Film nanostructure formation during low-temperature PVD deposition using partially ionized atomic fluxes

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Abstract. The method of molecular dynamics was employed to study the effect of low-energy irradiation with self-ions on the nanostructure and residual stresses arising in niobium films in the process of atomic-ion deposition. The ion flux constituted 10% of the total flux of deposited atoms and the ion energy was 20 and 100 eV. After thermal physical vapor deposition (TPVD) of the film at a temperature of 300 K up to a thickness at which a steady-state density is reached, computer simulation of ionized PVD (IPVD) of the film was performed. The growing film density increased under the ion action. It was established that this increase is provoked mainly by the film smoothing under ion bombardment that leads to a decrease in the number of “microcracks” below which pores are formed. The results of investigations show that under ion action the character of internal microstresses is changing. It is related with the formation of interstitial atom clusters. A correlation was found between the density of films formed, their nanostructure and the arising microstresses.

1. Introduction

Microstructure formation in films during physical vapor deposition (PVD) has been the object of intense studies for 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 established that for metals there are three different temperature ranges separated by the temperatures $T_1 \approx 0.3T_m$ and $T_2 \approx 0.5T_m$, where $T_m$ is the melting point. It is assumed that the processes of the coarse microcrystallite growth in Zone III ($T > T_2$) are associated with the bulk diffusion processes. The formation of a columnar structure in Zone II is generally related to the surface self-diffusion. The film growth at the temperature ($T < T_1$) is the low-temperature deposition Zone I. The low-temperature deposition permits one to obtain protective layers while avoiding degradation of the bulk properties in the products under treatment. At the same time, at low temperatures porous films are formed with weak adhesion to the substrate.

In view of improving the protective, hardening, friction and other properties of coatings different technologies of ion-beam assisted deposition have been recently applied making it possible to obtain compact coatings with good adhesion at low temperatures. One of the methods for forming films from atomic-ion fluxes is the method of IPVD. The essence of the IPVD method consists in the following: using the electron beam to heat the material one obtains partially ionized metal vapors to be deposited on the substrate. The ion current density is controlled by the degree of ionization vapors. The ion energy is varied by varying the potential applied to the substrate. The experimental data shows that by
changing the energy and the degree of ionization of the atomic-ion flux it is possible to influence appreciably the microstructure of the films, their density, residual microstresses etc. [6-10]. Despite the available experimental data and theoretical investigations carried out [11-17], the mechanisms of this ion irradiation effect are not fully understood.

The purpose of the present work is to study, using the methods of computer simulation, the mechanisms of ion radiation effect on the structural properties of films in the process of low-temperature atomic-ion deposition.

2. Simulation details

Niobium was chosen as the material to be investigated taking into account the available experimental data on the change of properties of niobium films during their deposition under different conditions [7, 11]. Niobium attracted increasing technological interest because of its use in manufacturing Josephson tunnel junctions [18-19]; thin niobium films are considered as a promising material for application in superconducting cavities for particle acceleration [20-21].

The niobium film deposition simulations were performed by the molecular dynamics method using the Sdyn program as an updated version of the DYMOD program [22] designed to study the material surface properties. The equations of motion were solved by a Verlet-like algorithm method with a time step \( \approx 0.25 \) fs. The interaction between metal atoms was described by the embedded-atom method (EAM) [23]. The simulations were conducted using the Johnson-Oh EAM-potential for Nb [24]. The Hartree-Fock potential in the Molièr approximation [25] was used at small distances between atoms.

Simulations were performed of atomic flux deposition onto the substrate of nine close-packed planes with \{110\} orientation. The first four layers were fixed in the positions of a perfect bcc lattice. To reach a required substrate temperature before the deposition onset, a kinetic energy was given to movable atoms of the next five layers. Thermal equilibrium was established in 1 ns. Thermal film deposition was carried out at a temperature of 300 K. The temperature control was achieved by scaling the atomic velocities [26]. TPVD atoms had kinetic energy of 0.2 eV and a momentum normal to the deposition plane. The deposition time of one monolayer \( t_{\text{mono}} \) was 0.904 ns. The characteristics of an ion flux in the computer simulation were the following: ion energy - 20 and 100 eV, ion concentration - 10% of the total quantity of impinging atoms. Incident atoms and ions were randomly distributed in the plane parallel to the deposition plane. The crystallites were growing in the \( Z \) axis direction. The \( X \) axis had the \[100\] crystallographic direction, \( Y - [011] \) direction and \( Z - [011] \) direction. Periodic boundary conditions were applied to both the \( X \) and \( Y \) directions. A computational cell was a rectangular parallelepiped with dimensions of 9.24, 9.34 and 27.6 nm along the \( X \), \( Y \) and \( Z \) axis, respectively.

The atomic structure and surface atom distribution of the film were analyzed using the algorithm described in [27]. This algorithm is based on the analysis of the electron density spatial distribution. The entire space of the computational cell was separated into the 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 of \( \rho_c \). Atoms neighboring with these cells were considered as surface ones. Successive analysis of neighboring cells from the upper point of the computational cell (certainly “blank”) allowed us to separate the atoms of the internal and external surfaces. The value of the parameter \( \rho_c \) was determined by test calculations so that atoms of the external flat surface and vacancy-neighboring atoms be selected correctly. The film material density in depth was characterized by the atomic layer occupation \( \theta(Z) \), where \( Z \) is the center coordinate \( Z \) of the atomic layer parallel to the substrate. The value of \( \theta = \theta_0 = 1 \) corresponds to the fully occupied \( (110) \) layer of the perfect lattice.

We calculated the microstress tensor on every atom for the stresses arising in the deposited films [15,28]:
\[ \sigma_{i}^{a\beta} = -\frac{1}{\Omega_i} \left( \sum_{j \neq i} \frac{1}{2} G_{ij}^{a} r_{ij}^{\beta} + M_{i} V_{i}^{a} V_{i}^{\beta} \right) \]  

(1)

\[ G_{ij}^{a} = \left[ \frac{\partial F_{i}(\rho_{i})}{\partial \rho_{i}} \frac{\partial \rho_{j}^{a}}{\partial r_{ij}} + \frac{\partial F_{j}(\rho_{j})}{\partial \rho_{j}} \frac{\partial \rho_{i}^{a}}{\partial r_{ij}} + \frac{\partial \phi_{i}(\rho_{i})}{\partial \rho_{i}} \frac{\partial \phi_{j}(\rho_{j})}{\partial \rho_{j}} \right] r_{ij}^{a} - r_{ij}^{a}. \]  

(2)

Here \( \sigma_{i}^{a\beta} \) is the stress tensor component at point \( r_{i} \), where the atom \( i \) is located, \( G_{ij}^{a} \) is the \( \alpha \) component of the force acting between atoms \( i \) and \( j \), \( \Omega \) is the atomic volume of atom \( i \), \( r_{ij}^{\beta} \) is the \( \beta \) component of the distance between atoms \( i \) and \( j \), \( M_{i} \) is the mass of atom \( i \), \( V_{i}^{a} \) is the \( \alpha \) component of the velocity of atom \( i \). The mean hydrostatic microstress in the film depth was determined by averaging over the atomic layer:

\[ \sigma_{g}(z) = \frac{1}{3N_{z}} \sum_{k}^{N_{z}} \left( \sigma_{k}^{xx} + \sigma_{k}^{yy} + \sigma_{k}^{zz} \right), \]  

(3)

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.

3. Results and discussion

To clarify the role of ion irradiation in the formation of a film structure, first the TPVD deposition of a niobium film was simulated. The methods of computer simulations have already been used for investigation of the processes taking place in forming such niobium films by TPVD [29]. It has been shown that the film structure in the process of low-temperature deposition is determined by the morphological instability of a smooth form of the film surface during deposition. On the surface of a growing film, a relief arises consisting of ripples mostly oriented along the crystallographic \(<100>\) direction. The development of this relief leads to 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 \( C(r,t) \):

\[ C(r,t) = \langle \left( z(x,t) - z(t) \right) \rangle \left( z(x+\mathbf{r},t) - z(t) \right) \rangle, \]  

(4)

where the vector \( x \) determines the coordinates of atoms, and the brackets refer to the averaging over the surface atoms. In figure 1, the hollow markers represent the plots of functions \( C_{y} = C(y,t) \) along the vector parallel to the computational cell edge \( Y \) of the film obtained by TPVD. 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 \( C(r,t) \) [30]. As it follows from the results of previous investigations, during the low-temperature deposition of niobium films along the \(<110>\) direction, the formation of a correlated structure with the same value of \( \lambda \approx 2.3 \text{nm} \) is observed [31]. In the same figure 1, the solid markers show the change in the height-height correlation function during the further IPVD Nb deposition onto the film. The presence of 20 eV ions in the flow being deposited does not provoke a change in the \( \lambda \) value. An ion energy increase up to 100 eV leads to a change in the correlation radius to \( \lambda \approx 3.0 \text{nm} \). Thus, by varying the value of the incident ion energy, one can influence the characteristics of a nanostructure formed on the film surface. The effect under consideration is similar to that observed previously in the case of changing the correlation length by increasing the substrate temperature [32]. However, unlike the case of increasing the temperature, the film surface roughness decreases with time during the process of IPVD deposition.
Often the dynamics of the surface morphology changes is described, along with the correlation length $\lambda (t)$, by the change in time of the roughness value ($W$). The film surface roughness is characterized by the mean-square deviation of the $Z$ coordinate of the surface atoms from the mean value of $W$:

$$W^2(t) = C(0,t) = \sum_i \left( Z_i^t - \langle Z_i^t \rangle \right)^2,$$

where the summation is performed over all atoms on the external surface. To simulate the roughness determination, we performed a selection among all atoms observed using a tunnel scanning microscope. Upon calculating the roughness, only those atoms were selected which did not overlap by themselves the underlying atoms [31]. Such a procedure is similar to roughness determination by a cylindrical probe whose transverse dimension is equal to the atomic size. Below, the roughness obtained by the above-described method will be denoted as $W_u$. The change of $W_u^2$ with the time of deposition by TPVD (open markers) and IPVD (solid markers) at the energy of 20 and 100 eV is shown in figure 2. As is seen from the figure, in the case of TPVD deposition during the initial period, the $W_u^2$ value increases linearly and then fluctuates above the stationary value reached. IPVD deposition leads to the surface roughness decreasing with time. However, after the period of time $8t_{mono}$ at the energy of 20 eV, the roughness takes a new stationary value, $W_u^2 \approx 0.2nm^2$. As the ion energy increases up to 100 eV, the stationary value of $W_u^2$ decreases down to $\approx 0.1nm^2$ approximately after $14t_{mono}$. In experiments, besides by using the $W_u$ value, the roughness is frequently characterized by the roughness coefficient: the ratio of the real surface area to the geometrical one, or the ratio of the number of surface atoms on the real surface $S$ to that on the ideal smooth surface $S_0$:

$$\eta = S/S_0 = N^S/N^S_0.$$

This has to do with the fact that the metal surface area can be properly measured by using the gas adsorption method. In figure 3, the open markers present the changes in the number of atoms on the external surface $N^S$ with time. It is seen that the change of the number of surface atoms is also well described by a linear function. At the same time, IPVD deposition leads to a decrease of the $\eta$ value. Then, similarly to $W_u^2$, the number of surface atoms reaches a new steady-state value corresponding to the given ion energy.
Consequently, the ions impede the formation of a correlated structure on the film surface in the process of deposition by blocking the mechanism of “microcracking” and formation of nanoblocks. It is known that one of the causes of instability arising during the film deposition is the presence of Ehrlich-Schwoebel barriers [32]. This is the energy necessary for an atom to perform a thermally activated jump from the upper atomic terrace onto the lower one. Irradiation of the film deposited with low-energy ions leads to an increase of the frequency of atomic transitions between the terraces in the nonequilibrium stage of atom-atom collision cascade. The calculation results show [33] that the probability of atomic displacements between the terraces increases several times. The analysis of the data obtained shows that during TPVD approximately every fifth atom undergoes the transition while forming one monolayer. Under IPVD, the number of atomic transitions is increasing. Every impinging ion with energy $E = 100 \text{ eV}$ provokes, in average, about 10 additional atomic transitions between the atomic layers. So, one of the mechanisms of low-energy irradiation effect on the film structure is the increase of the frequency of atomic transitions between the terraces; as a consequence, the appearance of the correlated structure “microcracking” is blocked.

It was shown in [29] that the porosity of the films obtained by low-temperature TPVD is due to microvoids being formed below the “microcracks” on the surface of a growing film. As a result, the film density decreases, as compared to the density of the solid material. The change of the density with the thickness of the TPVD deposited film is shown in figure 4 by the hollow markers. Subsequently, the atomic-ion flux was deposited upon this film. For comparison, the circular hollow markers show the values of the density of the thermally deposited film during further thermal deposition without ion assistance. As shown in figure 4, the density of the TPVD deposited film is 8% less than the density of solid niobium. The density of the film formed by the IPVD is marked on the plot by solid circles. Figure 4 also shows that the density of newly deposited layers is increased. At ion energy of 20 eV, the film density assumes the steady state value $\theta / \theta_0 \approx 0.97$. Increasing the ion energy to 100 eV results in the film density reaching the value of a solid material.

It should be noted that in the process of IPVD deposition not only the density of the newly formed layer increases, but the density in the film thickness is changing too. It is seen that the density of the film appears to exceed the density of the solid material. This has to do with the emergence of self-interstitial atoms in the film. The interstitial atoms are forming when the falling ions transfer to the film atoms kinetic energy exceeding the threshold energy of the specific material.

As a result of this process, Frenkel interstitial-vacancy pairs are created. 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 [34] when the lattice atom is displaced from the node into the position

![Figure 3](image3.png)

**Figure 3.** Time variation of $\eta = S / S_0 = N^S / N^S_0$ for TPVD and additional IPVD deposited films.

![Figure 4](image4.png)

**Figure 4.** Variation of the degree of atomic layer occupation $\theta$ in the depth of the film.
symmetric with the interstitial atom. Such an interstitial configuration is very movable, migrates easily even at low temperatures and can form complexes of defects. In the process of growth such complexes of defects can form interstitial dislocation loops. Figure 5 presents the cross-section of the film obtained by IPVD at ion energy of 100 eV in the ZY plane. The dark color marks the atoms forming one of the dislocation loops. At the same time, the film deposition at energies lower than the threshold energy does not lead to the formation of dislocation loops. Thus, the ion interaction can lead to formation of structural defects uncharacteristic for TPVD deposition of films. Experiments on IPVD film deposition have shown that, while in the case of thermal deposition preferably voids are formed, in the case of atomic-ion deposition a dislocation structure develops [7,11]. Figure 6 presents electron-microscopy images of niobium films deposited by IPVD with ion energies from 7 to 100 eV [7]. The photographs show that the ion energy increase leads to the formation of dislocation loops in the film volume. The present study provides a strong indication that the dislocation structure observed in experiments on the IPVD is formed as a consequence of the development of interstitial loops arising under ion irradiation.

Figure 6. Microphotographs of IPVD deposited Nb films: a - 7eV, b - 100 eV.
The change of the film microstructure leads to changes in the internal microstresses. A plot of the hydrostatic microstress distribution in the thickness of the film deposited is given in figure 7. The hollow markers present the microstresses in the TPVD film. The presence is seen of compressive microstresses in the film. These microstresses arise as a result of vacancies formation. The mechanism of vacancy formation was studied in [35]. The solid markers in the same plot denote the internal microstresses in the niobium film after additional IPVD. It is seen that IPVD with ion energy of 20 eV has changed only slightly the behavior of microstresses in the film, and the use of ions with energy of 100 eV has changed not only the value but the sign of microstresses, too. The compressive microstresses become tensile. At the same time, they remained compressive at the boundary of the growing film. The presence of compressive microstresses at the front of the growing film is brought about by the partial filling of the first several atomic layers in the process of thermal deposition and atomic-ion deposition. The conclusion can be drawn that the change of internal microstresses in the films irradiated is due to the formation of interstitials and their complexes, which are developing and transforming into dislocations thereby changing the films’ microstructure.

4. Conclusion
The effect of low-temperature irradiation with self-atoms on the nanostructure of niobium films is studied. It is shown that the ion action influences the relief of a growing film. The effect of ion densification is studied. It is established that at ion energy of 100 eV and degree of ionization of 0.1 the density of the films formed is equal to the density of the bulk material. It is demonstrated that the ion densification is provided mainly by blocking the “microcrack” formation at the surface of the growing film. The influence of ion action on the character of microstresses in the film deposited is studied. Changing of the sign of stresses in the film bulk from compressive to tensile is related to the formation of interstitial atom clusters. These clusters can be 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 the films formed, their microstructure and the arising microstresses.

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