Physical mechanisms of microstructure formation in niobium films under low temperature ionic-atomic deposition

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The molecular dynamics method has been used to study the effect of low-energy irradiation with self-ions on the microstructure and residual stresses arising in niobium films in the course of ion-atomic deposition. The ion flow constituted 10 % of the total atomic flow being deposited, the ion energy was 200 eV. After thermal deposition of the film at 300 K up to the thickness at which the steady-state density is attained, the ionic-atomic deposition of the film was performed. The growing film density was increased under ion action. This increase has been shown to be caused mainly by the film smoothing under ion bombardment that results in decreasing number of "micro-cracks" below which the pores are localized. The investigation results show that the ion action changes the character of internal microstresses. This is related with formation of interstitial atom clusters. A correlation has been found between the density of films formed, their microstructure and arising microstresses.

В работе методом молекулярной динамики исследовано влияние низкоэнергетического облучения собственными ионами на микроструктуру и остаточные напряжения, возникающие в пленках ниобия при атомно-ионном осаждении. Ионный поток составлял 10% от общего потока осаждаемых атомов, энергия ионов - 200 эВ. После термического осаждения пленки при температуре 300 К до толщины, при которой достигается стационарная плотность, проводилось атомно-ионное осаждение пленки. Ионное воздействие приводило к повышению плотности растущей пленки. Показано, что это происходит в основном благодаря сглаживанию поверхности пленки во время ионной бомбардировки, что приводит к уменьшению количества "микротрещин" под которыми располагаются поры. Результаты исследований свидетельствуют о том, что ионное воздействие изменяет характер внутренних микронапряжений. Это связано с образованием кластеров междоузельных атомов. Раскрыта корреляция между плотностью образуемых пленок, их микроструктурой и возникающими микронапряжениями.

The microstructure formation in films during the physical vapor deposition (PVD) is the object of intense study during many years [1–4]. Thin films exhibit a wide variety of microstructures depending on the substrate temperature T. Movchan and Demchishin developed the structure zone models which systematically categorize the self-organized structure evolution during PVD [5]. They have established that in the deposited metals, there are 3 different temperature ranges separated by the temperatures $T_1 \approx 0.3T_{ml}$ and $T_2 \approx 0.5T_{ml}$, where T_{mp} is the melting point. It is that the processes of coarse micro-crystallite growth in Zone III ($T > T_2$) are assumed to be associated with the bulk diffusion processes. The formation of a columnar structure in Zone II is generally associated with the surface self-diffusion. The film growth at the temperature ($T < T_1$) proceeds in the low-temperature deposition Zone I. The low-temperature deposition permits to obtain protective lay-

ers avoiding degradation of bulk properties in the products under treatment. At the same time, the films deposited at low temperatures are porous and show a weak adhesion to the substrate. Recently, various technologies of ion-beam assisted deposition are used to improve the protective, hardening, friction, and other properties of coatings. These methods make it possible to obtain compact coatings with a good adhesion at low temperatures. One of the methods to form films from atomic-ionic flows is the thermoionic deposition (TID) [6]. The essence of the TID consists in what follows: using an electron beam for material heating, partially ionized metal vapors are obtained to be deposited onto a substrate. The ion current density is controlled by the degree of vapor ionization in the low-voltage DC discharge. The ion energy is varied by the potential applied to the substrate. The experimental data evidence that changing the atomic-ionic flow energy and ionization degree, it is possible to influence appreciably the microstructure of films, their density, residual microstress level, etc. [7, 8]. Despite the available experimental data and the theoretical investigations [9–15], the mechanisms of this ion irradiation effect are not fully clear up to now. The purpose of this work is to study the mechanisms of ion irradiation effect on the structural properties of niobium films in the process of low-temperature atomic-ionic deposition using computer simulation.

Niobium was chosen as a material to be investigated taking into account the available experimental data on the changes of niobium film properties during the deposition under different conditions [8, 9]. Niobium attracts an increasing interest in engineering because of its use in manufacturing of Josephson tunnel junctions [16, 17], and thin niobium films are considered as a promising material for application in superconductive cavities for particle acceleration [18, 19]. The niobium film deposition was simulated by the molecular dynamics method using the Sdyn program as an updated version of the DYMOD program [20] designed to study the material surface properties. The equations of motion were solved by a Verlet-like algorithm method at the time step about 1 fs. The interaction between metal atoms was described by the embedded-atom method (EAM) [21]. The total energy of an elemental system is represented as

$$E = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{j \neq i} \varphi_{ij}(R_{ij}), \qquad (1)$$

where φ_{ij} is the pair potential as a function of the distance R_{ij} between atoms i and j; $F_i(\rho_i)$, the embedding energy as a function of the host electron density ρ_i induced at a site i by all other atoms in the system. The latter is given by:

$$\rho_i = \sum_{j \neq i} \rho_j^0(R_{ij}), \qquad (2)$$

where $\rho_j^0(R_{ij})$ is the electron density function. The simulations were conducted using the Johnson-Oh EAM-potential for Nb [22]. In small interatomic spaces, the Hartree-Fock potential was used in the Molier approximation [23].

The atomic flow deposition of 9 close-packed planes with {110} orientation onto a substrate was simulated. Four first layers were fixed in the positions of a perfect bcc lattice. To provide the required substrate temperature before the deposition onset, a kinetic energy was given to movable atoms of the next five layers. The procedure used to establish the thermal equilibrium has taken 1 ns. The thermal film deposition was carried out at 300 K. The temperature control was provided by scaling the atomic velocities [24]. The velocity correction was applied to all the atoms except for four last deposited monolayers. Thermally deposited atoms had kinetic energy of 0.2 eV and a pulse direction normal to the deposition plane. The deposition time of one monolayer t_{mono} was 0.142 ns. The ion flow characteristics in the computer simulation were as followis: ion energy 200 eV, ion number 10 % of the total number of impinging atoms corresponding to the maximum density of films observed in experiments. The incident atoms were distributed randomly in the plane parallel to the deposition plane. Crystallites were grown in the Z axis direction. The X axis had [100] the crystallographic direction, Y – the [001] and Z– the [0$\bar{1}$1] one. Periodic boundary conditions were applied in both X and Y directions. The simulating cell was a rectangular parallelepiped with dimensions of 4.63, 4.67, and 13.8 nm along X, Y and Z axes, respectively.

The atomic structure and surface atomic distribution in the film were analyzed using the algorithm described in [25] based on consideration of the electron density spatial distribution. The entire space of the simulating cell was separated into cubic blocks

with an edge much less then the atomic radius. The cell space was considered to be "blank" if the electron density was less than a certain value ρ_V. The atoms neighboring to these cells were considered as surface ones. Successive analysis of neighboring cells from the upper point of the simulating cell (certainly "blank") allows us to separate the atoms of the internal and external surfaces. The ρ_V parameter value was determined by test calculations so that atoms of the external planar surface and vacancy-neighboring atoms be selected correctly. The film material density in depth was characterized by the atomic layer occupation $\theta(Z_n)$, where Z_n is the center coordinate Z of the atomic layer parallel to the substrate. The value $\theta = 1$ corresponds to the fully occupied (110) layer of the perfect lattice.

We have calculated the microstress tensor on every atom for the stresses arising in the deposited films [26–27]:

$$\sigma_i^{(\alpha\beta)} = -\frac{1}{\Omega_i}\left(\frac{1}{2}\sum_{j\neq i} G_{ij}^{\alpha} r_{ij}^{\beta} + M_i V_i^{\alpha} V_i^{\beta}\right), \quad (3)$$

$$G_{ij}^{\alpha} = \quad (4)$$

$$= -\left[\frac{\partial F_i(\rho_i)}{\partial \rho_i}\frac{\partial \rho_j^0(r_{ij})}{\partial r_{ij}} + \frac{\partial F_j(\rho_j)}{\partial \rho_j}\frac{\partial \rho_i^0(r_{ij})}{\partial r_{ij}} + \frac{\partial \varphi_i(r_{ij})}{\partial r_{ij}}\right]\frac{r_i^{\alpha} - r_j^{\alpha}}{r_{ij}}.$$

Here, $\sigma_i^{\alpha\beta}$ is the stress tensor component in the point r_i where the atom i is positioned; G_{ij}^{α} is the α component of the force acting between the atoms i and j; Ω_i is the atomic volume of the atom i; r_{ij}^{β} is the β component of the distance between the atoms i and j; r_{ij} is the distance between the atoms i and j; M_i is the mass of atom i; V_i^{α} is the $\forall$ velocity component of atom i. The mean hydrostatic microstress over the film depth was determined by averaging over the atomic layer:

$$\sigma_g(z) = \frac{1}{3N_z}\sum_{k=1}^{N_z}(\sigma_k^{xx} + \sigma_k^{yy} + \sigma_k^{zz}), \quad (5)$$

where the summation was made over atoms k belonging to the layer having a center with Z coordinate; N_z is the number of atoms in the layer.

To clear up the role of ionic irradiation in the formation of a film structure, the thermal deposition of a niobium film was first simulated. The methods of computer simulation were used before to investigate the processes taking place in formation of such niobium films by vacuum deposition

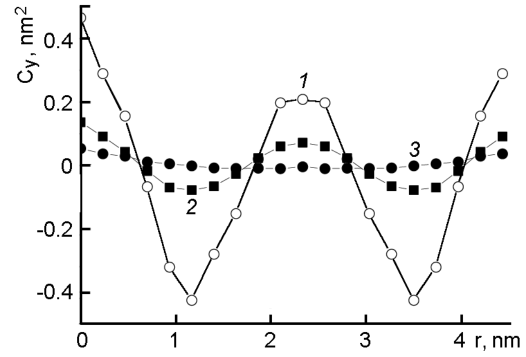

Fig. 1. The height-height correlation functions C_y along the direction Y in different moments of additional thermoionic deposition. *1* – moment of deposition onset; *2* – after $t = 2t_{mono}$; *3* – after $t = 7t_{mono}$.

[28]. It has been shown that in the process of low-temperature deposition, the film structure is defined by the instability of a smooth form of the film surface during deposition. On the surface of a growing film, a relief arises consisting of ripples oriented mainly along the <100> crystallographic direction. Development of this relief results in the roughness build-up and "microcracks" formation. The statistical measure of the surface morphology variation in time t along the direction determined by the vector **r** is the height-height correlation function:

$$C(\mathbf{r},t) = \langle(\langle z(\mathbf{x},t) - \langle z(t)\rangle)(z(\mathbf{x}+\mathbf{r},t) - \langle z(t)\rangle)\rangle, \quad (6)$$

where the vector **x** determines the atom coordinates and the brackets refer to the averaging over the surface atoms. In Fig. 1, the hollow markers represent the plots of functions $C_y = C(\mathbf{y},t)$ along the vector parallel to the simulating cell edge Y of the film obtained by PVD. The morphology of the statistically ordered surface structure is qualitatively described by the correlation length $\lambda(t)$, that is generally determined as the value r of the first maximum in the correlation function $C(\mathbf{r},t)$ [29]. As it follows from the previous investigations results, during the low-temperature deposition of niobium films along the <110> direction, the formation of a correlated structure with the unchanged $\lambda(t)$ value is observed. In the same Fig. 1, the solid markers show the change in the height-height correlation function during the further atomic-ionic flow deposition onto the film. As is seen from the Figure, the presence of ions in the flow being deposited

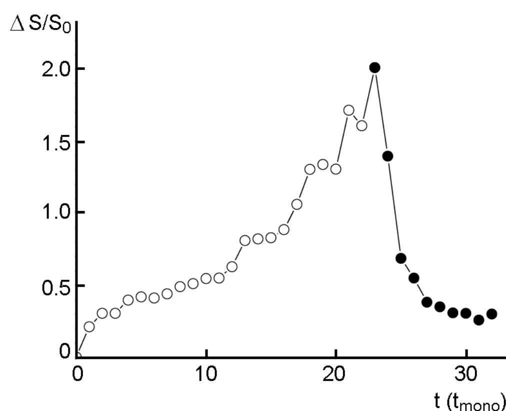

Fig. 2. Ratio of the external film surface area change $\Delta S = S - S_0$ to the perfectly smooth surface area S_0. (S is the current value of the surface area). Hollow circles, preliminary thermally deposited film; solid markers, after additional atomic-ionic deposition of 9 monolayers.

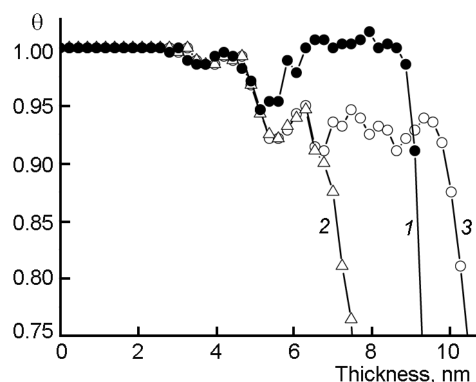

Fig. 3. Change of the atomic layer occupation $\theta(Z_n)$ characterizing the material density in the thickness of films deposited by PVD and TID. *1* (circular solid marker) – niobium film after additional thermoionic deposition during $8t_{mono}$. *2* (triangular markers) – niobium film preliminary obtained by PVD ($t = 24t_{mono}$); For comparison, the circular hollow markers (*3*) show the change in $\theta(Z_n)$ corresponding to the further thermal deposition during $8t_{mono}$.

results first in a decrease of the maximum $\lambda(t)$ and then in the full disappearance of the latter. Consequently, the ions hinder the formation of a correlated structure on the film surface in the course of deposition by blocking the mechanism of microcracking and formation of nanoblocks.

It is known that one cause of instability arising during the film deposition is the presence of Ehrlich-Schwoebel barriers [30]. This is the energy necessary to the atom to perform a thermally activated jump from the upper atomic terrace onto the lower one. Irradiation of the film deposited with low-temperature ions results in an increased frequency of atomic transitions between the terraces during the nonequilibrium stage of atom-atom collision cascade. The calculation results show [31] that the probability of atomic displacements between the terraces increases by several times. It follows from the analysis of data obtained that during thermal deposition, while forming one monolayer, approximately every fifth atom undergoes the transition. Under atomic-ionic action, the number of atomic transitions increases. Every impinging ion provokes in average about 20 additional atomic transitions between the layers. So, the main mechanism of low-energy irradiation effect on the film structure is the increase of the atomic transition frequency between the terraces; and, as a consequence, the blocking of the mechanism of correlated structure microcracking. The increase of atomic mobility between the layers results in smoothing of the surface and in decreasing number of surface atoms. The ratio of the film surface area change to its perfect value $\Delta S/S_0$ for two cases — during thermal film deposition of and after TID is given in Fig. 2. During thermal deposition, $\Delta S/S_0$ increases in time. In the case of atomic-ionic deposition, the film roughness decreases.

In [28], it is shown that the porosity of films obtained by low-temperature PVD is due to the microvoids being formed below the "microcracks" on the surface of a growing film. As a result, the film density is decreased as compared to that of solid material. The density change in the thickness of the thermally deposited film is shown in Fig. 3 by triangular markers. Subsequently, the atomic-ion flux was deposited upon this film. For comparison, the circular hollow markers show the density values of the thermally deposited film during further thermal deposition without ion assistance. From Fig. 3, it follows that the density of the thermally deposited film is 8 % lower than that of solid niobium. The density of the film formed by the TID is marked on the plot by solid circles. It is seen from Fig. 3 that the density of newly deposited layers is increased. After deposition of several monolayers from the atomic-ionic flow, the film density has reached that of solid material. It should be noted that in the course of thermoionic deposition, not only the density of newly formed layer is increasing, but

also the density in the film thickness changes. It is noteworthy that areas appear in the film exceeding in density the solid material. This is connected with the emergence of self-interstitial atoms in the film. The interstitial atoms are formed due to transferring to the film of atoms having the kinetic energy higher than the threshold displacement energy of the film atoms.

As a result of this process, the Frenkel interstitial-vacancy pairs are formed. As a rule, the vacancies are formed on the film surface. The interstitial atoms arising in the bulk of the growing film have the configuration of dumb-like interstitials elongated along the crystallographic <110> direction characteristic for bcc materials [32] when a lattice atom is displaced from the site into a position symmetric to the interstitial atom. Such an interstitial configuration is very mobile and migrates easily even at low temperatures. As a result, the interstitial atoms can arrive at the boundary of the growing film and can also heal the vacancy clusters in its bulk. So, one of mechanisms of ion densification at low energies is the "healing" of vacancy clusters by self interstitial atoms being formed. However, this effect is not determining one in the porosity suppression as well as in the film nanostructure formation. The important factor in the formation of interstitial atoms is that those can form clusters of defects. During the film growth, we observed the formation of clusters including six and more interstitial atoms. In the course of growth, such clusters of defects can form interstitial dislocation loops. Thus, the ion interaction may result in formation of structural defects not typical of thermal film deposition. In experiments on thermal ion deposition of films, it has been shown that while in the case of thermal deposition preferably voids are formed, in the case of atomic-ionic deposition, a dislocation structure is developed [8, 9]. The present study allows us to believe with good reason that the dislocation structure observed in the TID experiments is formed due to development of interstitial loops arising under ion irradiation.

The film microstructure change results in changing of internal microstresses. The plot of hydrostatic microstress distribution in the thickness of a deposited film is given in Fig. 4. The hollow markers present the microstresses in the PVD film. It is seen that there are compressive microstresses in the film. These microstresses result from formation of vacancies. The vacancy formation mechanism was studied in [33]. The solid markers in the same plot designate internal microstresses in the niobium film after additional TID of 8 layers. It is seen that the character of microstresses in the film bulk is changed appreciably. The compressive microstresses are converted into tensile ones. At the same time, at the boundary of the growing film they remained compressive. The presence of compressive microstresses at the growing film front is due to the non-compact filling of several first atomic layers in the course of thermal deposition and atomic-ionic deposition as well. A conclusion can be made that the change of internal microstresses in the films under irradiation is due to formation of interstitials and their clusters which develop and transform into dislocations, thereby changing the film microstructure.

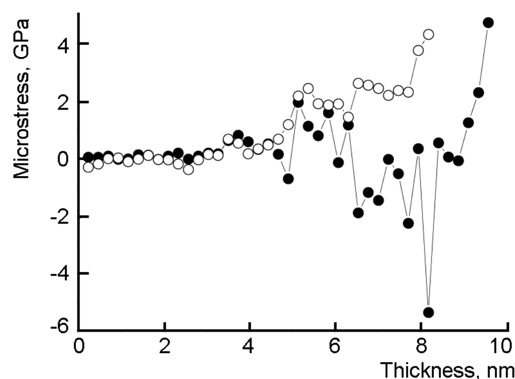

Fig. 4. Distribution of hydrostatic microstresses σ_g in thickness of the deposited niobium film. Hollow markers, microstresses in the preliminary thermally deposited film, solid markers, after additional atomic-ionic deposition of 8 monolayers.

Thus, the effect of low-temperature irradiation with self-atoms on the microstructure of niobium films has been studied. It is shown that the ion action influences the growing film relief. The effect of ion densification has been studied. It has been established that at the ion energy 200 eV and the ionization degree 0.1, the density of films formed is equal to that of the solid material. These data are well correlated with the experimental data obtained by TID of niobium films. It is demonstrated that the ion densification is provided mainly by blocking the "microcrack" formation at the growing film surface. The influence of ion action on the character of microstresses in the film deposited has been studied. Changing of the stress sign in the film bulk from compressive to tensile

ones is related with the formation of interstitial atom clusters. These clusters can act as nuclei of interstitial dislocation loops observed in the experiments studying the ion irradiation effect on the film properties. It is established that there is a correlation between the density of formed films, their microstructure and arising microstresses.

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Фізичні механізми впливу іонів на формування мікроструктури плівок ніобію при низькотемпературному осадженні

І.Г.Марченко, І.М.Неклюдов

У роботі методом молекулярної динаміки досліджений вплив низькоенергетичного опромінення власними іонами на мікроструктуру та залишкові напруги, що виникають у плівках ніобію при атомно-іонному осадженні. Іонний потік становив 10% від загального потоку атомів, що осаджують, енергія іонів - 200 еВ. Після термічного осадження плівки при температурі 300 K до товщини, при якій досягається стаціонарна щільність, проводилося атомно-іонне осадження плівки. Іонний вплив приводив до підвищення щільності зростаючої плівки. Показано, що це відбувається в основному завдяки згладжуванню поверхні плівки під час іонного бомбардування, що приводить до зменшення кількості "мікротріщин" під якими розташовуються пори. Результати досліджень свідчать про те, що іонний вплив змінює характер внутрішніх мікронапруг. Це пов'язане з утворенням кластерів міжвузлевих атомів. Розкрито кореляцію між щільністю утворених плівок, їхньою мікроструктурою й виникаючими мікронапругами.