Optimization of Implantation in the Surface Layers of Polycrystalline Materials by Ion Mixing Method under Irradiation by Ar^+ Ion Beam with a Wide Energy Spectrum

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Abstract – Various factors influencing the efficiency of ion-mixing are considered. It is shown that the energy transfer from ions and PKA of films to subsequent displacement cascades is responsible for the penetration of multi-layer film's atoms into the polycrystalline substrate. At that, the deeper penetration of implanting atoms into the material under investigation is determined by the density of defects, the radiation-stimulated migration of implanted atoms, and their physicochemical interaction with atoms of the matrix which can be described within the bounds of an isotropic-mixing model.

1. Introduction

As previously shown in [1,2], the radiation-stimulated processes allowing the penetration of implanting atoms into the substrate at a depth greater than the projected range Rp occur together with merely kinematic interaction between the ion, the implanting atoms of films and the substrate material under irradiation of "film-substrate" systems by a polyenergetic ion beam with a wide energy distribution.

The kinematic interaction at the energy range up to 100 keV is determined by the value of energy transfer $<E'>_{if}$ between Ar^+ ions, primarily knocked out atoms (PKA) of the films, and the substrate material $<E'>_{fs}$. These values can be characterized using a reduced mass [3]:

$$\mu_{if} = 2 \cdot \frac{M_{Ar} \cdot M_f}{(M_{Ar} + M_f)^2}, \quad \mu_{if} = 2 \cdot \frac{M_{Ar} \cdot M_f}{(M_{Ar} + M_f)^2}, \qquad (1)$$

where μ_{if}, μ_{fs} are the reduced masses of "ion-film" and "film-substrate" systems, respectively; M_{Ar} and M_f, the atomic mass of ions of Ar and the film material; M_s, the atomic mass of the substrate material; $<E'>$, the mean transferred energy, $<E'>=\mu E_i$; E_i, the energy of a bombarding particle.

The efficacy of a deeper implantation of atoms could be estimated as a function depending on the intensity of an ion beam, its energy and irradiation time [4]. In this connection it is of importance to determine the optimal irradiation conditions which provide a deeper penetration of implanting atoms under their maximum possible concentration, especially in case of alloying of polycrystalline substrates.

2. Experimental procedure

Polycrystalline substrates with various crystalline structures and atomic masses (^{9}Be(HCP), ^{27}Al(FCC), ^{56}Fe(BCC), ^{64}Cu(FCC), ^{91}Zr(HCP), ^{96}Mo(BCC)) were selected for investigation.

Mono-, double-, and three-layer films of Be, Al, Ti, Fe, Cu, Ni, and Mo at their different combination were deposited by thermal evaporation in vacuum ($p \leq 3 \cdot 10^{-4}$ Pa). The thickness x_t of a single layer of the films changed in the 40...50 nm range. Such the thickness was determined by the condition that the maximum penetration efficiency of primarily knocked out atoms into the substrate should be attained [3].

The irradiation of "multi-layer film -polycrystalline substrate" systems in the $D=1 \cdot 10^{17}-5 \cdot 10^{18}$ cm^{-2} fluence range was carried out on the installation "VOKAL" forming a polyenergetic Ar^+ ion beam with a Gaussian-type energy distribution. The energy of ions changed in the 3...15 keV range, their mean energy in a beam was 10 keV, the beam current density j was from 15 to 25 A/cm^2, and the residual pressure in the area of samples $p \leq 1 \cdot 10^{-5}$ Pa) [5].

The distribution profile of implanted atoms in depth was determined by the secondary ion (Ar^+ and O^+) mass spectrometry (SIMS) with an ion energy E=4.6 keV, using the PHI-600 device. The depth resolution error of the SIMS method was less than ±1 nm. The relative concentration error of the SIMS method was not more than $\pm 10^{-2}$ at %.

3. Experimental results and discussion

The experimental data of atom implantation from mono-, double-, and three-layer films into the polycrystalline substrates of Be, Fe, Cu, Mo, and Zr under irradiation by a polyenergetic Ar^+ ion beam show that it is expedient to carry out alloying of the near-surface layer at a relatively low temperature, $T<100-250$ °C. On the example of a "three-layer film – polycrystalline Zr-substrate" (Fig. 1), the con-

tent $C(x)$ of Al, Fe, and Mo atoms of multi-layer films in Zr is shown to change from the irradiation dose. The duration of irradiation is figured at relative units x/x_t; x is the thickness of a sputtered layer, x_t, the thickness of a single deposited layer of a multi-layer film, $x_t \approx 40–50$ nm.

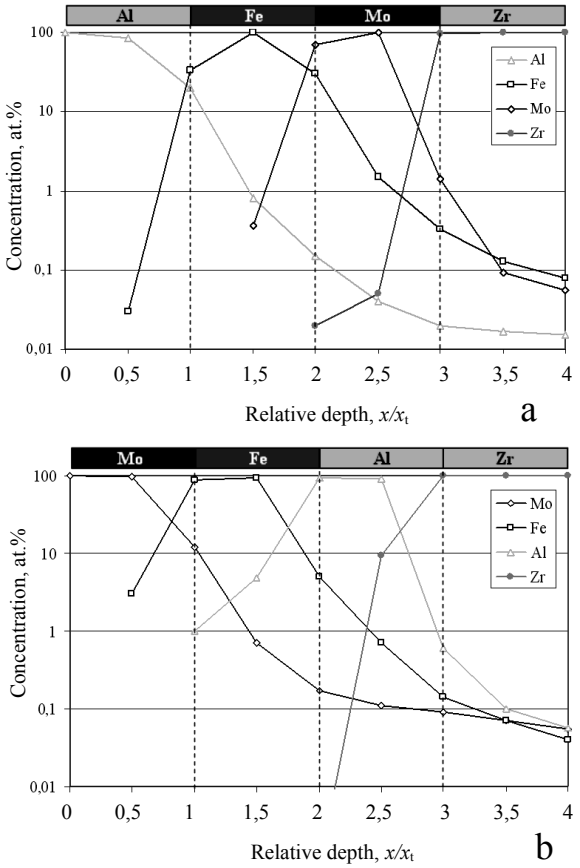

Fig. 1. Change in the composition of three-layer films under irradiation by an Ar^+ ion beam: a, the "Al-Fe-Mo on Zr" system; b, the "Mo-Fe-Al on Zr" system

It is seen from the $C(x)$-dependence that the atoms of films penetrate into both the underlying and overlying layers during the irradiation. And the atoms from a polycrystalline substrate are detected in the first film layer adjacent to that substrate.

After sputtering the third layer ($3x_t$), atoms of Al, Fe, and Mo with concentration up to 0.7, 0.5, and 2.0 ат.%, respectively, are present in the matrix. More optimal mutual arrangement of the films makes it possible to significantly increase the concentration of implanted atoms in the matrix, for example, under irradiation of the "MoFeAl-Zr" system (Fig. 1, *b*) the content of Mo-atoms in the external layer of the matrix is higher than that of Al under irradiation of the "AlFeMo-Zr" system (Fig. 1, *a*). Therefore the maximum quantity of implanted atoms from a film into the near-surface layer of the substrate can be observed when the external layer has a larger atomic mass than that of Ar^+ ions; the internal layer adjacent to the substrate surface has the least atomic mass.

One of the main parameters influencing the quantity of implanted PKA from a film under irradiation by an ion beam is the sputtering rate of a film $d_x/d_t = S_p * J * N_o$, where S_p is the sputtering coefficient; J, the current density of an ion beam; N_o, the atomic density of a film [6, 7]. Thus, it's expedient to decrease the S_p-value due to an optimal selection of the energy, the atomic mass of ions in a beam, as well as the arrangement of layers in the multi-layer film.

Investigation of concentration distributions $C(x)$ of implanted atoms from three-layer films in different polycrystalline substrates (Be, Cu, Zr) revealed that the ion mixing under irradiation of "film-substrate" systems by a polyenergetic Ar^+ ion beam leads to penetration of implanted atoms at depth 5–20 times greater than the corresponding projective range of primarily knocked out atoms of a film [8, 9, 10]. The total quantity of atoms implanted into the matrix reaches 1–10 %. The distribution maximum X_c is located at the depth that is several times greater than the projective range R_p typical for the knocked out atoms (PKA).

As an example, the measured distribution profiles of Al, Ti, and Mo $C(x)$ in Be and their distribution only at the expense of radiation-stimulated migration are presented in Fig. 2, *a*.

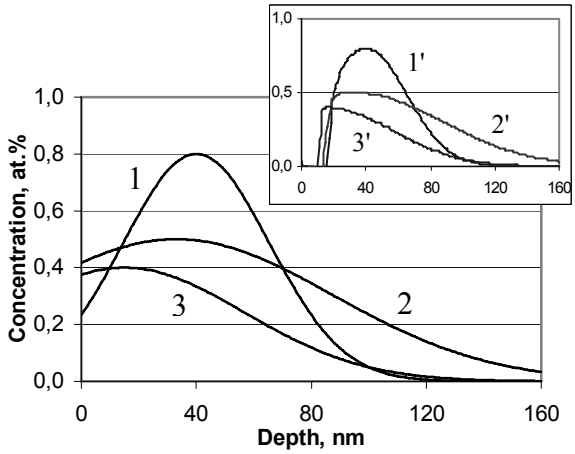

Fig. 2. Distribution of implanted atoms of a three-layer film at depth (for Be-substrate). 1, 2, 3, the concentration dependence $C(x)$ for Al, Ti, and Mo, respectively. 1', 2', 3', the contribution of radiation-stimulated processes

Table 1 shows the typical values for the location depth of the distribution maximum X_c and the maximum penetration depth X_m of implanted atoms from multi-layer films into polycrystalline substrates of Be, Cu, and Zr.

According to the data presented, the penetration depth X_m significantly exceeds the projective range R_p of PKA in corresponding substrates. The X_m/R_p ratio reaches its maximum value under alloying of Zr-samples ($X_m/R_p \approx 15–50$).

The earlier experiments showed that the model of isotropic mixing suggested by P. Sigmund and A. Gras-Marti [4, 11, 12] can be used as the basic

model describing deep penetration of atoms from a film into a polycrystalline substrate under irradiation by ion beams with a wide energetic spectrum. The comparison of experimental and calculated data made it possible to obtain an analytical expression for a large number of "film-substrate" systems, including such parameters as the ratio of atomic masses of ions in a beam, that of the atoms of films and the substrate, the energy release F_q in the implanted layer and the values of electronegativity $\Delta\chi$ [13].

$$\frac{X_m}{R_p} = C_o \frac{M_i M_f}{(M_i + M_f)^2} \times \left[0,202 \frac{F_q(x) D}{N_o E_d (1 - \mu_{if})} \right]^{0,3} \Phi(|\Delta\chi|^n),$$

where:

$\Phi(|\Delta\chi|^n) = \sum_{k=0}^{k=2} A_k \chi_k^{\,n_k}$; $F_q(x)$, the energy release in a substrate at the depth x, eV/nm; D, the radiation dose, ion/cm^2; R_p, the projective range of PKA from a film, nm; N_o, the density of a substrate material, at/cm^3; E_d, the displacement energy of the atoms of a substrate, eV; C_o, the sensitivity threshold of measuring the concentration of atoms, C_o=0,001–0,002; A_k, coefficients depending on the material of a film; χ_0, χ_1, the electronegativity of the material of a substrate and a multi-layer film, respectively.

Table 1. Penetration parameters of PKA from films into substrates under Ar^+ irradiation with a mean energy $<E>$=10 keV

Film's atom	Substrate material	R_p, nm	X_c, nm	X_m, nm	X_m/R_p
Al	Be	20	40	100	5
Ti		17	33	150	9
Mo		11	15	100	9
Al	Cu	6	11	45	8
Fe		5	20	75	15
Mo		4	7	50	13
Al	Zr	7	50	100	15
Fe		6	150	300	50
Mo		3	300	500	(170)

R_p, the projective range of PKA from films;
X_c, the location depth of a distribution maximum $C(x)$;
X_m– maximum depth of implanted atom penetration ($C(X_m)$≥0,1 ат.%).

It is necessary to point out that in contrast to work [12] in which it was proposed to use the reduced mass if as a parameter of energy exchange under elastic interaction, in the given work it was proposed to use its difference $(1-\mu_{if})$ that takes into account the energy transferred to the atoms of a film in subsequent collisions.

According to [13, 14], the conditions for radiation-enhanced migration of implanted atoms can be reached in the event if the atoms are in the matrix in the form of a solid solution. The electronegativity and the radius ratio of these atoms are used as criteria of the formation of a solid solution between the implanted atoms and the matrix. For example, the diagrams of Darken-Gurry-Sood (DGS-diagram) allow making a conclusion of the possibility to form solid solutions under alloying by ion-mixing if the ratio of atom radiuses r_f/r_s is in the 0.85–1.40 range (r_f is the radius of film atoms, r_s, the substrate atom radius) and the difference of their electronegativity $\Delta\chi$ is less than or equal to 0.5 (Polling units) – $\Delta\chi \leq 0,5$ Polling units [15].

The atom radiuses ratio of implanting elements (Al, Ti, Fe, Mo) and Be-, Cu-, and Zr-matrices, as well as the corresponding values of their electronegativity are presented in Table 2. The conditions to form solid solutions (the DGS-criteria) are true for Al and Ti in a Be-matrix, Al, Fe, and Mo in a Cu-matrix, and Al and Fe in a Zr-matrix. However, a deep penetration of implanted atoms into matrices under ion mixing is observed for all the cited atoms of a three-layer film (Al, Fe(Ti), Mo), which seems to be connected to the features of implanted atom redistribution during the alloying and in the process of a change in the parameters of a matrix modified layer [16,17].

Table 2. Ratio between the radii of implanted atoms and matrix atoms, and electronegativity of elements

Film's atom	Substrate material	r_f/r_s	χ_f	χ_s	$\lvert\Delta\chi\rvert$
Al	Be	1,30	1,61	1,57	0,04
Ti		1,43	1,54	1,57	0,03
Mo		1,44	2,16	1,57	0,59
Al	Cu	1,16	1,61	1,9	0,29
Fe		1,10	1,83	1,9	0,07
Mo		1,28	2,16	1,9	0,26
Al	Zr	0,84	1,61	1,33	0,28
Fe		0,80	1,83	1,33	0,50
Mo		0,93	2,16	1,33	0,83

The efficiency of ion-mixing can be estimated by the following formula [18]: $B=<X_m>2/D^*F_q$, where $<X_m>$ is the maximum depth of atom penetration; D, the dose of irradiation; F_q, the energy release in the material of a substrate. It is evident from the equation that increasing the efficiency of ion-mixing consists in increasing the penetration depth of alloying atoms with decreasing the radiation dose D and the energy release in a substrate F_q (i.e. decreasing the thickness of a sputtered layer and the density of defects).

Table 3. The energy release in a substrate, the irradiation dose (Ar^+, $<E>$=5keV, $D=4\cdot10^{17}$ cm^{-2}), and the efficiency of ion-mixing B

Film's atom	Substrate material	X_c, nm	D^*F_q, eV/nm^3	B^*10^{-3}, nm^5/eV
Al	Be	62	1.9	1.9
Ti		92	2.4	3.6
Mo		62	3.1	1.2
Al	Cu	28	6.0	0.1
Fe		46	7.9	0.3
Mo		31	8.4	0.1
Al	Zr	62	5.6	0.7
Fe		185	6.6	5.2
Mo		308	11.2	8.4

The calculated B-values for mean energies $<E>$=5, 10 and 20 keV of an ion beam are presented in tables 3–5. As the tables show for the energy range involved, the B-parameter and the maximum pen-

etration depth of atoms, except for Fe and Mo atoms in Zr, increase with the energy of irradiation and decrease with the energy release F_q in the substrate. Fe and Mo atoms in Zr have very large values of X_m and B at high values of F_q, which is partly connected to a high diffusion mobility of these atoms in Zr [16].

Table 4. The energy release in a substrate, the irradiation dose (Ar^+, $<E>$=10 keV, D=2·10^{17} cm^{-2}), and the efficiency of ion-mixing B

Film's atom	Substrate material	X_m, nm	D^*F_q, eV/nm^3	B^*10^{-3}, nm^5/eV
Al	Be	100	1.0	10.3
Ti		150	1.2	19.0
Mo		100	1.5	6.5
Al	Cu	45	3.2	0.6
Fe		75	3.9	1.4
Mo		50	4.2	0.6
Al	Zr	100	2.8	3.6
Fe		300	3.3	27.4
Mo		500	5.6	44.6

Table 5. The energy release in a substrate, the irradiation dose (Ar^+, $<E>$=20 keV, D=1·10^{17} cm^{-2}), and the efficiency of ion-mixing B

Film's atom	Substrate material	X_m, nm	D^*F_q, eV/nm^3	B^*10^{-3}, nm^5/eV
Al	Be	162	0.5	54.2
Ti		244	0.6	100.5
Mo		162	0.8	34.5
Al	Cu	73	1.6	3.3
Fe		122	2.0	7.5
Mo		81	2.1	3.1
Al	Zr	162	1.4	19.0
Fe		487	1.6	144.7
Mo		812	2.8	235.3

The B-parameter dependence on the energy release in a substrate is presented in Fig. 3 for three values of mean ion energies of 5, 10, and 20 keV which illustrate an increase of B with a decrease of F_q for each value $<E>$. At that, an increase of B with increase of $<E>$ from 5 up to 10 keV is lower than that from 10 up to 20 keV. However an increase of the energy of ions lead to an increase of the sputtering rate and consequently the total quantity of implanted atoms to matrix decreases. For example [19], at a simultaneous alloying of a zirconium substrate by Mo, Ti, and Al atoms by ion mixing, increasing the mean Ar^+ ion energy from 10 to 20 keV results in decreasing the concentration of Mo atoms in the near-surface layer from 0.07 to 0.03 at.%; Ti, from 0.10 to 0.05 at.%; Al, from 0.04 to 0.02 at.%.

The one of possible ways of term realization of optimal alloying by ion-mixing method may be simultaneous irradiation by ions of two masses (light and heavy). For example, the irradiation by two-component beam of He^++Ar^+ ions on the one hand reduces value F_q and on the other hand reduces sputtering rate, since effective mass of beam decreases as $m=(c_1m_1+c_2m_2)$, where c_1, m_1, c_2, m_2 – concentration and mass of He^++Ar^+ ions respectively. Besides, as experiments show, effect of "ion polishing" of surface is observed under irradiation by polyenergetic beam containing ions of two types – He^+ и Ar^+.

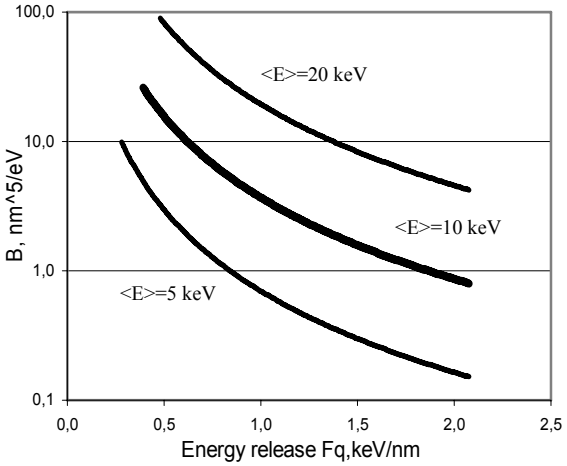

Fig. 3. Dependence of the efficiency parameter of ion mixing B on the energy release in a substrate at $<E>$=5, 10, 20 keV

As an example, the photo of the surface of technically pure zirconium Zr-100 sample after an irradiation by polyenergy beam of Ar^+ and He^+ (C_{Ar}:C_{He}=10:1) up to dose of 2,3·10^{18} ions/cm^2 is presented in Fig. 4, which shows that second phase and crystal boundaries are revealed during irradiation and the sputtering rate of separate crystals is practically identical (the destruction of surface is not observed).

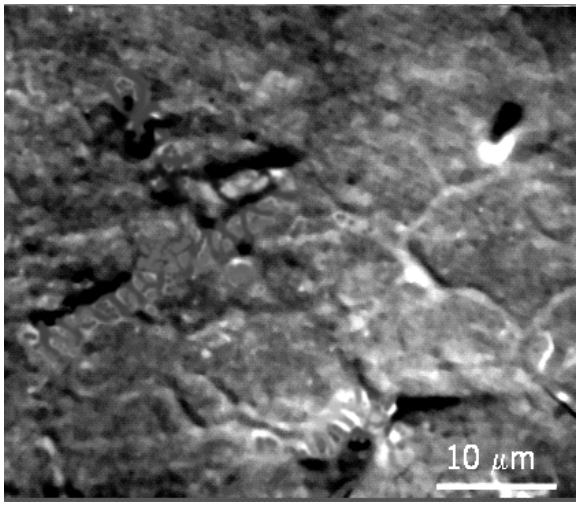

Fig. 4. The surface of technically pure zirconium Zr-100 sample after an irradiation by polyenergy beam of Ar^+ and He^+ (C_{Ar}:C_{He}=10:1) up to dose of 2,3·10^{18} ions/cm^2

4. Conclusion

Thus, the performed experiments on alloying the near-surface layers of Be, Cu, Zr with Al, Ti, Fe, and Mo atoms and an analysis of the results obtained make it possible to conclude that the basis for penetra-

tion of the atoms of multi-layer films into polycrystalline substrates under ion-mixing is the energy transfer from the ions of a polyenergetic beam and primarily knocked out atoms to subsequent displacement cascades.

The penetration of implanted atoms at large depths is determined by following:

- the release of energy in the modified layer of a substrate F_q;
- the radiation-enhanced migration of implanted atoms and their physicochemical interaction with the matrix atoms that can be described in the context of the isotropic-mixing model.

It is suggested to confirm the terms Darken-Gurry-Sood, i.e. the ratio of atom radii (film/substrate) and the values of electronegativity as the parameters characterizing the formation of solid solutions promoting the process of radiation-enhanced migration in polycrystalline substrates.

The one of possible ways of increasing of ion-mixing method efficacy and realization of term of optimal alloying may be simultaneous irradiation of "multi-layered film – polycrystalline substrate" systems by ions of several masses, for example, two-light and heavy (He^++Ar^+).

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