the interatomic distance a, then it is senseless to talk about the stress formation in each of these 'layers', because the size of the ion NTP considerably exceeds the layer thickness [2]. In this case, we can assume that the coating is formed by a mixture of ions of two different energies (the approximation of mixed beam), and relative fractions of ions with energies E_2 and E_1 are ft_p and $1 - ft_p$, accordingly. The condition of realization of the last case has the form:

$$f = Ra^2\,.\qquad(3)$$

Taking for estimations $R = 5$ mA/cm$^2 \sim 3\cdot10^{20}$ ions·m^{-2}s^{-1}, $a = 2.5\cdot10^{-10}$ m, we get from (3): $f > 20$ Hz. In known experiments on coating deposition in the pulse potential mode this requirement is surely satisfied.

The considered 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 ions, and density of defects formed as a result of ion scattering on the target atoms. In [6] based on the linear theory of cascade collisions it is shown that a generation rate of defects on unit area $\dot{n}_i$ is related to the flux density of bombarding ions j and ion energy E by relationship $\dot{n}_i \sim jE^{1/2}$. One should note that the above dependence arising from model assumptions is only analytical approximation presenting satisfactorily process of a defect formation only at enough high energy of the bombarding ion $E \gg E_d$, where E_d is the energy of defect formation. However direct calculation of the part of ion energy spent on formation of vacancies $\upsilon(E)$ can result in the change of the dependence $\dot{n}_i(E)$. We assume that each vacancy corresponds to an interstitial, composing the Frenkel pair with it. According to definition of function $\upsilon(E)$, number of point defects (Frenkel pairs) forming by the primary ion is equal to $E\upsilon(E)/E_d$. It is necessary to consider also the contribution Υ to volume strain of a primary ion which is constant for all ions with energy E, exceeding surface energy $E_s \sim 10$ eV. As the result, expression for generation rate of defects can be presented as:

$$\dot{n}_i \sim j\left[\frac{E\,\upsilon(E)}{E_d} + \Upsilon\right], \quad (E > E_s).$$ (4)

If ions of two various energies E_1 and E_2 are presented in flux, then (4) can be written in the form:

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

where we introduce the notation $\zeta(E_i) = (E_i\upsilon(E_i)/E_d + \Upsilon)$.

According to expression (2) stress relaxation is determined by the number of thermally activated transitions of atoms in the ion NTP. The relaxation rate $\dot{n}_R$ per unit area is proportional to the number of thermally activated transitions of atoms in the ion NTP $w(E,u,T_0)$, to relative fraction of defects n/n_0, and to the flux of implanted ions j:

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

where n and n_0 are the defect and atom concentrations, accordingly.

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

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

At plasma-ion deposition intrinsic stress in the coating can be calculated 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 with 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 growing film. On the other hand, the resultant rate of defects formation is 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]:

$$\dot{n}_i - \dot{n}_R = R(n/n_0).$$ (8)

Substituting $\dot{n}_i$ and $\dot{n}_R$ in (8), we obtain the part of the implanted ions in a film n/n_0 :

$$\frac{n}{n_0} \sim \frac{ft_p\zeta(E_2)+(1-ft_p)\zeta(E_1)}{\xi+ft_pw(E_2)+(1-ft_p)w(E_1)}.$$ (9)

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

$$\sigma(U) = B\frac{E_Y}{1-\Pi}\frac{ft_p\zeta(E_2)+(1-ft_p)\zeta(E_1)}{\xi+ft_pw(E_2)+(1-ft_p)w(E_1)},$$ (10)

where B is the normalizing constant depending, generally, on a material and technology of coating. Assuming $ft_p = 1$ in (10) we obtain expression (1) for intrinsic stress in the case of DC bias potential mode.

3. Results and discussion

Expression (10) allows to determine the value of intrinsic compressive stress in ta-C coating deposited from C^+ ion flux in modes of DC and pulse bias potentials at energies of ions $E < 1$ keV.

In the figure 1 dependences of internal compressive stresses in deposited ta-C coating on potential U in modes of DC (the curve 1) and pulse (curves 2, 3) bias potential are presented. Calculation of stresses was carried out by formula (10) at following values of parameters: $U_0 = 16$ V, $E_0 = 20$ eV, $u = 0.3$ eV, $\xi = 1$; curve 2: $t_p = 5$ μs, $f = 24$ kHz; curve 3: $t_p = 20$ μs, $f = 1.2$ kHz. Calculation of function $\zeta(E_i)$ and $w(E_i)$ for combination C^+ - ta-C was carried out using program SRIM2000 [7]. In calculations $E_d = 35$ eV and $E_s = 10$ eV were accepted.
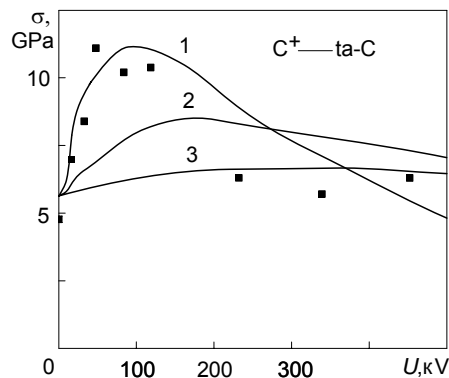

Figure 1. Dependences of intrinsic compressive stresses in deposited films ta-C on DC bias potential (the curve 1) and pulse bias potential (curves 2, 3), calculated at deposition temperature $T_0 = 370$ K. ■ - the experimental data obtained in DC bias potential mode from work [4].

At calculation of intrinsic stress in deposited coating it is necessary to consider deposition temperature T_0 which can essentially change with energy of deposited ions because the ion flux heats up coating surface. One can show that in approximation of linear heat equation with a constant heat conductivity and in steady conditions deposition temperature T_0 is associated with potential U by a linear relation: $T_0(U) = \lambda[q(U+U_0)+E_0]+T_{00}$, where T_{00} is the temperature of unirradiated substrate. The charge q of the ion C^+, according to experimental data [8], with adequate accuracy is equal to proton charge.

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 experimental data given in [4] we accepted $T_0(0\text{ V}) \approx 300$ K and $T_0(450\text{ V}) \approx 380$ K. That gives an estimation of $\lambda \approx 0.1$ K/eV.

Dependence of intrinsic stress in deposited ta-C film, obtained at deposition temperature $T_0 = 293$ K in mode of DC bias potential (curve 1) qualitatively agrees with experimental data from [4]. Curve 1 is normalized on maximum of experimentally observed stress ~ 11.1 GPa that determines the scale of all other stress curves. In DC bias potential mode the maximum of calculated compressive stress $\sigma_m \sim 11.1$ GPa is situated at $U \sim 100$ V (the curve 1). The maximum experimental value σ in ta-C coatings also was observed at $U = 100$ V [4]. Also, calculation has shown that intrinsic stress sharply decreases at increase of deposition temperature.

In mode of pulse bias potential for ft_p =0.12 (0.024) the maximum of intrinsic stress $\sigma_m \sim$ 8.5(6.6) GPa is placed at $U \sim 170$ (350) V (the curve 2(3) in fig. 1) at the same deposition temperature, i.e. the maximum shifts to higher energies. One should be noted that at $U <270$ (370) V (the curve 2 (3) in figure 1) the deposition in mode of pulse potential results in smaller stresses than deposition in mode of DC bias potential. The obtained results qualitatively agree with the experimental data from [9,10].

Noted features remain at other deposition temperatures.

CONCLUSIONS

1. In model of the nonlocal thermoelastic peak with a glance of defect formation the expression for the internal stress in the coating deposited in the plasma environment with simultaneous bombardment of ion flux is derived. The expression is valid in regimes both DC and pulsed bias potential.

2. Comparison of the calculation results of internal stresses in ta-C coating deposited from C^+ ion beam in DC bias potential with the experimental data demonstrates their qualitative agreement.

3. It is shown that in the mode of pulse bias potential the deposition of ta-C coatings for low-energy ions (E < 500 eV) leads to a lower value of compressive stress than the deposition in DC bias potential at the same temperature. The maximum internal stress in the coating increases with ft_p parameter. The bias voltage corresponding to stress maximum decreases with ft_p parameter. Pulse potential mode allows to obtain ta-C coatings with low internal stress at appropriate choice of the deposition temperature.

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