

## MODIFICATION OF SILICON UNDER SYNERGY OF HIGH-INTENSITY IMPLANTATION OF TITANIUM IONS AND ENERGY INFLUENCE OF A HIGH-POWER ION BEAM ON A SURFACE

*Alexandr Valerievich Gurulev<sup>1a</sup>, Anna Ivanovna Ivanova<sup>1</sup>,  
Dimitri Olegovich Vakhrushev<sup>1</sup>, Olga Sergeevna Korneva<sup>1</sup>,  
Dmitri Davidovich Efimov<sup>2</sup>, Artem Alexeevich Chernyshev<sup>3</sup>*

<sup>1</sup> National Research Tomsk Polytechnic University, 30 Lenin pr., Tomsk 634050 Russia

<sup>2</sup> Immanuel Kant Baltic Federal University, 14 A. Nevsky str., Kaliningrad 236041 Russia

<sup>3</sup> National Research Tomsk State University, 36 Lenin pr., Tomsk 634050 Russia

<sup>a</sup> avg72@tpu.ru

### ABSTRACT

Methods of modifying surface and near-surface layers of materials and coatings by ion beams can be applied in many fields of science and technology. To practically implement the technologies for the targeted improvement of the performance properties of parts and products for various purposes, it is of great interest to develop the methods of deep ion doping of near-surface layers of semiconductor materials, as well as metals and alloys due to the enhancement of radiation-stimulated diffusion under conditions when the irradiated sample's deep layers are not subjected to significant temperature impact. This work studies the features and regularities of the implementing the synergy of high-intensity titanium ion implantation at current densities of several hundred milliamps per square centimeter with simultaneous energy impact of a submillisecond ion beam with a power density reaching several tens of kilowatts per square centimeter on the surface. This work is the first to show that the synergy of high-intensity ion implantation and the energy impact of a high power density ion beam, taking the titanium implantation into silicon as an example, provides the possibility of increasing the ion doping depth from fractions of a micron to 6 microns by increasing the irradiation time from 0.5 to 60 min.

### KEYWORDS

Ion implantation; energy impact; temperature field dynamics; radiation-stimulated diffusion; deep ion doping; synergy; titanium ions; silicon; surface modification; vacuum arc; infrared pyrometer.

## МОДИФИКАЦИЯ КРЕМНИЯ В УСЛОВИЯХ СИНЕРГИИ ВЫСОКОИНТЕНСИВНОЙ ИМПЛАНТАЦИИ ИОНОВ ТИТАНА И ЭНЕРГЕТИЧЕСКОГО ВОЗДЕЙСТВИЯ МОЩНОГО ИОННОГО ПУЧКА НА ПОВЕРХНОСТЬ

*Александр Валерьевич Гурулев<sup>1a</sup>, Анна Ивановна Иванова<sup>1</sup>,  
Дмитрий Олегович Вахрушев<sup>1</sup>, Ольга Сергеевна Корнева<sup>1</sup>,  
Дмитрий Давидович Ефимов<sup>2</sup>, Артем Алексеевич Чернышев<sup>3</sup>*

<sup>1</sup> Национальный исследовательский Томский политехнический университет, Россия, 634050, Томск, пр. Ленина, 30

<sup>2</sup> Балтийский федеральный университет имени Иммануила Канта, Россия, 236041, Калининград, ул. Александра Невского, 14

<sup>3</sup> Национальный исследовательский Томский государственный университет, Россия, 634050, Томск, пр. Ленина, 36  
<sup>a</sup> avg72@tpu.ru

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## АННОТАЦИЯ

Методы модификации поверхностных и приповерхностных слоев материалов и покрытий ионными пучками находят применение во многих областях науки и техники. Развитие методов глубокого ионного легирования приповерхностных слоев полупроводниковых материалов, а также металлов и сплавов благодаря усилению радиационно-стимулированной диффузии в условиях, когда глубокие слои облучаемого образца не подвергаются значительному температурному воздействию, представляет значительный интерес для практической реализации технологий направленного улучшения эксплуатационных свойств деталей и изделий различного назначения. Настоящая работа посвящена исследованию особенностей и закономерностей реализации синергии высокоинтенсивной имплантации ионов титана при плотностях тока в несколько сотен миллиампер на квадратный сантиметр с одновременным энергетическим воздействием на поверхность пучка ионов субмиллисекундной длительности с плотностью мощности, достигающей нескольких десятков киловатт на квадратный сантиметр. Впервые показано, что синергия высокоинтенсивной имплантации ионов и энергетического воздействия пучка ионов высокой плотности мощности, на примере имплантации титана в кремний, обеспечивает возможность роста глубины ионного легирования от долей мкм до 6 мкм за счет увеличения времени облучения от 0,5 до 60 мин.

## КЛЮЧЕВЫЕ СЛОВА

Ионная имплантация; энергетическое воздействие; динамика температурных полей; радиационно-стимулированная диффузия; глубокое ионное легирование; синергия; ионы титана; кремний; модификация поверхности; вакуумная дуга; инфракрасный пирометр.

## Introduction

Methods of modifying the surface of metals, alloys, and semiconductor materials by ion beams [1–18] are of considerable interest for directed change in physical, mechanical, and electrophysical properties in many fields of science and technology. An increase in the thickness of ion-modified layers expands the possibilities of practical application of ion implantation both in semiconductor materials and in metals and alloys. The method of high-intensity low-energy ion implantation proposed in [19] demonstrated the possibility of increasing the ion-doped layer depth due to radiation-stimulated diffusion to several tens

and hundreds of micrometers. The high current density in the ion beam and 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, heating irradiated samples to high temperatures during ion implantation causes a negative change in the microstructure both in the doped layer and in the entire volume of the material.

The study [20] considers the possibility of modifying the near-surface layer by 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 assumes the synergy

of high-intensity ion implantation and energy impact on the surface of ion beams with a high-pulsed power density. At that, the mean temperature of the irradiated target can be limited to values at which its microstructure does not deteriorate.

This work studies the features and regularities of implementing the synergy of high-intensity titanium ion implantation at current densities of several hundred mA/cm<sup>2</sup> with simultaneous energy impact of a submillisecond ion beam with a power density reaching several tens of kW/cm<sup>2</sup> on the surface. This work is the first to show that the synergy of high-intensity ion implantation and the energy impact of a high power density ion beam, taking titanium implantation into silicon as an example, increase the ion doping depth from fractions of a micron to 6 microns due to increasing the irradiation time from 0.5 to 60 min.

### **1. Experimental setup and research methods**

The experimental study was carried out on a complex installation equipped with a modified ion source Raduga-5, described in [18]. A vacuum-arc evaporator generated titanium plasma in a continuous mode at a discharge current of 130 A. For ion extraction a single grid electrode in the form of a part of a sphere with a radius of 130 mm, a grid cell size of 1×1 mm<sup>2</sup> and a transparency of 64% was used. As in work [18], a disk electrode located along the ion source axis was used to cut off the deposition of the microdroplet fraction of the vacuum arc discharge during the titanium plasma generation on the irradiated surface. The beam was generated in a repetitively-pulsed mode using a pulsed voltage generator with a pulse duration of 500 μs and a bias potential amplitude of 30 kV. Silicon wafers with sizes of 40×10 mm<sup>2</sup> and thickness of 380 μm were used as samples. The samples had a polished surface with low roughness, which made it possible to obtain good depth resolution in pulsed diffusion studies.

For pulse measurement of the sample surface temperature a high-speed infrared pyrometer KLEIBER KGA 740-LO was used.

Ultra-high-dose implantation of titanium ions under conditions of partial heating of the entire sample by an ion beam and significant pulsed heating of the surface provided diffusion doping of silicon with titanium depending on the time and irradiation fluence.

The concentration and spatial distribution of implanted titanium were studied using the methods of RBS (Rutherford Back Scattering) of alpha-particles and transmission electron microscopy.

To analyze the implanted structures by the Rutherford backscattering (RBS) method, an accelerator based on a high-voltage electrostatic generator of the Van de Graaff type was used. Helium ions with an energy of 1.5 MeV were used as a probing beam, the angle between the beam and the normal to the sample was 5°, the scattering angle was 160°.

The distribution of titanium and silicon over the irradiated target depth was studied using a transmission electron microscope JEM-2100F.

### **2. Experimental results and discussion**

At the first stage, the studies were carried out on the titanium coating deposition on the silicon sample surface using a disk electrode located along the ion source axis. The disk electrode prevented the direct passage and deposition of both macroparticles and titanium plasma on the sample. The presence of thermal energy in the ions expanded the plasma and its deposition in the region of the ion beam focusing. The experimentally measured rate of titanium film deposition on a silicon substrate at the center of the target was about 2.7 Å/s.

The patterns of changes in the spatial distribution of titanium in silicon at the synergy of repetitively-pulsed high-intensity implantation and simultaneous energy impact of an ion beam on the surface were studied at a high-voltage bias pulse frequency of up to four

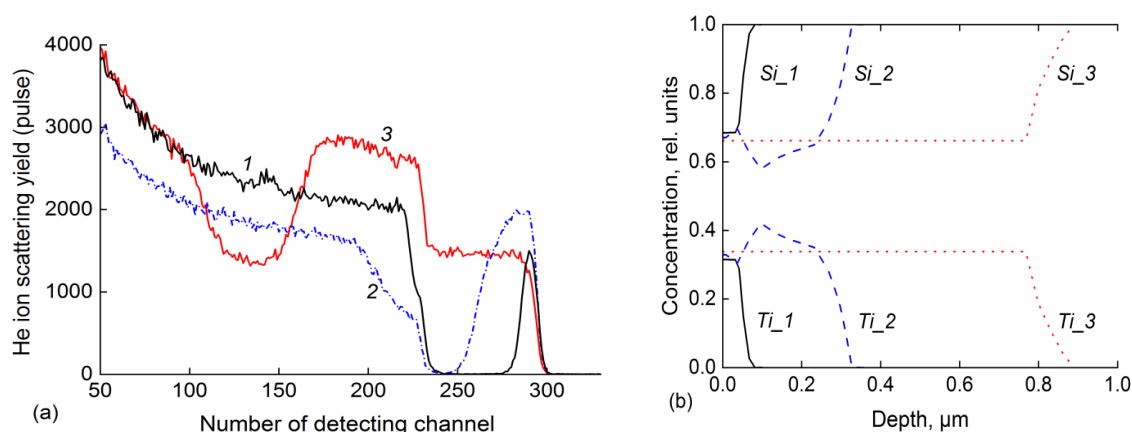
pulses per second, depending on the irradiation time from 0.5 to 15 min and a bias potential amplitude of 30 kV.

The use of a pulse pyrometer KLEIBER 740-LO with a lower limit of the measured temperature of 300 °C predetermined the experimental conditions. The samples were irradiated with their integral heating to a temperature near the pyrometer's lower sensitivity limit.

The first sample was irradiated for 0.5 min at an accelerating potential of 30 kV. The ion irradiation fluence, taking into account the pulse repetition rate and ion current density, slightly exceeded  $2 \times 10^{17}$  at./cm<sup>2</sup>. Fig. 1, *a*, curve 1, shows the RBS spectrum of the irradiated sample. Fig. 1, *b*, curve Ti\_1, shows the distribution profile of implanted titanium in silicon reconstructed from the spectrum data. The shape of the titanium distribution profile indicates a high-dose mode of ion implantation, when the concentration maximum appears on the irradiated target surface due to ion sputtering. Measurement of the surface temperature with a pulse pyrometer showed that

by the end of irradiation, the maximum surface temperature in the pulse reached 348 °C. The RBS spectrum and distribution profile indicate no significant titanium diffusion in silicon under these conditions.

An increase in the irradiation time to 5 min with a corresponding increase in the ion implantation fluence, while maintaining the remaining beam parameters, significantly changed the implanted titanium distribution in silicon. Fig. 1, *a*, curve 2, shows the RBS spectrum with a significant increase in the number of channels detecting titanium and a characteristic change in the channels detecting silicon. Fig. 1, *b*, curves Ti\_2 and Si\_2, shows the distribution profiles of titanium and silicon reconstructed using the SIMNRA program (version 7.03). These distributions indicate high-intensity implantation with titanium diffusion to a depth of more than 0.3 μm. The titanium concentration is quite uniform over the implanted layer depth, it is about 32 at.% and approximately coincides with the concentration level that was achieved during implantation for 0.5 min.



**Fig. 1.** Rutherford backscattering spectra (a), titanium dopant distribution over the silicon sample depth (b). 1 – 0.5 min, 2 – 5 min, 3 – 15 min

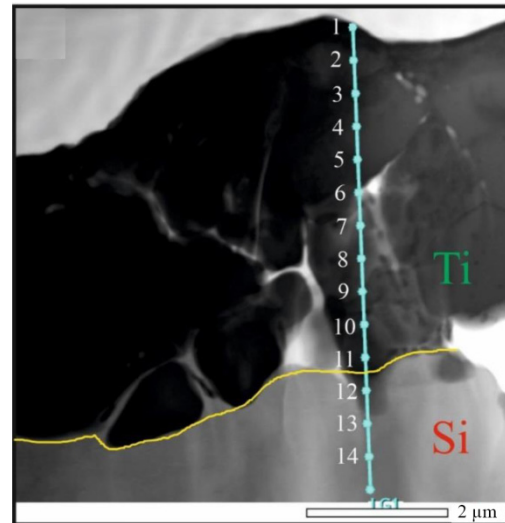
**Рис. 1.** Спектры обратного резерфордского рассеяния (a), распределение примеси титана по глубине образца кремния (b). 1 – 0,5 мин, 2 – 5 мин, 3 – 15 мин

A further increase in the irradiation time to 15 min significantly increased the ion-doped layer thickness. Irradiation was carried out under conditions of varying the pulse frequency of the accelerating potential. At the beginning of irradiation, the pulse frequency was 4 p.p.s. After the sample temperature reached 450 °C, its further stabilization was maintained by changing the pulse frequency. Fig. 1, *a*, curve 3, shows the RBS spectrum for the given irradiation mode. The spectrum of complex shape indicates a very wide titanium layer. Fig. 1, *b*, curves Ti\_3 and Si\_3, shows the spatial distributions of titanium and silicon corresponding to this spectrum. It is obvious that titanium diffuses to a depth of more than 0.7 μm, which exceeds by several orders of magnitude the projective range of implanted titanium ions, having an average energy of about 60 keV in silicon, taking into account the charge composition of the ions. It is characteristic that the ratio of titanium and silicon concentrations remains constant throughout the entire ion-doped layer thickness.

A further increase in the high-intensity ion implantation time with simultaneous energy impact of the ion beam on the silicon surface to 30 and 60 min formed the ion-doped layers with a thickness significantly exceeding one micrometer. Using alpha particles to analyze ion-doped layers by the RBS method limited the analyzed layer depth within one micrometer. The data obtained by the RBS method during implantation for 30 min showed that the titanium concentration in the doped layer with a thickness of more than one micron is 32 at.%. With an increase in the implantation time to 60 min, the titanium concentration slightly increased and reached 39 at.%.

A silicon sample irradiated with titanium ions for 60 min was studied by transmission electron microscopy.

Fig. 2 shows the data of transmission electron spectroscopy of a silicon sample irradiated with titanium ions for 60 min, over depth. The data show a doped layer with a thickness of 6 μm.



**Fig. 2.** Image obtained using a transmission electron microscope, indicating the recording of spectra

**Рис. 2.** Изображение, полученное с помощью просвечивающего электронного микроскопа, с указанием регистрации спектров

## Conclusion

Thus, this work is the first to show the possibility of realizing the synergy of high-intensity titanium ion implantation at current densities within 0.5 A/cm<sup>2</sup> with simultaneous energy impact of a submillisecond ion beam with a power density reaching 50 kW/cm<sup>2</sup> on the surface. Ultra-high-dose titanium ion implantation under conditions of partial heating of the entire sample by an ion beam and significant pulsed heating of the surface provided diffusion doping of silicon with titanium depending on the irradiation time (fluence) from fractions of a micron to 6 μm. The obtained results are of interest for developing the techniques and technologies of the deep ion doping of semiconductor materials' near-surface layers, as well as metals and alloys due to the enhancement of radiation-stimulated diffusion under conditions when the irradiated sample's deep layers are not subjected to significant temperature impact.

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#### 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-Uspexhi*. 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. DOI: 10.1007/978-3-540-71488-0.
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 of radiation upon diffusion in metals // *Journal of Nuclear Materials*. 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, Iss. 2. 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, Iss. 2. 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. Anishik V. M., Uglov V. V. Modification of Instrumental Materials by Ion and Plasma Beams. Minsk: BSU, 2003. P. 191.
19. Ryabchikov A. I., Ananin P. S., Dektyarev S. V., Sivina 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.
20. 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.