The effect of low-energy ion bombardment on residual stress in thin metal films due to the generation of surface defects and their migration to the grain boundary

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Abstract. A kinetic model that describes the evolution of residual stress in thin polycrystalline films during bombardment by ions with energies below the sputtering threshold is presented. The mechanisms responsible for the change in stress are the generation of point defects on the surface and their redistribution over the film thickness along grain boundaries. The presented model was used to explain the experimental data on the change in stress in thin Cr films after treatment in Ar plasma of low-pressure RF induction discharge with ion energy of 15-30 eV.

1. Introduction
The ability to influence on mechanical stress in thin metal films is an actual task that has many applications in MEMS and other areas related to coatings. In our previous works [1, 2] it was shown that ion-plasma treatment (IPT) with ion energy below the sputtering threshold can have a significant effect on residual stress in Cr films. Depending on the ion energy IPT can both reduce average stress $\sigma_0$ and stress gradient $\sigma_1$ and increase them (figure 1) that allows to use IPT as a non-destructive tool for stress regulation. However, this requires an understanding of the mechanisms that occur during IPT and ability to predict their behavior depending on treatment conditions and initial stress state.

Figure 1 (a, b, c). Dependences $\sigma_0(t)$ (a) and $\sigma_1(t)$ (b) obtained by x-ray diffractometry and by measuring the bending of the cantilevers respectively at $\varepsilon_i = 15$ eV and 30 eV. Dependences $\Delta \sigma_1(t)$ (c) in films with different initial stress gradients at $\varepsilon_i = 25$ eV. The straight dotted lines mean the value in the original film. Curved lines are theoretical.
In [3,4], the effect of bombardment by inert gas ions with an energy of ~ 1 keV on residual stress in Cu and Pt is explained by the generation of point defects in a thin surface layer and their subsequent movement deep into the film. The change in stress is associated with the concentration profiles of interstitial atoms, vacancies and implanted ions. In [5], the decrease in tensile stress in Cu films after bombardment with He ions is explained by the incorporation of atoms from the surface into the grain boundary. The authors took this mechanism from [6], which describes the evolution of residual stress during the deposition of polycrystalline films. Unfortunately, both of these models are not able to explain the results presented in figure 1. In the framework of these models, the result of treatment with ion energy of 15 eV and 30 eV will differ only in the magnitude of the change in $\sigma_0$ and $\sigma_1$. However, we can see that the result of their influence is radically qualitatively different.

The aim of this work was to develop a theoretical model suitable for describing the effect of bombardment by ions with energies below the sputtering threshold on stress in thin metal films.

Figure 2. The scheme of the junction of the grains surfaces and the grain boundary; the transition to a one-dimensional coordinate system.

2. Theoretical model

Ion bombardment during IPT leads to the formation of a pair of point defects (surface atoms and vacancies) on the surface of grains (figure 2). Then due to surface diffusion they move to the junction of two grains (point O) and penetrate into the grain boundary (GB) where due to grain-boundary diffusion and drift due to the stress gradient they are distributed over the film thickness. As can be seen, in contrast to [3,4], we take into account the polycrystalline structure of the film. And unlike the work [5], we take into account that during the bombardment not only atoms move to the GB but also vacancies and before that they must pass along the grain surface. Since the coefficient of bulk diffusion is approximately $10^6$ times smaller than the coefficients of surface and grain boundary diffusion [7], the movement of defects inside the grain can be neglected. The flows of defects along the surface and GB, respectively [8]:

$$j^s_{a,v} = -D^s_{a,v} \frac{\partial C^s_{a,v}}{\partial x}$$

$$j^{gb}_{a,v} = -D^{gb}_{a,v} \frac{\partial C^{gb}_{a,v}}{\partial x} + D^{gb}_{a,v} \frac{\partial \sigma}{kT} \frac{\partial \sigma}{\partial x}$$

(1)

(2)
where $D_{ab}$—diffusion coefficients, $\Omega$ — atomic volume. The distribution of stress in the film during IPT $\sigma(x,t)$ is related with the concentrations of defects $C_{av}^{gb}$ and $C_{vs}^{gb}$ penetrating in GB:

$$
\sigma(x,t) = \sigma_0^{in} + \sigma_1^{in} \left(1 - \frac{x}{h/2}\right) - \frac{1}{2} \frac{E}{1-\nu} \frac{\Omega}{L} (C_{av}^{gb}(x,t) - C_{vs}^{gb}(x,t))
$$

(3)

where $\sigma_0^{in}$ — initial average stress in the film, $\sigma_1^{in}$ — initial stress gradient. To obtain $\sigma(x,t)$ we must solve the kinetic equations for atoms and vacancies on the surface and in GB [9]:

$$
\frac{\partial C}{\partial t} = K - \frac{\partial j_i}{\partial x} - 4\pi\lambda(D + D')CC' - k_r^2DC
$$

(4)

where $K$ — generation coefficient, $\lambda$ — recombination length, $k_r$ — sink strength, an apostrophe above the letter indicates the opposite defect. Thus we have obtained a system of four differential equations (5) and (6). The solution of this system was carried out by the finite difference method. As a result, the system of partial differential equations was replaced by a system of nonlinear algebraic equations, which was solved numerically by the Newton method. $D_{av}$ and $k_r$ were adjustable parameters.

$$
\begin{aligned}
\frac{\partial C_i}{\partial t} &= K + D_i \frac{\partial^2 C_i}{\partial x^2} - 4\pi\lambda(D_i + D_i')C_i'C_i' - k_r^2D_i'C_i' \\
\frac{\partial C_i'}{\partial t} &= K + D_i' \frac{\partial^2 C_i'}{\partial x^2} - 4\pi\lambda(D_i + D_i')C_i'C_i' - k_r^2D_i'C_i'
\end{aligned}
$$

(5)

$$
\begin{aligned}
\frac{\partial C_{av}^{gb}}{\partial t} &= D_{av} \frac{\partial^2 C_{av}^{gb}}{\partial x^2} - D_{av} \frac{\partial \Omega}{kT} \left(\frac{\partial C_{av}^{gb}}{\partial x} \frac{\partial \sigma}{\partial x} + C_{av}^{gb} \frac{\partial^2 \sigma}{\partial x^2}\right) - 4\pi\lambda(D_{av} + D_{av}')C_{av}^{gb}C_{av}'^{gb} \\
\frac{\partial C_{vs}^{gb}}{\partial t} &= D_{vs} \frac{\partial^2 C_{vs}^{gb}}{\partial x^2} + D_{vs} \frac{\partial \Omega}{kT} \left(\frac{\partial C_{vs}^{gb}}{\partial x} \frac{\partial \sigma}{\partial x} + C_{vs}^{gb} \frac{\partial^2 \sigma}{\partial x^2}\right) - 4\pi\lambda(D_{vs} + D_{vs}')C_{vs}^{gb}C_{vs}'^{gb}
\end{aligned}
$$

(6)

3. Results and discussion

The adjustable parameters were selected by the least squares method according to the experimental data presented in [2]. Figure 1a,b dots show the change in average stress $\sigma_0$ and stress gradient $\sigma_1$ on the treatment time with ion energies 15 eV and 30 eV obtained experimentally. Also in figure 1a,b, the dashed lines show the curves obtained as a result of numerical calculations. As a result of the selection of parameters, those dependences of the distribution of defect concentration along the grain boundary on time $C_{av}^{gb}(x,t)$ and $C_{vs}^{gb}(x,t)$ were found at which calculated curves were as close as possible to the experimental points.

Figure 3 shows the change in the distribution of defects along the grain boundary with an increase in the treatment time with ion energy $\epsilon_0 = 15$ eV. As can be seen, the number of atoms penetrating into the GB substantially exceeds the number of vacancies due to the fact that the diffusion coefficient of the atoms is more than two orders of magnitude higher. With increasing IPT time the predominance of the contribution of atoms to average stress increases (equation (3)) as a result of which compressive stress increases in the film (figure 1a). At the same time, the stress gradient increases slightly due to the fact that the surface region of the film still contains a sufficiently large number of vacancies whose contribution outweighs the bending moment created by the atoms (figure 1b).
Figure 3 (a, b, c, d). The distribution of defects in GB at $\varepsilon_i = 15$ eV. (a) 15 min, (b) 30 min, (c) 45 min, (d) 60 min. $D_i = 1,3\cdot10^{-16}$ m$^2$s$^{-1}$, $D_v = 0,97\cdot10^{-18}$ m$^2$s$^{-1}$, $k_s = 1,4\cdot10^8$ m$^{-1}$.

Figure 4 (a, b, c, d). The distribution of defects in GB at $\varepsilon_i = 30$ eV. (a) 15 min, (b) 30 min, (c) 45 min, (d) 60 min. $D_i = 2,2\cdot10^{-16}$ m$^2$s$^{-1}$, $D_v = 3,7\cdot10^{-17}$ m$^2$s$^{-1}$, $k_s = 1,3\cdot10^8$ m$^{-1}$.
Figure 4 shows the change in the defect distribution along the grain boundary with increasing IPT time with ion energy $\varepsilon_i = 30$ eV. At this ion energy, the diffusion coefficient of atoms is still greater than for vacancies but less than an order of magnitude. As a result, significantly more vacancies penetrate in the grain boundary. The initial stress gradient, or rather its contribution to the drift component of the flow, also contributes to this. As a result, as the IPT time increases, the contribution of vacancies to average stresses gradually increases and at $t = 60$ min exceeds the contribution of atoms. Therefore, at this point, the compressive stress is less than in the original film (figure 4а). At the same time, the contribution of vacancies to the stress gradient exceeds the contribution of atoms during the entire treatment time, as a result of which its significant growth occurs (figure 4b).

Similar calculations were performed for study of the effect of the initial stress gradient on the IPT result. In figure 4c, the dots show the change in the stress gradient $\sigma_1$ from the treatment time with ion energy $\varepsilon_i = 30$ eV, obtained experimentally, the dashed lines show the dependences obtained as a result of calculations. Figure 5 shows the distribution of defects along the grain boundary after 60 min of IPT of films with different initial stress gradients: 385 MPa, 900 MPa and 1615 MPa. It can be seen that, as in the IPO results considered earlier with $\varepsilon_i = 30$ eV, the number of vacancies penetrating in the grain boundary exceeds the number of atoms. Moreover, the larger the initial gradient, the more vacancies. As already mentioned, this is due to the presence of drift under the action of the stress gradient. Since in our films the near-surface region has lower compressive stress than the region near the substrate, vacancies are drawn deep into the film, while the penetration of atoms is, on the contrary, difficult. The larger the initial stress gradient, the greater the contribution of drift to the final result.

From the distributions of defects shown in figures 3, 4 and 5, it can be seen that the depth of their introduction into the GB is comparable with the film thickness, which leads to rather large changes in the average stress and stress gradient. Similar estimates of the depth of influence were shown by us earlier in the experimental work [2].
The values obtained as a result of the calculation show that the diffusion coefficients of atoms and vacancies increase with increasing ion energy (figure 6). Moreover, the higher the ion energy, the closer their values are to each other. This is probably caused by radiation-stimulated diffusion. Under radiation exposure, the diffusing particles acquire some energy $Q(\varepsilon_i)$, which is greater than $kT$ and increases with increasing ion energy. As a result, with an increase in the ion energy, the diffusion coefficient also increases.

$$D = D_0 \exp \left( - \frac{\varepsilon_a}{Q(\varepsilon_i)} \right)$$  \hspace{1cm} (7)

Since it is characteristic of metals that the activation energy $\varepsilon_a$ of atoms is several times greater than that of vacancies, the diffusion coefficient of the former is greater than that of the latter. However, with the growth of the denominator under the exponent, their values will become closer to each other, which we see in figure 6.

4. Conclusions
The model presented in the work agrees quite well with the experimental results. Unlike the models available in the literature, it takes into account the polycrystalline structure of thin films, as well as the influence of the initial stress gradient on the treatment result. However, its further use is still hindered by the lack of information in the literature (both experimental and MD modeling) about the values of the coefficients of radiation-stimulated diffusion of atoms and vacancies on the film surface for the studied ion energies, which is why these values have to be adopted as adjustable parameters.

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References
[1] Babushkin A, Uvarov I, Amirov I 2018 Technical Physics 63 1800
[2] Babushkin A, Selyukov R, Amirov I 2019 Proceedings of the SPIE 11022 1102223
[3] Chan WL, Chason E 2008 J. Vac. Sci. Technol. A 26 44
[4] Chan WL, Zhao K, Vo N, Ashkenazy Y, Cahill DG, Averback RS 2008 Phys. Rev. B 77 205405
[5] Fu EG, Wang YQ, Nastasi M 2012 J. Phys. D: Appl. Phys 45 495303
[6] Chason E, Sheldon B W and Freund L B 2002 Phys. Rev. Lett. 88 156103
[7] Johnson DL 1969 Journal of Applied Physics 40 192.
[8] Mullins WW 1995 Metallurgical and Materials Transactions 26 1917
[9] Was GS 2007 Fundamentals of radiation materials science (Heidelberg: Springer-Verlag. Berlin) p 1