

The multicomponent doping of surface layers of materials under the influence of ion beams with a broad energy spectrum

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Abstract. The paper discusses the various factors that influence the efficiency of ion mixing. It was found that in the base of penetration of atoms multilayer films in polycrystalline substrate is the process of energy transfer from ions and primary knocked-on atom (PKA) of films to subsequent displacement cascade. At the same time the penetration of implanted atoms to great depths determined by the density of defects, radiation-stimulated migration of interstitial atoms and their physico-chemical interaction with the atoms of the matrix, which can be described by the model of an isotropic mixing. It is shown that doping atoms of the multilayer films, possibly the formation of gradient layers, which are determined by radiation traces in the substrate implanted atoms and their migration under irradiation by the ion beam with a broad energy spectrum.

1. Introduction

The use of new implant techniques to create a gradiently structurally-phase state of construction and functional materials with improved operating and electro-physical properties, is an important problem of materials science.

Previously shown [1,2] that irradiation of systems "film-substrate" by ion beam with a broad energy spectrum, along with purely kinematic interaction between the ion implanted atoms films and the substrate material contains radiation-induced processes to penetrate deep into the implanted atoms in the substrate the depth is much greater than the projected range R_p .

Kinematic interaction in the energy range up to 100 keV is determined by the energy exchange $\langle E \rangle_{if}$ between ions Ar^+ , primary knock-on atom (PKA) films and the substrate material $\langle E \rangle_{fs}$, which can be accounted for by the reduced mass μ [1,3]:

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

$$\mu_{fs} = 2 \cdot \frac{M_f \cdot M_s}{(M_f + M_s)^2}, \quad (2)$$

where μ_{if} , μ_{fs} – reduced masses of the interaction of atoms "ion-film" and "film-substrate", respectively; M_{Ar} и M_f – atomic mass of ions Ar^+ and film; M_s – atomic mass of substrate material; $\langle E' \rangle$ – average transmitted power $\langle E' \rangle = \mu E_i$; E_i – the energy of the incident particle Ar^+ .



The effectiveness of the implementation of atoms at great depths can be estimated as a function that depends on the intensity of the ion beam, its energy and irradiation time [4]. In this regard, it is important to determine the optimum exposure conditions that ensure penetration of the implanted atoms to greater depths in their maximum possible concentration, especially in case of doping the polycrystalline substrates.

This paper presents the results of studying laws of formation of a given structural-phase state of the depth of the surface layers in a multilayer film and polycrystalline Ti (Zr) substrates at various modes of irradiation beams of ions He^+ and Ar^+ ions with a broad energy spectrum with an average energy of 10 keV.

2. Materials and tools

Were selected for study polycrystalline samples of Zr and Ti. The doping atoms of Si, Al, Fe, Mo, Zr and W formed as atoms of one kind or more atoms at the same time of the multilayer films in the following combinations: SiAl; AlFe; AlMo; TiSiAl-Me; MoFeAl-Me; MoFeTiAl-Me; MoFeTiSiAl-Me; MoFeAlTiSi-Me, where Me - a matrix material, i.e. Zr or Ti.

Samples were standard treatment consisting in mechanical grinding and polishing, electropolishing in the respective electrolytes. Some samples undergo additional purification by ion-beam treatment and the vacuum annealing ($p=3 \times 10^{-4}$ Pa) at a temperature of $0.7T_m$ for 1 hour.

The multicomponent doping carried out by ion mixing of the film when irradiated beams of ions He^+ and Ar^+ ions with a broad energy spectrum on the "VOKAL" [5], the average energy of the ions in the beam $\langle E \rangle = 10$ keV, the ion current density $j = 25 \text{ mA} \cdot \text{cm}^{-2}$, dose $F \approx (1-5) \times 10^{18} \text{ cm}^{-2}$, the temperature of the samples under irradiation $T \leq 500^\circ \text{C}$, residual gas pressure $p \approx 1 \times 10^{-6}$ Pa. For more information about the distribution of interstitial atoms in the depth $C(x)$ and polycrystalline Ti- and Zr-matrix method was used to measure the precision spectrometer SA-2000 (c. LECO) with a depth resolution of $\pm 5 \text{ nm}$.

3. Experimental results

3.1. Surface roughness

The experiments to study the dependence of change of surface roughness R_a of the dose of irradiation beams of ions He^+ , Ar^+ and $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:1, 1:2, 1:5, 1:10$) with a broad energy allowed to identify the most optimal conditions exposure (Figure 1) $R_a < 0.6$ micrometers.

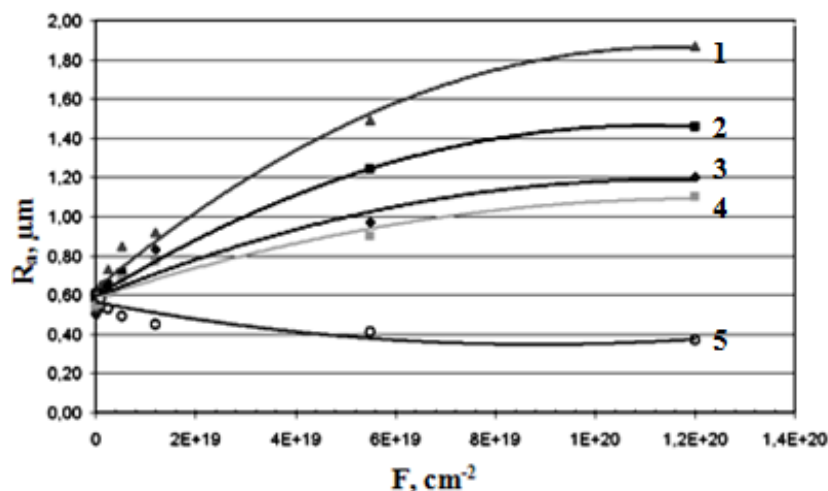


Figure 1. Dependence of surface roughness on exposure dose:
 1 – Ar^+ , 2 – He^+ , 3 – $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:1$), 4 – $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:5$) 5 – $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:10$).

From which it follows that the two-component ion beam irradiation of $\text{He}^+ + \text{Ar}^+$ with the content in the beam of He^+ ions at 10% (Figure 1, curve 5) creates favorable conditions for spraying the surface of the alloy in the "ion polishing". In this mode, a multi-component alloying matrix allows you to minimize distortions in the distribution of interstitial atoms, arising from the different rates of dispersion of individual crystallites, which is especially important when irradiated with high doses.

3.2. Single-component implementation

Figure 2 shows the typical distribution of atoms of Si, Al, Fe and Mo in polycrystalline zirconia after irradiation with Ar^+ ions dose of $1.3 \times 10^{18} \text{ cm}^{-2}$. As seen from the figure Mo and Fe atoms penetrate the greatest depth of 400-420 and 250-280 nm, respectively, and the atoms of Si and Al are arranged mainly close to the surface of <200 nm. The maxima of distributions of atoms Si, Fe and Mo are located at the surface at a depth of 20-40 nm, and the Al atoms at a depth of 60-80 nm. Distribution $C(x)$ of Si atoms and Mo has the form of a monotonically decreasing dependence, and Al atoms distribution corresponds to the dome depending on (asymmetric). Form distributions of embedded Fe atoms is more complex relationship and has two segments monotonic decrease in the concentration - 40-160, and 180-280 nm. Their appearance may be due to the processes of radiation exposure while stirring (first section) and radiation-stimulated diffusion under irradiation (second section) [3,6].

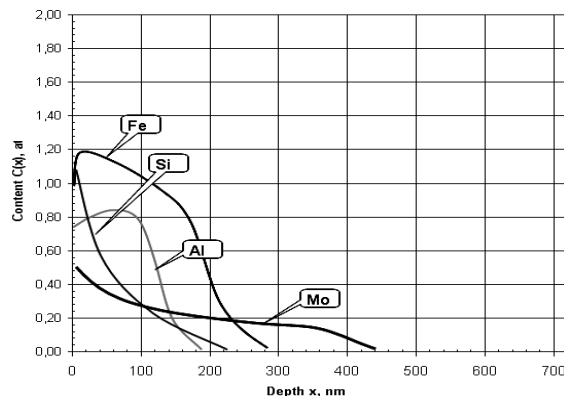


Figure 2. Distribution interstitial atoms in zirconium of monolayer films by irradiating a beam of Ar^+ ions with an average energy $\langle E \rangle = 10 \text{ keV}$, dose $F = 1.3 \times 10^{18} \text{ cm}^{-2}$, irradiation temperature $T < 100^\circ \text{C}$.

3.3. Multi-component implementation

Figure 3 shows the dependence of the distribution of atoms Al, Ti and Fe from which it is clear that the function $C(x)$ are characterized by several maxima of distributions: Al - 0-120 nm, Ti - 10-30 and 80-120 nm, Fe - 40-60, 200-220 and 380-420 nm. There is a deep penetration of Fe atoms (to $x_m = 500 \text{ nm}$).

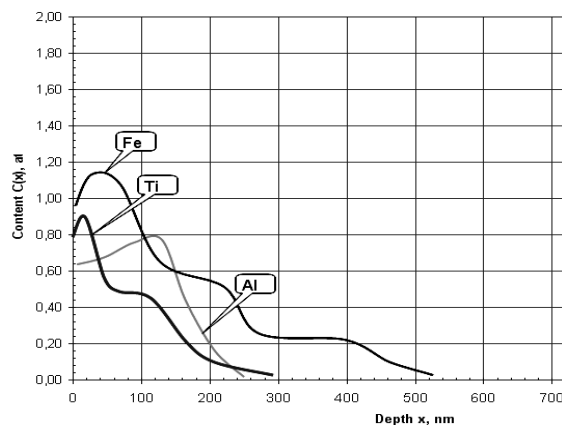


Figure 3. Distribution atoms Fe, Ti, Al in a polycrystalline sample Zr100 after irradiation with Ar^+ , dose $F = 2.1 \times 10^{18} \text{ cm}^{-2}$, temperature $T \leq 100-150^\circ \text{C}$, three-layer films FeTiAl- Me.

Changes in the mutual arrangement of the layers in a multilayer film MoFeTiSiAl-Me (Figures 4 and 5) is only one Al-layer (MoFeAlTiSi-Me) significantly changes the form of the functions $C(x)$. On the distribution of $C(x)$ (Figure 5) atoms Al, Ti, Fe concentrations appear secondary maxima located at great depths (Al - 80-100 nm, Ti - 100-120 nm, Fe - 160-180 nm). This is accompanied by the penetration of Si atoms and Mo to make greater depth (Si - 200-220 nm and Mo - 600-620 nm) compared with the distributions given in Figure 3 for a three-doping. Analysis of the distribution $C(x)$ of interstitial atoms represented in Figure 5, reveals three specific areas: 1 - the area of radiation exposure, 2 - radiation-stimulated migration of interstitial atoms, 3 - area of diffusion processes in the fields of internal stress.

For example, for the atoms Al, Si, Ti, Fe concentration maxima located in the first region (depth of 20-30, 0-10, 20-40, 40-60 nm, respectively), further extends the area of radiation-stimulated migration of physico-chemical interaction between interstitial atoms and the atoms of the substrate (for Al, Si, Ti, Fe, it extends to the 100-120, 120-140, 160-180, 220-240 nm, respectively), the diffusion region extends to depths of Al - 220-240 nm, Si - 220 nm, Ti - 300-320 nm, Fe - 360-380 nm. Distribution molybdenum atoms $C(x)$ has a maximum at a depth of 80-120 nm, and extends to a depth of 600 nm with a monotonic decrease of the largest concentration.

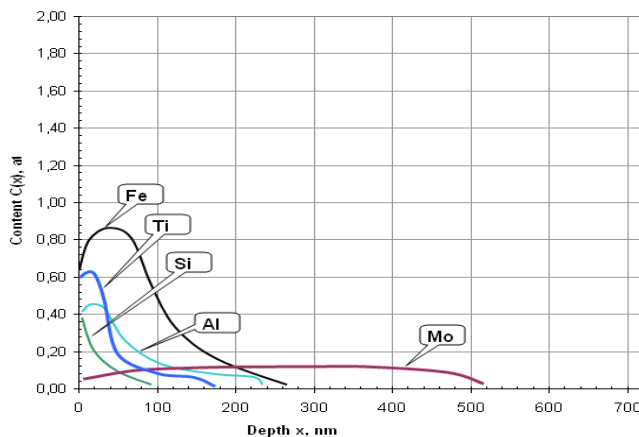


Figure 4. Distribution atoms Si, Al, Ti, Fe, Mo in a polycrystalline sample Zr-100 after irradiation ions $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:10$), dose $F = 5,5 \times 10^{18} \text{ cm}^{-2}$, temperature $T \leq 100-150^\circ\text{C}$, five-layer films MoFeTiSiAl – M.

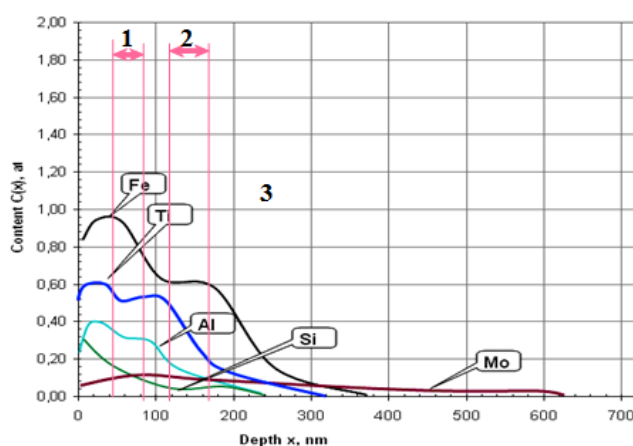


Figure 5. Distribution Si, Al, Ti, Fe, Mo atoms in Zr polycrystalline substrate (Zr-100) after the exposure to the ion beam $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:10$), dose $F = 5.5 \times 10^{18} \text{ cm}^{-2}$, temperature $T \leq 100 - 150^\circ\text{C}$, five-layer film MoFeAlTiSi - Me: 1-region of radiation exposure, 2-radiation-stimulated migration of interstitial atoms, 3-area diffusion processes in the fields of internal stress.

4. Discussion

Earlier experiments [7,8] showed that for more effective implementation of the atoms of the films on the one hand it is necessary to reduce speed of dispersion films $V_{\text{Spf}} = dx_f/dt$, on the other hand seek to increase the speed of implementation of their atoms $V_{\text{implf}} = dx_m/dt$ in matrix. As part of the cascade

theory of sputtering and isotropic mixing it is possible to show that these quantities are related as follows [7-9]:

$$V_{Spf} = \frac{A}{\pi^2 \rho N_A s_o} \times \frac{\Delta x j F_q}{U_o} \quad (3)$$

$$V_{implf} \cong \sqrt{\frac{B j F_q}{4t}}, \quad (4)$$

where B - gram mole, ρ - the proportion of the film material, N_A - Avogadro's number, s_o - irradiated area, U_o - the binding energy of the atoms on the surface, - the coefficient of ion mixing, F_q - the energy in the substrate material, j - current density ion beam, t - time of exposure.

From these relations we can draw the following conclusions:

- speed reduction sputtering films possible by reducing energy F_q and increasing the energy of the atoms U_o ;
- implantation rate increase may be accomplished by increasing the energy F_q and the coefficient of ion stirring B .

It is also one of the essential factors to increase the value of B can also be an optimum relative positioning of the layers of the films themselves [6-11]. For example, the outer layer of the multilayer films is expedient to spray with heavier atoms, and an inner, adjacent to the surface of the matrix - the lighter.

In this case, the conditions are favorable for intensification of atomic mixing and spraying rate of the film is reduced.

To explain the observed laws of change of the maximum depth of penetration of the atoms of the film substrates used in different model of an isotropic mixing proposed by Sigmund Peter and Andreas Grass Marty [3]. In the case of irradiation of the ion beam with a broad energy spectrum introduced these features. The amount of energy in the implanted layer F_q calculated from the condition that the thickness of the layer is equal to twice the projected range of ions in a suitable substrate - $2R_p$. Kinematic parameters μ_0 was replaced by $1 - \mu^*$, where $\mu^* = 0,5\mu_{fs}$. The value of $(1 - \mu^*)$ is responsible for maintaining the kinetic energy of interstitial atoms.

At the same time we have discussed various physical and chemical mechanisms of interaction between the implanted atoms and the atoms of the substrate that allowed to enter into the expression for the calculation of the relative depth migration (x_m/R_p electronegativity of the atoms of the multilayer film and the substrate in the form of a power function $\Delta\chi = \sum(A_i \times \chi_i^{mi})$, and the expression for the relative depth of migration of interstitial atoms can be written as:

$$\frac{x_m}{R_p} = C_o \frac{M_i M_f}{(M_i + M_f)^2} \times \left[0.202 \frac{F_q(x)\Phi}{N_o E_d (1 - \mu_{if}^*)} \right]^{0.3} \times \Phi_{fs} \left(|\Delta\chi|^n \right), \quad (5)$$

где x_m - depth migration of interstitial atoms; R_p - projected range of interstitial atoms; F_q - energy release in implantable layer; Φ - exposure dose; N_o - density target material; E_d - energy atomic

displacements; μ_{if} - linkage parameter, C_o - coefficient; $\Phi_{fs} \left(|\Delta\chi|^n \right) = \sum_{k=0}^k A_k \chi_k^{n_k}$ - function

describing the physical and chemical interaction (A_k - coefficients depending on the film material; χ_o , χ_i - electronegativity substrate and film material, respectively, tl. Pauling). For single-layer film $k=3$, a two-layer film - $k = 4-5$, a three-layer film - $k = 6$, five-layer film - $k = 7-8$ (Al-Fe-Mo-Y-Zr on Be, Fe, Cu, Zr и Ti alloys).

In multilayer systems, the distribution of interstitial atoms may issue contribute diffusion and radiation-induced processes. For example, in the "three-layer film - polycrystalline Zr-substrate" found that the mutual arrangement of layers significantly affects the amount of implanted atoms. The optimal relative positioning film layers allows substantially increase the concentration of interstitials in the

matrix, e.g., by irradiation system «MoFeAl-Zr» atoms content in the matrix of the outer layer (Mo) is higher than the Al upon irradiation system «AlFeMo-Zr», i.e. the maximum number of interstitial atoms in the surface layer of the film substrate was observed for the case where the outer layer has a higher atomic weight with respect to the atomic weight of the ions Ar^+ , and an inner layer adjacent to the substrate surface smallest atomic mass.

Experimental data on the introduction of atoms from one-, two-, three- and five-layer films in polycrystalline zirconia substrate and its alloys under irradiation with a beam of Ar^+ ions and $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:10$) shows that in the range of doses irradiation $(1-100) \times 10^{18} \text{ ion} \cdot \text{cm}^{-2}$ doping the surface layers is advantageously carried out at relatively low temperatures of $<100-250^\circ\text{C}$. Wherein assessment of the effectiveness of the ion mixing in can be carried out according to the formula [6,7] $B = \langle x_m \rangle / 2 / \Phi \cdot F_q$, where $\langle x_m \rangle$ - the maximum depth of penetration of the atoms, Φ - dose, F_q - the energy in the substrate material. From the expression that improving the efficiency of ion mixing is to increase the penetration depth of the dopant atoms with decreasing radiation dose Φ (ie, the thickness of the sprayed layer) and reducing energy F_q in the substrate where $F_q \approx \langle E \rangle / R_p$, $\langle E \rangle$ - the average energy of the ions in the beam, R_p - projected range of ions in the matrix. This condition managed to fulfill in experiments by irradiating an ion beam with a broad energy spectrum, and the use of the beam containing ions $\text{He}^+ + \text{Ar}^+$, the coefficient of efficiency of ion mixing in reaching a value $B = (5-20) \times 10^{-3} \text{ nm}^5 \text{ eV}^{-1}$.

In the case of irradiation of five-layer film Mo, Fe, Al, Ti, Si beam of Ar^+ ions and $\text{He}^+ + \text{Ar}^+$ ($C_{\text{He}^+} : C_{\text{Ar}^+} = 1:10$) repositioning the Al-layer relative to the other layers leads to both a deeper penetration of Fe atoms and the Mo and the appearance of secondary maxima distribution atoms Fe, Al, Ti. These changes can be explained by taking into account the processes of ion mixing, radiation-stimulated migration and physico-chemical interactions of atoms introduced both among themselves and with the atoms of the matrix, ie, condition Darken-Guri-Sud (DGS) [1,5,12].

Analysis of changes in dependencies $C(x)$ for a variety of one, two, three and five-layer films leads to several conclusions:

- with increasing depth of penetration into the matrix of implanted atoms concentration gradient $\text{grad } C(x)$ is minimal;
- less deep penetration of the interstitial atoms in a matrix corresponding to the maximum value of $\text{grad } C(x)$;
- doping allows to create multicomponent fibers at greater depths with the value $\text{grad } C(x)$ similar as in the one-component alloying $\text{grad } C(x) \approx 5-10 \text{ at.}\% \cdot \mu\text{m}^{-1}$;

As follows from the data presented, the introduction of single-layer film the maximum penetration depth x_m , e.g., in the Zr-matrix is observed for the Mo atoms (440 nm), Minimal - Ti (150 nm), and the concentration gradient is maximal for the atoms of Si and Ti ($20 \pm 3 \text{ at.}\% \cdot \mu\text{m}^{-1}$), the minimum - Fe and Mo. Alloying Zr-matrix from bilayer films shows that the maximum depth of penetration is observed for the Fe atoms (460 nm) and Mo (420 nm), and the minimum - Al (75 nm) film AlTi-Me. The concentration gradient for a maximum of Si atoms and Al ($10 \pm 2 \text{ at.}\% \cdot \mu\text{m}^{-1}$) of the film SiAl-Me, AlTi-Me, AlFe-Me and the minimum for the Mo atoms ($1.0 \pm 0.1 \text{ at.}\% \cdot \mu\text{m}^{-1}$).

Doping of Zr-matrix of three-layer film offers insight to the maximum depth of atoms of Fe (520 nm) film FeTiAl and Mo (460 nm) film MoAlSi-Me. The minimum depth of penetration is observed in atoms Al (220 nm) film MoAlSi-Me. The concentration gradient maximum atoms Si ($12 \pm 1 \text{ at.}\% \cdot \mu\text{m}^{-1}$) film MoAlSi-Me, and the minimum of the atoms Mo ($3 \pm 1 \text{ at.}\% \cdot \mu\text{m}^{-1}$), the film MoFeAl-Me for atoms Si, Ti, Fe ($11 \pm 1 \text{ at.}\% \cdot \mu\text{m}^{-1}$), and the minimum for Mo atoms ($1.0 \pm 0.1 \text{ at.}\% \cdot \mu\text{m}^{-1}$). Simultaneous introduction of a five-layer film enables to introduce a maximum depth of atoms of Mo (620 nm) film MoFeAlTiSi-Me, a minimum depth to penetrate atoms Si (100 nm). The concentration gradient with a maximum ($12 \pm 1 \text{ at.}\% \cdot \mu\text{m}^{-1}$).

5. Conclusion

The experiments showed that irradiation of the "film-substrate" change of value relative depth of penetration of the interstitial atoms (x_m/R_p) is satisfactorily described by the model of an isotropic

mixing and physico-chemical interaction with its environment. In the case of the introduction of the matrix atoms of the multi-layer film (two, three and five -ply) physico-chemical interaction between the implanted atoms and the atoms of the matrix can be accounted for by the value of the electronegativity of elements, presented in the form of a power series.

It was revealed that multicomponent doping can create gradient layers at greater depths with the value of $\text{grad } C(x) \approx 5\text{-}10 \text{ at.\% } \mu\text{m close}$, as in the one-component doping.

Due to the presence of multiple peaks of concentration in multicomponent doping in the matrix formed by several sections (layers) of a high concentration gradient of the interstitial atoms, which are formed as a result of redistribution of flows of displaced atoms of the multilayer film and substrate.

Analysis of the data suggests that the basis of the penetration of the atoms in the oxide film at the ion-doped multicomponent stirring under irradiation with ion beams of He^+ and Ar^+ with a broad energy spectrum lies several processes including:

- transfer of energy from the primary ions and sputtered atoms to subsequent displacement cascade;
- radiation-induced migration and physico-chemical interaction between the implanted atoms and the atoms of the substrate;

The effectiveness of penetrate of the implanted atoms to great depths B is defined energy release in implantable layer F_q , which is suitable to reduce the largest. One of the possible ways to implement the optimal conditions of doping by ion mixing the irradiation of the ion beam with a broad energy spectrum, and improve the efficiency of penetration into the substrate implanted atoms can be an increase in energy of the ions in the beam with a simultaneous decrease in the reduced atomic mass of the beam, which can be realized while irradiating ions of several mass For example, light and heavy ions ($\text{He}^+ + \text{Ar}^+$) to determine their ratio ($C_{\text{He}^+} : C_{\text{Ar}^+}$) and the optimal arrangement of the layers in the multilayer film, i.e. outer layer - heavy atoms, the lower layer the lightest atoms.

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