EFFECT OF TIME PARAMETERS OF PULSED BIAS POTENTIAL ON INTRINSIC STRESS IN TiN COATING DEPOSITED FROM INCLINED ION BEAM

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In the model of the nonlocal thermoelastic peak of low-energy ion, the formation of intrinsic stress in the coating deposited from inclined ion beam at the pulsed bias potential with different values of pulse frequency f and duration t_p is analyzed. The stress in the TiN coating deposited from Ti ion flux in the mode of the pulsed bias potential at various angles of incidence α and different values of time parameter $\tau = f\,t_p$ is calculated. It is established that in the region $0.01 < \tau < 0.2$ the stress σ varies nonmonotonically with increasing α, decreasing up to angles of incidence $\alpha \sim 70^o$ with subsequent growth. The calculated curve $\sigma(\tau)$ coincides with the experimental data at U = 1.5 kV and $\alpha = 0$.

PACS: 61.80.Az, 81.65.-b

INTRODUCTION

Various methods of plasma-ion deposition, which are used for coatings, are characterized by appearance of significant intrinsic stresses in coatings. Intrinsic stress in the coating is one of the key characteristics, which, in turn, determines a number of other important physical properties and technological parameters of the coating – density, hardness, adhesion of coating to the substrate [1]. In particular, high stresses can lead to the destruction of deposited coatings. The use of the pulsed bias potential permits reducing value of arising intrinsic stress. It is known that, in case of normal incidence, the intrinsic stress depends considerably on the parameters of the pulsed potential (duration t_p, repetition frequency f, amplitude U). However, the deposition of coatings on objects of complex geometric shape requires investigation of influence of the pulse potential parameters and the angle of incidence on the intrinsic stress. The effect of surface orientation was revealed experimentally [2] and was confirmed by simulation with the molecular dynamics method [3].

Earlier, we developed the theory of intrinsic stresses formation in coatings at plasma-ion deposition, based on the model of the nonlocal thermoelastic peak (NTP) of the low-energy ion (see, for example, [4–6]). The theory describes intrinsic stresses arising in the coatings at the normal incidence of the ion beam as a function of deposition temperature, species, energy, and charge of the deposited ions in DC and pulsed potential modes. Comparison of the results of stress calculations with experimental data has shown their qualitative agreement for a number of practically important cases, in particular, for diamond-like and nitride coatings [5, 6].

The influence of the pulsed potential amplitude on the value of the intrinsic stress in TiN coatings at oblique incidence of the ion beam was investigated in [7]. However, the influence of the time parameter $\tau = ft_p$ on the intrinsic stress value was not investigated. The parameter τ characterizes the average flux of energy of the ion beam.

The purpose of this paper is the investigation intrinsic stresses in TiN coatings deposited from the inclined beam of Ti^+ ions, depending on the time parameter τ of pulse potential and comparison of the calculation results with the experimental data.

INTRINSIC STRESS IN COATING DEPOSITED FROM INCLINED ION BEAM

The use of the NTP model for inclined ion beam (angle of incidence α ≠ 0) will require the modification of the formulas, taking into account changes in the geometric parameters and energy content of the NTP ions, ion flux density falling on the surface and causing the change in its mean temperature, the number of point defects, formed by the primary ion and determining the deformation of the deposited coating. To take into account the change in the geometric parameters and the energy content of the NTP, it is necessary to carry out the complex of computer experiments using the SRIM2000 program package [8] simulating cascades of excited atoms. The analysis of the geometric and energy characteristics of the resulting model cascades will allow us to modify the previously developed NTP model for the oblique incidence of the ion on the irradiated surface.

Simulation results using the SRIM 2000 software package have shown that under normal incidence of the low-energy ion, its NTP can be approximated by the spherical segment adjacent to the target surface. The radius of the NTP is determined by the relation:

$$R(t,E) = l(E)/2 + R_T(t), \qquad (1)$$

where $l(E)$ is the average projective range of an ion with energy E; $R_T(t)$ is the radius of the “smearing sphere” of the point thermal source for time t. The NTP center lies at the middle of the average projected range of the ion. The analysis of the geometric characteristics of the cascades of excited atoms generated by the ion at various energies and incidence angles α has shown that the radius of the NTP weakly depends on α. But the position of the NTP with respect to the boundary varies and is determined by the rotation of the NTP by angle α around the ion's entry point in the plane determined by the normal to the target surface and by the ion velocity vector (Fig. 1).

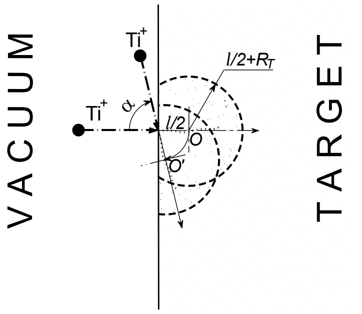

Fig. 1. Scheme of NTP transformation with the change of the angle of ion incidence

At the arbitrary incidence angle, the NTP volume is determined by the expression:

$$V=\frac{4\pi}{3}R^3-\frac{\pi}{3}\left[R-\frac{l}{2}\cos\alpha\right]^2\left[2R+\frac{l\cos\alpha}{2}\right]. \quad (2)$$

As follows from (2), the volume of the peak decreases monotonically with α increase from 0 to 90°. At normal incidence α = 0° expression (2) coincides with the expression for V given in [6].

The energy content of the peak is determined by the phonon loss of the ion, which now depends on the angle, and has the form:

$$E_{ph}(E,\alpha)=\eta(E,\alpha)E\,. \quad (3)$$

Functions $l(E)$ and $\eta(E,\alpha)$ are defined using the SRIM2000 software package. The calculated functions $V(t,E,\alpha)$ and $E_{ph}(E,\alpha)$ allow us to calculate the average temperature of the NTP with oblique incidence of the ion beam

$$T(t,E,T_0,\alpha)=\frac{E_{ph}(E,\alpha)}{\rho CV(t,E,\alpha)}+T_0\,, \quad (4)$$

where ρ, C, and T_0 are the density, specific heat and deposition temperature of the coating, respectively. We note that at temperatures above room temperature, the dependence of the heat capacity C on temperature can be neglected, taking it equal to its high-temperature limit.

The values obtained were used to calculate the relaxation rate of intrinsic stresses in the coating, determined by the number of thermally activated transitions $w(E, u, T_0, \alpha)$ in the NTP of the ion:

$$w(E,u,T_0,\alpha)=n_0\nu\int_0^{\tau_c}V(t,E,\alpha)\,\mathrm{e}^{-\frac{u}{k_BT(t,E,T_0,\alpha)}}\,dt\,, \quad (5)$$

where k_B is the Boltzmann constant; n_0 is the target atom concentration; ν is the vibrational frequency of the atom; τ_c is the lifetime of the NTP, and u is the activation energy of the defect migration process [5, 6].

When determining the deposition temperature T_0 in the steady-state regime, it is necessary to take into account the change in the flux density of ions j falling on the surface. As the first approximation for oblique incidence, it can be assumed that the ion flux density on the substrate is varied in proportion to the cosine of the incidence angle α. Then the value of T_0, which depends on the potential on the substrate U, and the incidence angle α, is given by:

$$T_0(U,\alpha)=T_{00}+\mu j_\alpha\left[\tau\sum_i Q_i(U)+(1-\tau)\sum_i Q_i(U_1)\right], \quad (6)$$

where T_{00} is the temperature of the non-irradiated substrate; $j_\alpha = j\cos\alpha$; μ is the fitting parameter chosen from the equality condition of the deposition temperature to the experimentally observed value; $Q_i(U) = i\chi_i\left(U+U_f+E_{0i}\right)$; χ_i and E_{0i} is the fraction of ions with charge i (in proton charge units) and the initial ion energy per unit of charge, respectively; U_f is the floating potential; U_1 is the potential applied to the substrate between pulses. Summation is carried out over n charge states of ions (as a rule, $n \le 5$).

Intrinsic stresses are formed as a result of the defect formation at ion implantation and stress relaxation during the migration of defects into NTP ions [1, 4–6]. When deriving the formula for stresses, a linear dependence was assumed between the volume deformation of the target and the density of long-lived defects formed as a result of the scattering of the primary ion by target atoms. The resulting rate at which defects are introduced into the film is determined by the difference between the rate of appearance of defects due to ion implantation and the rate of their loss due to thermally activated migration. Calculations of the rate of defect formation lead to the following formula for calculating of intrinsic stresses in coatings deposited from the inclined beam of differently charged ions:

$$\sigma(U,\tau,\alpha)=A\frac{E_Y}{1-\Pi}\frac{\tau G(U,\alpha)+(1-\tau)G(U_1,\alpha)}{1+\tau W(U,\alpha)+(1-\tau)W(U_1,\alpha)}\,, \quad (7)$$

where E_Y and Π are the Young's modulus and the Poisson's ratio of the coating material,

$$G(U,\alpha)=\sum_i\chi_i\zeta^*\left(i\left(U+U_f+E_{0i}\right),\alpha\right)$$

and

$$W(U,\alpha)=\sum_i\chi_i w\left(i\left(U+U_f+E_{0i}\right),\alpha\right).$$

Parameter A, as well as the value of the activation energy of defect migration u, are determined from the comparison of the theoretical dependence with the experimental data for the normal incidence of the ions α = 0°. The function $\zeta^*(E,\alpha)$ is determined by the density of interstitial defects $\zeta(E,\alpha)$ generated by the primary ion, minus those that are removed during the ion sputtering of the coating material. Let the total number of defects created by both the primary ion and all secondary ions be given by the function $\zeta_{total}(E,\alpha)$, and the total number of sputtered atoms is function $\psi_{total}(E,\alpha)$. Both these functions, as well as the function $\zeta(E,\alpha)$, can be obtained using the SRIM2000 software package. Then the part of the stable defects that is not removed from the material as a result of sputtering can be determined by the expression:

$$\zeta^*(E,\alpha)=\zeta(E,\alpha)\left(1-\psi_{total}(E,\alpha)/\zeta_{total}(E,\alpha)\right). \quad (8)$$

Formula (7) defines the intrinsic stress that arises in the coating during deposition of the one-component beam of charged ions at both the constant (τ = 1) and the pulsed (τ < 1) potentials on the substrate.

RESULTS AND DISCUSSION

Calculation of intrinsic stresses in the TiN coating was carried out at the following values of the parameters: u = 0.58 eV, U_f = 20 V, U_1 = 0, T_{00} = 300 K. In accordance with the experimental conditions, the pulse frequency f and duration t_p were selected from intervals 2.5...12 kHz and 5...20 μs, respectively. The NTP parameters of Ti ions in the TiN coating material, necessary for calculating the functions $\zeta(E)$ and $w(E)$ were determined using the software package SRIM2000. The calculations also assumed $\mu j = 0.223$ K/V, which corresponded to the average deposition temperature T_0 (0.12)=400 K in the pulsed potential mode and the normal incidence of the deposited beam on the coating surface. The values of the parameters χ_i and E_{0i} for Ti ions were taken from the monograph [9].

In Fig. 2 the shape of the function $\gamma(E,\alpha) = \psi_{total}(E,\alpha)/\zeta_{total}(E,\alpha)$ is shown for the case of Ti ions bombarding the TiN target for different values of the incidence angle of ions α. The functions $\zeta, \zeta_{total}, \psi_{total}$ were calculated using SRIM2000.

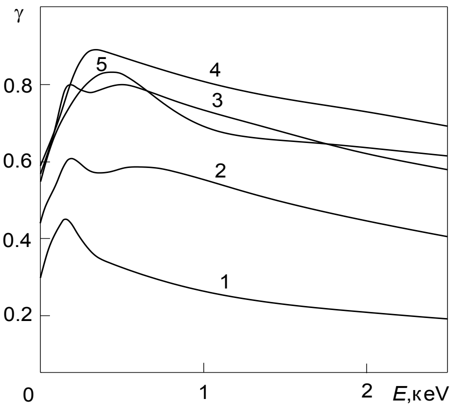

Fig. 2. Function $\gamma(E,\alpha)$ for different values of the incidence angle α of Ti ion, α = 0, 45, 60, 70, 80° (curves 1–5, respectively)

As can be seen from Fig. 2, the relative decrease in the number of long-lived defects due to their sputtering in the case of the normal incidence of the ion is relatively small and varies slowly from 0.4 to 0.2 in the ion energy range from 0.2 to 2.5 keV. For qualitative analysis, it is possible to replace the function $\gamma(E,0)$ with constant $\gamma \approx 0.3$. In the accepted approximation, account of the sputtering at normal incidence changes the shape of the stress curve $\sigma(E)$ only slightly, leading only to the renormalization of the fitting parameter A in expression (7). Thus, the obtained previously results of calculations of intrinsic stresses in the TiN coating at normal incidence of the Ti ion beam [5, 6], in which sputtering is not taken into account, qualitatively correctly describe the stresses arising at α = 0 and need only in an insignificant correction. We note that for the fixed ion energy, the number of sputtered atoms increases with α for α < 70º and decreases for α > 70º (see Fig. 2).

Fig. 3 displays the dependences $\sigma(\tau)$ in TiN coatings bombarding by Ti ions for U = 1.5 kV at different angles of incidence of α, calculated using formula (7).

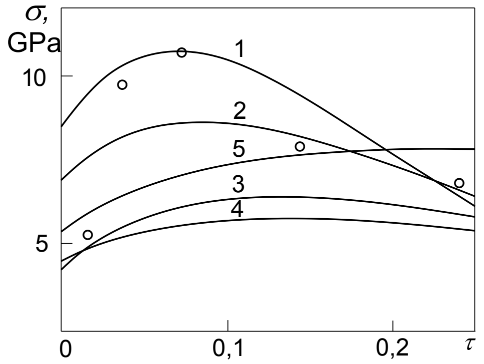

Fig. 3. Intrinsic stresses $\sigma(\tau)$ in TiN coating deposited from Ti ion beam in the pulsed potential mode for U = 1.5 kV at incidence angles α = 0, 45, 60, 70, 80°, curves 1–5, respectively. The symbols ○ are experimental points at α =0°[10]

It can be seen from Fig. 3 that at $\alpha = 0$º the calculated curve coincides qualitatively with the experimental data [10]. In the region 0.01 < τ < 0.2, as the angle of incidence α is increased, the stress σ varies nonmonotonically, decreasing up to angles of incidence $\alpha \sim 70°$ with subsequent growth. This behavior is associated with different influence of processes of defect formation, sputtering and the deposition temperature at different angle of incidence of ions. When approaching the regime of constant potential (τ ~ 1), calculations show that the stresses increase monotonically with increasing angle of incidence, remaining small enough.

CONCLUSIONS

1. In the framework of the model of the nonlocal thermoelastic peak, intrinsic stresses in the coating deposited from the inclined ion beam are analyzed at different values of angle of incidence α and time parameter τ of the pulse bias potential.

2. The calculation of intrinsic stresses in the TiN coating deposited from the inclined beam Ti^+ at different values of angle of incidence α and time parameter τ of the pulse bias potential is carried out.

3. It is shown that in the mode of pulsed bias potential at $\alpha = 0$, $U = 1.5$ kV; and $0 < \tau < 0.25$, the calculated curve $\sigma(\tau)$ coincides qualitatively with the experimental data.

4. It is established that in the region $0.01 < \tau < 0.2$ the stress σ varies nonmonotonically with increasing α, decreasing up to angles of incidence $\alpha \sim 70$º with subsequent growth. This behavior is due to different contributions in σ of deposition temperature and processes of defect formation and sputtering at different angles of incidence.

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Article received 02.11.2017

ВЛИЯНИЕ ВРЕМЕННЫХ ПАРАМЕТРОВ ИМПУЛЬСНОГО ПОТЕНЦИАЛА СМЕЩЕНИЯ НА ВНУТРЕННИЕ НАПРЯЖЕНИЯ В ПОКРЫТИИ TiN, ОСАЖДАЕМОМ ИЗ НАКЛОННОГО ПУЧКА ИОНОВ

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В модели нелокального термоупругого пика низкоэнергетического иона проанализировано формирование внутренних напряжений в покрытии, осаждаемом из наклонного пучка ионов при импульсном потенциале смещения с различными значениями частоты f и длительности t_p импульсов. Проведен расчет напряжений σ в TiN-покрытии, осаждаемом из потока ионов Ti в режиме импульсного потенциала при различных углах падения ионов α и различных значениях временного параметра $\tau = f\ t_p$. Установлено, что в области $0{,}01 < \tau < 0{,}2$ при увеличении α напряжение σ изменяется немонотонно, уменьшаясь вплоть до углов падения $\alpha \sim 70^{o}$ с последующим ростом, причем при U = 1,5 кВ и α = 0 ход расчетной кривой $\sigma(\tau)$ совпадает с экспериментальными данными.

ВПЛИВ ЧАСОВИХ ПАРАМЕТРІВ ІМПУЛЬСНОГО ПОТЕНЦІАЛУ ЗМІЩЕННЯ НА ВНУТРІШНЮ НАПРУГУ В ПОКРИТТІ TiN, ЩО ОСАДЖУЄТЬСЯ З ПОХИЛОГО ПУЧКА ІОНІВ

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У моделі нелокального термопружного піку низькоенергетичного іона проаналізовано формування внутрішніх напружень в покритті, що осаджується з похилого пучка іонів при імпульсному потенціалі зміщення з різними значеннями частоти f і тривалості t_p імпульсів. Проведено розрахунок напружень в TiN-покритті, що осідає з потоку іонів Ti в режимі імпульсного потенціалу при різних кутах падіння іонів α і різних значеннях часового параметра $\tau = f\ t_p$. Установлено, що в області $0{,}01 < \tau < 0{,}2$ при збільшенні α напруга σ змінюється немонотонно, зменшуючись аж до кутів падіння $\alpha \sim 70^{o}$ з наступним ростом, причому при U = 1,5 кВ і α = 0 хід розрахункової кривої $\sigma(\tau)$ збігається з експериментальними даними.