MATERIALS. TECHNOLOGIES. DESIGN

УДК 533.93:537.525
P.A.C.S. 68.55.Ln

DOI 10.54708/26587572_2023_5313123

FEATURES OF THERMAL PROCESSES AND THE INFLUENCE OF PULSED HEATING OF SURFACE LAYERS OF TITANIUM ON THE DIFFUSION TRANSFER OF DOPANTS DURING HIGH-INTENSITY ION IMPLANTATION

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ABSTRACT

Methods for modification of surface and near-surface layers of materials and coatings by ion beams have prospects for application in many fields of science and technology. The method of high-intensity implantation by high-power density ion beams with submillisecond duration involves significant pulsed heating of the irradiated target's surface layer, followed by its rapid cooling due to heat removal into the material due to thermal conductivity and the implementation of repetitively-pulsed radiation-enhanced diffusion of atoms to depths significantly exceeding the projective ion range. This paper considers features of thermal processes and the effect of pulsed heating of near-surface titanium layers on diffusion transfer under conditions of synergy of high-intensity titanium ion implantation and energy impact of a high-power density repetitively-pulsed beam on the surface to increase ion doping depth due to radiation-enhanced diffusion under conditions of limited heating of the entire sample. The paper presents the data of numerical simulation of dynamic changes in temperature fields in titanium and titanium self-diffusion under the action of ion beams with a submillisecond duration and a pulse power of tens of kW/cm^2 and fluence of ions in a pulse 1.25×10^{15} ion/cm^2.

KEYWORDS

Ion implantation; energy impact; modification of surface; near-surface layers; diffusion of atoms; numerical simulation; titanium; self-diffusion; thermal processes; dynamics of temperature fields; radiation-stimulated diffusion; deep ion doping.

ОСОБЕННОСТИ ТЕПЛОВЫХ ПРОЦЕССОВ И ВЛИЯНИЯ ИМПУЛЬСНОГО НАГРЕВА ПОВЕРХНОСТНЫХ СЛОЕВ ТИТАНА НА ДИФФУЗИОННЫЙ ПЕРЕНОС ПРИМЕСЕЙ ПРИ ВЫСОКОИНТЕНСИВНОЙ ИОННОЙ ИМПЛАНТАЦИИ

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АННОТАЦИЯ

Методы модификации поверхностных и приповерхностных слоев материалов и покрытий ионными пучками имеют перспективы применения во многих областях науки и техники. Метод высокоинтенсивной имплантации пучками ионов высокой плотности мощности субмиллисекундной длительности предполагает значительный импульсный разогрев приповерхностного слоя облучаемой мишени, с последующим быстрым его охлаждением за счет отвода тепла внутрь материала благодаря теплопроводности и реализацию импульсно-периодической радиационно-усиленной диффузии атомов на глубины, существенно превышающие проективный пробег ионов. В настоящей работе исследуются особенности тепловых процессов и влияние импульсного разогрева приповерхностных слоев титана на диффузионный перенос в условиях синергии высокоинтенсивной имплантации ионов и энергетического воздействия импульсно-периодического пучка высокой плотности мощности на поверхность с целью увеличения глубины ионного легирования за счет радиационно-стимулированной диффузии в условиях ограниченного разогрева всего образца. Приведены данные численного моделирования динамического изменения температурных полей в титане и самодиффузии титана при воздействии на поверхность пучков ионов субмиллисекундной длительности с импульсной мощностью в десятки кВт/см^2, флюенс ионов в импульсе 1,25×10^{15} ион/см^2.

КЛЮЧЕВЫЕ СЛОВА

Ионная имплантация; энергетическое воздействие; модификация поверхности; приповерхностные слои; диффузия атомов; численное моделирование; титан; самодиффузия; тепловые процессы; динамика температурных полей; радиационно-стимулированная диффузия; глубокое ионное легирование.

Introduction

The ion implantation method has unique opportunities for changing the elemental composition, conductivity, microstructure, and properties of a wide range of materials, including semiconductors, metals, and alloys [1–17]. The wide-scale application of ion implantation is limited by the short ion range in a solid.

Radiation enhanced diffusion as applied to ion implantation can expand the possibilities of its practical application for deep ion doping of both semiconductor materials and metals and alloys. In [18], for the first time, the possibility of forming high-intensity ion beams with a current density up to 1 A/cm^2 at the ion energy of a few keV was experimentally shown. The method of high-intensity implantation of low-energy ions using such beams showed the possibility of increasing the ion-doped layer depth due to radiation enhanced diffusion to several tens and even hundreds of micrometers [19, 20]. The high current density in the ion beam and the significant heating of the irradiated materials contribute to the implanted atoms' diffusion to depths many times greater than the ion projective range. At the same time in many cases, the heating of irradiated samples to high temperatures during ion implantation negatively changes the microstructure of entire volume of the material. Paper [21] proposes a new method of modifying the near-surface layer with a high-intensity repetitively-pulsed beam without a significant change in the microstructure and properties of the irradiated material outside the doped layer. The method involves the synergy of high-intensity ion implantation and energy impact on the surface of ion beams with a high-pulsed power density [22]. In this case, the irradiated target's average temperature can be limited to values at which its microstructure does not deteriorate.

For a more detailed study of these processes, modern science cannot do without mathematical simulation of physical processes, reducing the time of research when carrying out a physical experiment. Simulation is an indispensable tool in the study of regularities and features of various physical processes under conditions of replacing the real process with a model similar to the original.

This paper considers thermal processes' features and the effect of pulsed heating of near-surface titanium layers on diffusion transfer under conditions of synergy of high-intensity titanium ion implantation and energy impact of a high-power density repetitively-pulsed beam on the surface to increase ion doping depth due to radiation enhanced diffusion under conditions of limited heating of the entire sample.

1. Studying the dynamics of changes in the spatial distribution of implanted dopant

1. 1. Description of the numerical model

The study is carried out within the development of a new method for modifying the surface properties of various materials by implanting dopant atoms as a result of irradiation with an intense repetitively-pulsed ion beam.

The power density of a similar beam is such that the surface layers can be significantly heated. Consequently, the diffusion transfer of implanted atoms should be enhanced. In high-intensity implantation, it is important that the deeper layers of the irradiated material do not undergo recrystallization or melting. To implement this, it is required to identify the range of operating beam parameters that will ensure a noticeable diffusion penetration of dopant atoms into the deep layers of the processed material.

To solve the problem, a mathematical simulation of thermal and diffusion processes in a metallic material was carried out, developing under the action of a repetitively-pulsed ion beam with operating parameters corresponding to the technical capabilities of the experimental setup. The most appropriate working parameters of ion irradiation were determined using an ion beam with energies up to *ZeU* ~100 keV (Z is average ion charge state; for titanium in DC vacuum arc plasma, Z is about 2) as an example. Current pulse repetition rate is 1 p.p.s., pulse duration (τ_{imp}) is 500 μs. The experimentally obtained shape of the current density distribution over the beam cross-section radius is shown in Fig. 1.

The diffusion transfer change was studied using the example of titanium self-diffusion (i.e., a titanium ion beam acts on the titanium target surface).

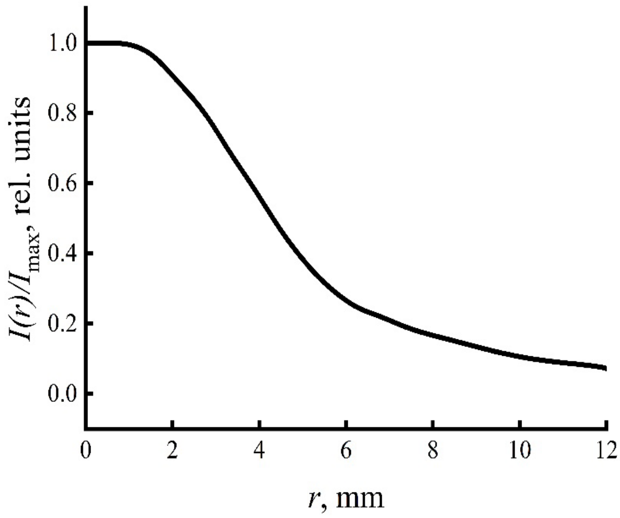


Fig. 1. Shape of the current density distribution along radius (*r*) of the ion beam cross-section

Рис. 1. Форма распределения плотности тока по радиусу (*r*) поперечного сечения ионного пучка

A joint solution of the thermal problem was carried out based on the heat conduction equation (described in [23]) and the diffusion equation in the following form:

$$\frac{\partial C(z,t)}{\partial t} - v_{sput}\frac{\partial C}{\partial z} D(T(t))\frac{\partial C(z,t)}{\partial z} + S(z,t).$$

Initial and boundary conditions: $C(z,0) = 0$.

$$D\frac{\partial C(z,t)}{\partial t}\bigg|(z=0) = D\frac{\partial C(z,t)}{\partial z}\bigg|(z=back) = 0.$$

Here $T(t)$ – temperature change during the repetition period of beam current pulses; $C(z,t)$ – function of spatiotemporal distribution of the implanted atom concentration, which will be referred to as dopant atoms; v_{sput} – sputtering rate of the irradiated target surface, $v_{sput} = Y_{sput} \times I(t)/q_e$; Y_{sput} – sputtering ratio; $I(t)$ – current density during a pulse; q_e – electron charge (here it is assumed that all ions are double-charged with energy 100 keV);

$$S(z,t) = \frac{I(t)}{q_e\sqrt{2\pi\Delta R_p^2}}\exp\left(-\frac{(z-R_p)^2}{2\Delta R_p^2}\right)$$

– embedding power density of dopant atoms; R_p и ΔR_p – average projective range and straggling of the projective range of beam ions.

In the frequency-pulse mode of impact, the energy release in the surface layers of the substance due to the beam ion deceleration occurs during the action of a current pulse with duration τ_{imp}, then there is a pause in the bombardment of the target until the end of the period in the repetition of pulses (i.e. until $T_{per} = 1/\nu$). In this case, the change in the target temperature (including in its surface layers (T_{surf})) can be represented as follows:

$$T_{surf}(t) = T_{back} + \Delta T_{imp}(t).$$

Here T_{back} – temperature against the background of which the target is heated by ΔT_{back} during the action of one current pulse.

1.2. Numerical simulation of the target temperature field evolution during pulsed and repetitively-pulsed high-power density ion beam implantation

Fig. 2 shows the stabilization of the residual temperature T_{back} in a titanium target with a thickness of 3 mm at different beam powers, averaged over the period (Q_{av}). It can be seen that the greater the power, the faster T_{back} stabilizes. For each Q_{av}, T_{stab} reaches its definite constant value.

Fig. 3 shows the evolution of $T(t)$ on the titanium target surface during one ion beam current pulse. The calculation was carried out under conditions of a steady temperature T_{back} for Q_{av} = 50 W and T_{back} = 300 K (this corresponds to the initial irradiation or a situation with intense cooling of the sample's back surface). Temperature evolution analysis shows that the maximum heating in the target surface layers is reached by the pulse end. Then they cool down due to thermal conductivity into depth and thermal radiation of the target. The residual temperature T_{back}, which takes place by the beginning of the next pulse, depends on their repetition frequency, as well as the energy introduced by the beam into the target material during the pulse, the sample size, and the intensity of its heat exchange with the environment. In any case, it stabilizes as the beam impacts the target due to the establishment of a thermal balance with the environment. For the case of frequency-pulsed mode with T_{back} = 918 K, a melting temperature of 1940 K is reached on the surface. When heated by one current pulse against a background of 300 K, T_{max} = 1402 K. Obviously, a higher power will increase T_{max}.

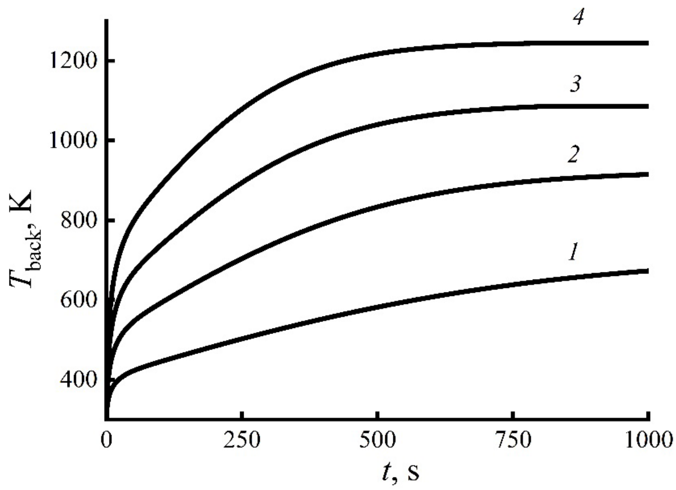


Fig. 2. Temperature stabilization of a titanium target with a thickness of 3 mm during its irradiation with an ion beam with different power averaged over the period Q_{av}:
1 – 25 W; 2 – 50 W; 3 – 75 W; 4 – 100 W

Рис. 2. Стабилизация температуры титановой мишени толщиной 3 мм в процессе ее облучения ионным пучком с разной мощностью, усредненной по периоду $Q_{ср}$:
1 – 25 Вт; 2 – 50 Вт; 3 – 75 Вт; 4 – 100 Вт

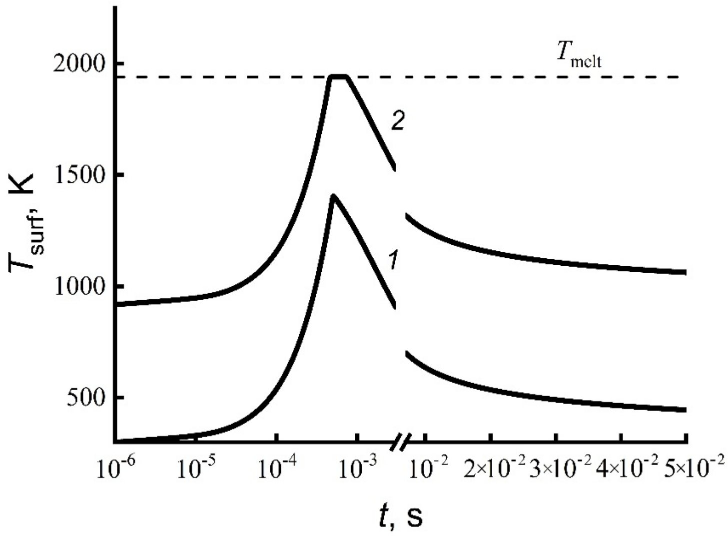


Fig. 3. Temperature evolution on the Ti target surface during one period of beam current pulses with the power averaged over the period, 50 W:
1 – $T_{back} = T_{stab} = 918$ *K; 2 –* $T_{back} = 300$ *K*

Рис. 3. Эволюция температуры на поверхности титановой мишени в течение одного периода импульсов тока пучка с мощностью, усредненной по периоду, 50 Вт:
1 – $T_{back} = T_{stab} = 918$ *K; 2 –* $T_{back} = 300$ *K*

Table 1 summarizes the data on the maximum heating of the target's surface layers under the action of a beam with different power, averaged over the period, at $\tau_{imp} = 500$ μs. Two cases of steady heating are presented here.

Repetitively-pulsed beam with $Q_{av} \geq 50$ W ($W_{imp} \geq 2\times10^8$ W/m^2) is the most promising in terms of enhancing diffusion mass transfer due to high-temperature heating. However, the power of 100 W ($W_{imp} = 4\times10^8$ W/m^2) seems to be too high due to the need to comply with the restrictions on the level of heating. Nevertheless, against a background of 300 K, irradiation may be quite acceptable.

Table 1. Maximum temperature on the titanium target surface as a result of the action of one current pulse under conditions of a steady residual temperature T_{back} in the repetitively-pulsed irradiation mode and against a background of 300 K

Таблица 1. Максимальная температура на поверхности титановой мишени в результате действия одного импульса тока на фоне установившейся остаточной температуры T_{back} в частотно-импульсном режиме облучения и на фоне 300 К

Q_{av}, Вт / Q_{av}, W	W_{imp}, 10^8 Вт/м^2 / W_{imp}, 10^8 W/m^2	Частотно-импульсный режим / Repetitively-pulsed mode		T_{max} при $T_{back} = 300$ К / T_{max} at $T_{back} = 300$ К
		$T_{стаб}$, К / T_{stab}, K	$T_{макс}$, К / T_{max}, K	
25	1	695	1260	864
50	2	918	1940	1402
75	3	1085	2222	1940
100	4	1243	2968	1971

1.3. Numerical simulation of pulsed self-diffusion of titanium

Fig. 4 shows the concentration profiles of dopant atoms embedded in the surface layers during one beam current pulse for Q_{av} = 50 W. It can be seen that in the case of T_{back} = 918 K, the dopant propagated into the deep layers of the target rather noticeably even by the end of the pulse. After its completion, diffusion transfer continues for some time (up to about 5 ms from the beginning of the period). To determine the self-diffusion coefficient of titanium, the following parameters were used in the simulation: diffusion factor (pre-exponential factor) – 6.4×10^{-8} cm²/s; activation energy – 123 kJ/mol [24].

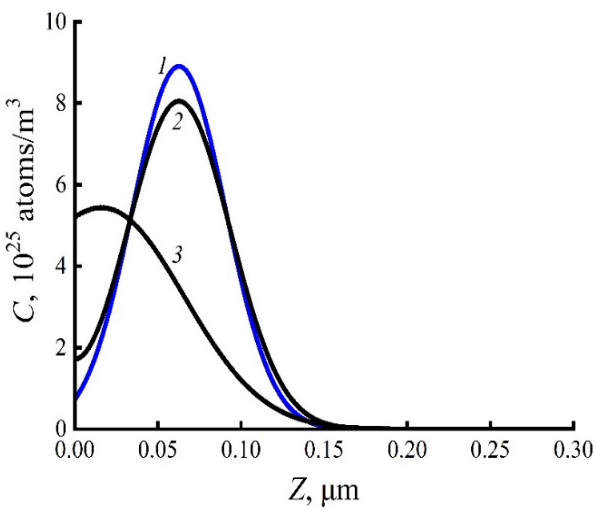
When irradiated under conditions of 300 K, a slight dopant redistribution occurs in the most surface layers; i.e. in the area of primary implantation of particles.

To estimate the diffusion transfer level for different operating parameters of the beam, the diffusion transfer's intensity index of the dopant is introduced in the following way:

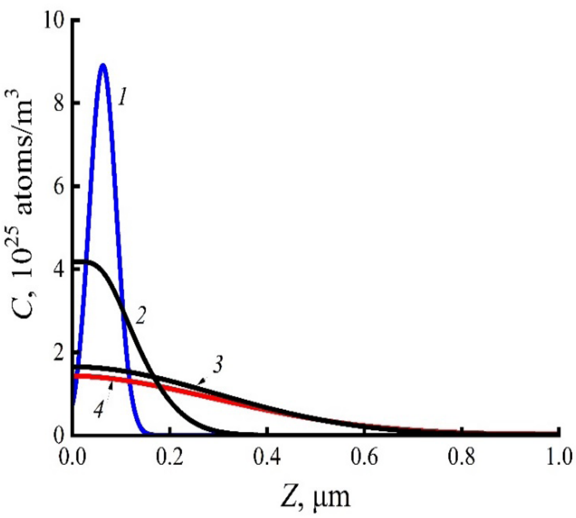
$$K_{diff} = (h_{diff} - R_p)/R_p,$$

where R_p – ion projective range; h_{diff} – diffusion length, which is defined as depth (Z) at which at the current moment of time (t) the dopant concentration C (t, Z) is $0.3\times C(t, R_p)$.

The dependences of K_{diff} on the beam power density averaged over a pulse with duration of 500 μs are shown in Fig. 5. It can be seen here that at $W_{imp} \geq 1.5\times10^8$ W/m², the diffusion length is several times greater than the depth of the initial embedding of dopant atoms.



a



b

Fig. 4. Change in the concentration profile (C) of the implanted dopant in the surface layers of titanium target during the ion beam current period with the power density averaged over the period, Q_{av} = 50 W ($W_{imp} = 2\times10^8$ W/m²) under conditions of a residual temperature of 300 K (*a*) and T_{stab} = 918 K (*b*)

Рис. 4. Изменение профиля внедренной примеси в поверхностных слоях титановой мишени в течение периода тока ионного пучка с плотностью мощности, усредненной по периоду, $Q_{ср}$ = 50 Вт ($W_{imp} = 2\times10^8$ Вт/м²) на фоне остаточной температуры 300 K (*a*) и T_{stab} = 918 K (*b*)

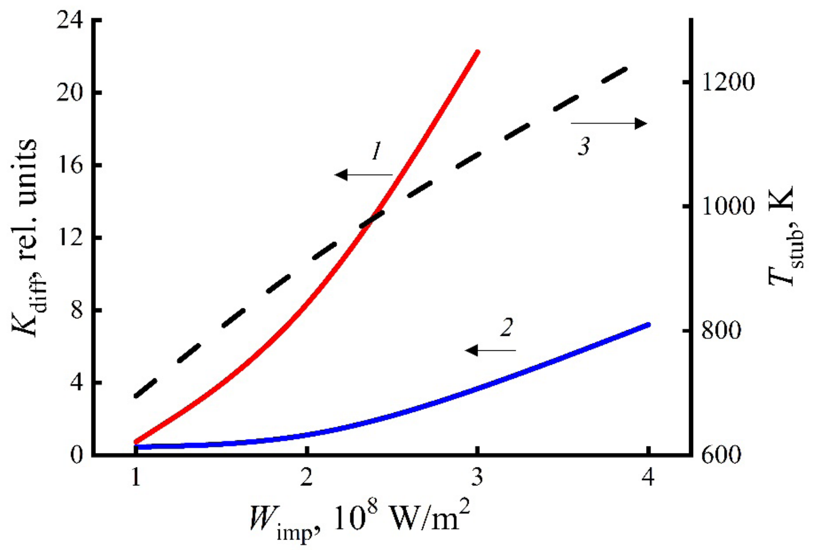


Fig. 5. Dependence of the diffusion transfer intensity index on the ion beam power density in the repetitively-pulsed mode of irradiation under conditions of residual heating T_{stab} (1) and 300 K (2); dependence of the steady-state residual temperature of the target surface layer (T_{stab}) on the beam power density (3)

Рис. 5. Зависимость показателя интенсивности диффузионного переноса от плотности мощности ионного пучка в частотно-импульсном режиме облучения на фоне остаточного нагрева T_{stab} (1) и 300 К (2); зависимость установившейся остаточной температуры T_{stab} поверхностного слоя мишени от плотности мощности пучка (3)

The maximum values of K_{diff} reach 20 in the admissible range of power density (i.e., in terms of compliance with the restrictions on the target heating level) during one beam current pulse against the background of $T_{back} = T_{stab}$. Diffusion transfer by single pulses against a background of 300 K is characterized by K_{diff} from 3 to 7 in the range $W_{imp} = (3–4)\times10^8$ W/m^2.

Conclusions

A model has been developed for numerical simulation of the dynamics of changes in temperature fields in a solid and diffusion of dopants under conditions of high-intensity ion implantation and simultaneous energy impact of an pulsed ion beam on the surface.

Numerical simulation showed that exposure of the titanium surface to a submillisecond ion beam (500 μs) at a power density in the range of 1.5×10^8 to 3×10^8 W/m^2 provides pulsed heating of the near-surface layer to temperatures approaching the melting temperature, while the temperature does not rise significantly throughout the entire volume of the target material.

It has been established that in the specified range of power density and pulse duration, even at a frequency of 1 p.p.s., the diffusion transfer of the dopants increases by almost an order of magnitude. It is shown that under conditions of target forced cooling or in the single-pulse mode, i.e. when the residual heat is at the level of 300 K, the pulse power density above $(3–4)\times10^8$ W/m^2 should produce a noticeable diffusion dopants transfer.

Acknowledgments / Благодарности

Исследование выполнено за счет гранта Российского научного фонда № 22-79-10061, https://rscf.ru/project/22-79-10061/.

This work was carried out with the financial support of the Russian Science Foundation (grant No. 22-79-10061).

REFERENCES

1. Ryssel H., Ruge I. Ion implantation. New York: John Wiley and Sons Inc., 1986. P. 478. DOI: 10.1002/sia.740100409.

2. Williams J. S., Poate J. M. Ion Implantation and Beam Processing. First Edition. V. 1. New York: Academic Press Inc., 1984. P. 419.

3. Komarov F. F. Defect and track formation in solids irradiated by superhigh-energy ions // Physics-Uspekhi. 2003. V 46, Iss. 12. P. 1253–1282. DOI: 10.1070/PU2003v046n12ABEH001286.

4. Mehrer H., Diffusion in solids: fundamentals, methods, materials, diffusion-controlled processes. First Edition. V. 1. Berlin: Springer Science & Business Media, 2007. P. 651.

5. Valiev S. H., Pugacheva T. S., Jurabekova F. G., Lem S. A., Miyagawa Y. The radiation stimulated diffusion role in high dose, low energy, high temperature ion implantation. // Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 1997. V. 127–128. P. 265–268. DOI: 10.1016/S0168-583X(96)00937-8.

6. Ho P. S. Effects of enhanced diffusion on preferred sputtering of homogeneous alloy surfaces // Surface Science. 1978. V. 72, Iss. 2. P. 253–263. DOI: 10.1016/0039-6028(78)90294-7.

7. Miotello A., Mazzoldi P. Enhanced diffusion processes during ion implantation: A numerical analysis // Journal of Applied Physics. 1983. V. 54. P. 4235–4237. DOI: 10.1063/1.332528.

8. Eltoukhy A. H., Greene J. E. Diffusion enhancement due to low-energy ion bombardment during sputter etching and deposition // Journal of Applied Physics. 1980. V. 51. P. 4444–4452. DOI: 10.1063/1.328265.

9. Sizmann R. The effect if radiation upon diffusion in metals // Journal of Nuclear Materiarls. 1978. V. 69–70. P. 386–412. DOI: 10.1016/0022-3115(78)90256-8.

10. Shockley W. Forming semiconductive devices by ionic bombardment. Patent US No. 2787564. Publ. 02.04.1957.

11. Poate J. M., Foti G. Jacobson D. C. Surface Modification and Alloying by Laser, Ion, and Electron Beams, First Edition. V. 1. Berlin: Springer, 2013. P. 413.

12. Ryabchikov A. I., Stepanov I. B., Dektjarev S. V., Sergeev O. V. Vacuum arc ion and plasma source Raduga 5 for materials treatment // Review of Scientific Instruments. 1998. V. 69. P. 893–895. DOI: 10.1063/1.1148585.

13. Nikolaev A. G., Oks E. M., Savkin K. P., Yushkov G. Yu., Brown I. G. Upgraded vacuum arc ion source for metal ion implantation // Review of Scientific Instruments. 2012. V. 83. Article number 02A501. DOI: 10.1063/1.3655529.

14. Anders A. Handbook of Plasma Immersion Ion Implantation and Deposition, First Edition. V. 1. New York: John Wiley & Sons, 2000. P. 111.

15. Widner M., Alexeff I., Jones W. D., Lonngren K. E. Ion Acoustic Wave Excitation and Ion Sheath Evolution // Physics of Fluids. 1970. V. 13. P. 2532–2540. DOI: 10.1063/1.1692823.

16 Anders A. Metal plasma immersion ion implantation and deposition: a review // Surface and Coatings Technology. 1997. V. 93, Iss. 2–3. P. 158–167. DOI: 10.1016/S0257-8972(97)00037-6.

17. Wei R. Low energy, high current density ion implantation of materials at elevated temperatures for tribological applications // Surface and Coatings Technology. 1996. V. 83, Iss. 1–3. P. 218–227. DOI: 10.1016/0257-8972(95)02828-5.

18. Ryabchikov A. I., Ananin P. S. Dektyarev S. V., Sivin D. O., Shevelev A. E. High intensity metal ion beam generation // Vacuum. 2017. V. 143. P. 447–453. DOI: 10.1016/j.vacuum.2017.03.011.

19. Ryabchikov A. I., Sivin D. O., Korneva O. S., Bozhko I. A., Ivanova A. I. Modification of the microstructure and properties of martensitic steel during ultra-high dose high-intensity implantation of nitrogen ions // Surface and Coatings Technology. 2020. V. 388. Article number 125557. DOI: 10.1016/j.surfcoat.2020.125557.

20. Ryabchikov A. I., Shevelev A. E., Sivin D. O., Bozhko I. A., Kashkarov E. B., Bleykher G. A., Stepanov I. B., Ivanova A. I. Ultra high fluence implantation of aluminum ions into CP-Ti // Journal of Alloys and Compdound. 2019. V. 793. P. 604–612. DOI: 10.1016/j.jallcom.2019.04.179.

21. Ryabchikov A. I. High-Intensity Implantation With an Ion Beam's Energy Impact on Materials // IEEE Transactions on Plasma Science. 2021. V. 49, Iss. 9. P. 2529–2534. DOI: 10.1109/TPS.2021.3073942.

22. Ryabchikov A. I., Dektyarev S. V., Korneva O. S., Vakhrushev D. O. Formation of High-Power Pulsed Titanium Ion Beams of Submillisecond Duration from Vacuum Arc Plasma // Russian Physics Journal. 2023. V. 65. P. 1940–1946. DOI: 10.1007/s11182-023-02854-y.

23. Иванова А. И., Сивин Д. О., Корнева О. С., Блейхер Г. А. Моделирование температурных полей в мишенях при совмещении импульсно-периодической высокоинтенсивной имплантации ионов и энергетическом воздействии на поверхность // Материалы 8-го Международного конгресса по потокам энергии и радиационным эффектам (EFRE–2022), 2022. С. 820–825. DOI: 10.56761/EFRE2022.C2-P-018602.

24. Babichev A. P., Babushkina N. A., Bratkovskiy A. M. Physical values: reference book. 1st. Ed. Moscow: Energoatomizdat, 1991. P. 1232.