


EXAMPLE(MODEL) of submitting an article to the scientific magazine of University of Tashkent for Applied Sciences

Obtaining Manganese Silicide Films on a Silicon Substrate by the Diffusion Method

Nurullo F. Zikrillayev¹  [orcid: 0000-0002-6696-5265](#)
e-mail: zikrillaev.n@gmail.com

M.M. Shoabdurahimova¹  [orcid: 0000-0002-1879-6751](#)
e-mail: shoabduraximova.m@gmail.com

E.B. Saitov²  [orcid: 0000-0001-7691-6849](#)
e-mail: elyor.saitov@utas.uz

¹Tashkent State Technical University, Tashkent, 100095, Republic of Uzbekistan

²University of Tashkent for Applied Sciences, Tashkent, 100149, Republic of Uzbekistan

Abstract: Investigation of auto-oscillation currents in compensated silicon doped with impurity atoms of manganese, zinc, sulphur or selenium can observe several types of current instabilities with different natures and excitation conditions. The boundary regions of auto-oscillation currents such as temperature instabilities, recombination waves and injection instabilities in temperature, electric field, intensity of illumination as well as in resistivity and conductivity type of compensated silicon samples were determined. From the analysis of the results of the data obtained the possibility of using the detected auto-oscillation currents in compensated silicon for creating solid-state generators and sensors of physical quantities is shown.

Keywords: auto-oscillation currents, electric field strength, illumination, temperature, compensated silicon, amplitude, frequency, heterogeneity, photon energy.

1 Introduction.

The study of the diffusion distribution of impurities in semiconductor materials, in particular, in silicon, is necessary to elucidate the mechanism of the diffusion process, as well as to determine the role of impurity atoms on the electrical and photoelectric parameters of the source material [1–4].

The process of diffusion of impurity atoms into silicon is carried out in a relatively wide range of high temperatures ($T=800\div1300^{\circ}\text{C}$), which leads to the formation of additional thermal defects, which strongly affect the fundamental parameters of silicon. In addition, during diffusion, silicides and other metal and dielectric film layers are formed on the silicon surface. The surface state of silicon after diffusion doping with impurity atoms has not been studied in detail. Some authors, when studying the processes of diffusion of impurity atoms into a semiconductor, removed near-surface layers and did not pay attention to studying the surface properties of diffusion-doped silicon [5, 6].

This paper presents the results of a study of silicon doped with impurity manganese atoms, in which higher manganese silicides were formed on the surface. Films of manganese silicides on silicon were obtained in an evacuated quartz ampoule of evacuated high vacuum, about $P=10^{-5} \div 10^{-6}$ mm Hg. Art. [7]. Single-crystal silicon grades KDB-1 and KDB-10, $10 \times 10 \times 0.8$ mm³ in size, with the [111] crystallographic axis orientation, were used as substrates. The surface of the substrates was cleaned mechanically and chemically before loading into ampoules. The amount of manganese diffusant in the quartz ampoule was based on the calculation of the evaporation time and is sufficient for complete deposition on the silicon substrate. The samples were cooled slowly in air to room temperature without violating the vacuum level in the ampoule. The results of the study showed that by controlling the modes (temperature, time) of the technological process, it is possible to obtain films of manganese silicides with different thicknesses and

electrical parameters. These results made it possible to determine the optimal temperature and time for the formation of silicide with the desired parameters.

2 Technology for obtaining materials and research method

The electrical parameters of the obtained films were measured by the Van der Pauw method on the Ecopia HMS-3000 Hall Measurement System, and the electrical resistance and Hall coefficient were determined as a function of temperature. The Hall coefficient in all silicide layers of the obtained silicon samples, regardless of the diffusion temperature and additional thermal annealing, was positive, the concentration of current carriers was equal to $\rho \approx 10^{20} \text{ cm}^{-3}$. The dependence of the structure of the formed films on the substrate temperature was also studied. X-ray and electron microscopic methods were used to control the composition and structure of the obtained films. The phase analysis of manganese silicide films was carried out by taking X-ray reflection spectra on a DRON-1 instrument. The topology of the resulting films of manganese silicides and their elemental composition were evaluated using an X-ray microanalyzer in a Ukha-840 scanning electron microscope.

From the analysis of the obtained X-ray patterns, it was found that in the temperature range of thermal annealing $T=800\div 1100^\circ\text{C}$, polycrystalline films corresponding to the phases of higher manganese silicides (HSM) are formed. The composition of the films grown in the temperature range $T=910\div 1040^\circ\text{C}$, obtained using an X-ray microanalyzer, turned out to be close to the composition of bulk HSM (MnSi). It is established that the formed film microstructures depend on the substrate temperature ($T_{\text{subs.}}$). An amorphous film of manganese silicides formed at temperatures $T \leq 880^\circ\text{C}$, with a subsequent increase in temperatures above $T \geq 970^\circ\text{C}$, forms a single-crystal layer consisting of manganese monosilicide. The surface topology of the obtained films was studied using a scanning electron microscope. Grain sizes were determined from the surface images of manganese silicide films. For example, in the samples obtained at $T=1070^\circ\text{C}$, the grain sizes are $\sim 5\div 20 \mu\text{m}$. The electron diffraction patterns for reflection from the surface of the obtained films indicate that they mainly constitute the HSM phase, but, in addition, lines belonging to manganese monosilicide were detected.

It is known that a banded structure is observed in massive HSM crystals, this is due to the precipitation during the growth of interlayers of silicon-depleted manganese monosilicide. An analysis of the structural data suggests that the resulting films, at $T \geq 970^\circ\text{C}$, the HCM film grows in the form of grains. Thus, in the process of diffusion of manganese atoms into silicon, a flow of atoms is formed, which are deposited on substrates and, as a result of diffusion, form compounds of the $\text{Mn}_x\text{Si}_{1-x}$ type. Structural studies, depending on the technological modes of manganese diffusion, made it possible to optimize the conditions for obtaining manganese silicide films with specified electrophysical parameters.

3 Experimental results and their discussion

An analysis of literature data [8-12] shows that the phase of higher manganese silicides $\text{Mn}_{0.25}\text{Si}_{1-0.25}$ (HSM) formed at a thermal annealing temperature in the range $T=1050\div 1150^\circ\text{C}$ is the most promising material for thermoelectric generators (converters) in photoelectronics. A correlation between the phase composition of silicide films and the coefficient of anisotropic thermal EMF has been established, and the possibility of obtaining polycrystalline films approaching in electrical and kinetic parameters to a massive HSM single crystal has been shown. It was shown that technological factors such as vacuum level, substrate temperature, quartz ampoule volume, substrate surface treatment, and cooling conditions are important for the production of HCM films. Table - 1 shows the values of some physical parameters of the obtained films of higher manganese silicides in silicon, where you can see the systematic dependence of the parameters of the obtained films of manganese silicides on the substrate temperature.

Table 1.

**Physical parameters of manganese silicide films
(vacuum $P \sim 10^6 \text{ mm Hg}$, rapid cooling)**

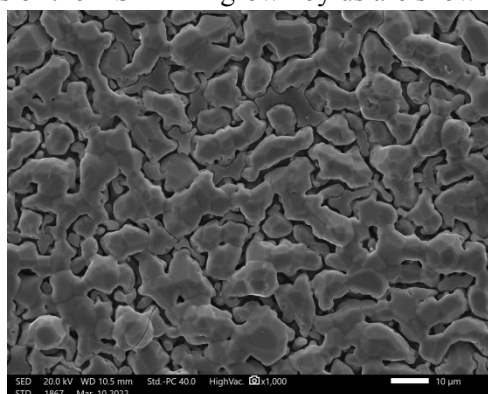
Diffusion temperature, $^\circ\text{C}$	Surface resistance, R_r, Om	Surface resistivity $\rho, \text{Ohm} \times \text{cm}$	Conversion factor, $S_v, \mu\text{V/W}$	Hall coefficient, $R_x, 1/\text{Ohm} \cdot \text{cm}^{-1}$
1120	264	0,004	266	0,065
1110	180	0,012	310	0,059

1070	165	0,023	486	0,062
1040	115	0,026	1880	0,066

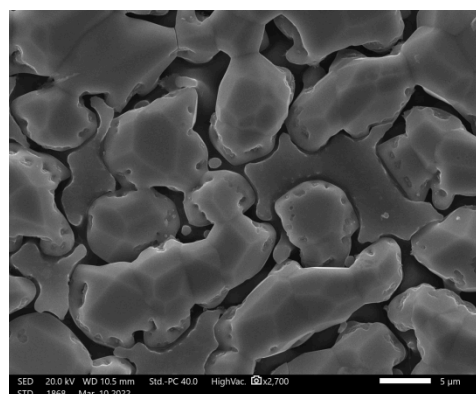
It has been established that the films grown on the basis of the initial KDB-1 and KDB-10 silicon in the temperature range $T=1040\div1070^{\circ}\text{C}$ contained predominantly the HSM polycrystalline phase; in the films grown in the temperature range $T=1100\div1200^{\circ}\text{C}$, monosilicides were the dominant phase; at temperatures below $T\leq900^{\circ}\text{C}$, the films were amorphous.

The study of the phase composition of the films over the thickness showed that during the evaporation of impurity Mn atoms in a quartz ampoule with a diameter of 10 - 12 mm in vacuum, $P\approx10^{-5}$ mm Hg. Art. in the temperature range $T=1050\div1100^{\circ}\text{C}$ with subsequent slow cooling of the samples, polycrystalline films were formed, which near the silicon surface consisted of a mixture of two phases - manganese monosilicide and higher manganese silicides with a predominance of monosilicide, in the upper layer there are mainly HSM phase layers. Interesting scientific results were obtained [13,14] when conducting diffusion in a quartz tube of evacuated vacuum $P\approx10^{-2}$ mm Hg. Art. during the entire process of diffusion of manganese atoms into silicon and subsequent slow cooling in air. Under these conditions, films were formed consisting of HSM grains up to 10 μm thick. Additional thermal annealing of the samples in the temperature range $T=350\div800^{\circ}\text{C}$ led to the enlargement of the formed HSM grains. It has been established that such films have a high conversion coefficient [15], and anisotropic properties of kinetic and thermoelectric parameters corresponding to the parameters of bulk HSM single crystals have been found in them.

When studying the topology of the silicon surface with films of higher manganese silicides, it was found that, on average, the grain size is 4–5 μm , although individual crystallites reach up to ≈10 μm . Micrographs of the HSM film grown by us are shown in Fig. 1.



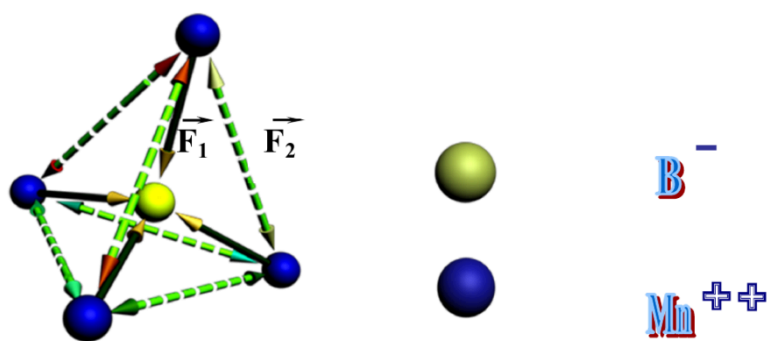
a) at a resolution of 10 μm .



b) at a resolution of 5 μm .

Rice. Fig. 1. Electron diffraction patterns "for reflection" from a polycrystalline film of manganese silicides on silicon.

An analysis of the results of complex studies of the physical properties of higher manganese silicide on the silicon surface, carried out by various modern methods, shows that all numerous crystalline structures have a tetragonal syngony (Fig. 2) and exhibit a superperiodic structure in the direction of the c axis (c is the main crystal growth axis of silicon). The HSM crystal lattice is usually described on the basis of the concept of a "hard" manganese sublattice and a relatively "soft" silicon sublattice. In the manganese sublattice, for all detected HSM phases, one can single out a subcell or nanocluster containing four Mn atoms with a lattice constant parameter along the c axis, which is approximately equal to 4.36 Å. Silicon atoms in adjacent layers, perpendicular to the c axis, are arranged in pairs in adjacent squares, which also makes it possible to isolate a subcell of four manganese atoms in the silicon sublattice (Fig. 2).



Rice. 2. Structure of a nanocluster of manganese atoms in a silicon lattice $[(Mn)_4^{+8}B^{-}]^{+7}$.

After analyzing the main regularities of the crystal structure of the studied phases, based on the results obtained, it was concluded that, in reality, the set of structures that can arise in the homogeneity region of HSM is much wider, since a change in the composition of HSM does not lead to the formation of structural defects, but only to a change in the ratios of characteristic sublattice parameters along the *c* axis. A universal method of description was proposed and all commensurate structures located in the domain of HSM existence were calculated.

4 Conclusions

The crystal axis with the orientation of the tetragonal cell of the manganese sublattice and the pitch of the helix along which the silicon atoms are arranged are incommensurable. It is known that the interaction of periodic subsystems with mutually incommensurable periods leads to the formation of incommensurate structures, which are something intermediate between crystalline and disordered structures. However, despite the absence of periodicity along the axis with any finite period, the diffraction patterns from such structures contain reflections with a small width.

Electron microscopic studies have confirmed the presence of incommensurate superstructures on the silicon surface of higher manganese silicides Mn_xSi_{1-x} . In [16], the authors analyzed the diffraction effects appearing in electron diffraction patterns from crystals with incommensurate modulated structures and orientational anomalies associated with them.

An analysis of the results obtained using a transmission electron microscope showed that, in the grown HSM films with grain sizes on the order of $\sim 10 \mu m$, manganese monosilicide can be present as a polycrystalline phase on the silicon surface as a crystallite.

As a result of the studies carried out, the mechanism of manganese diffusion into silicon was established, leading to the formation of higher manganese silicides on the silicon surface. It has been established that the films grown on the silicon surface consist of HSM grains with the predominant orientation of the *c* axis perpendicular to the substrate. On the surface of HSM crystallites, manganese monosilicide is present as a polycrystalline phase. Such films have a high conversion coefficient, anisotropic properties of kinetic and thermoelectric parameters are found in them, depending on the direction of the crystallization axis of the silicon substrate.

The possibility of creating efficient thermopiles based on the obtained structures of the type $Mn_xSi_{1-x} - Si < Mn > - Mn_xSi_{1-x}$ based on silicon, the operating parameters of which are not inferior to existing thermopiles, and sometimes have certain advantages, is shown.

The work was financially supported by the Ministry of Innovative Development of the Republic of Uzbekistan within the framework of the project F-OT-2021-497 - "Development of the scientific foundations for the creation of solar cogeneration plants based on photovoltaic thermal batteries".

References

1. Boltaks B.I. Diffusion and point defects in semiconductors. Science, Leningrad. 1972, p. 384.
2. Milvidsky M.G., Chaldyshev V.V. Nanosized atomic clusters in semiconductors - a new approach to the formation of material properties. Physics and technology of semiconductors, 1998, vol. 32 no. 5, p. 513-522.
3. Boltaks B.I., Bakhadirkhanov M.K., Gorodetsky S.M., Kulikov G.S. Compensated silicon. Leningrad, Nauka, 1972, p. 122.
4. Zainobiddinov S. Physical foundations of the formation of deep levels in silicon. Tashkent, Fan, 1984, p. 160.

5. Tasnin A.A., Tishkovsky E.G. Formation of complexes associated with selenium atoms in silicon. *Physics and Technology of Semiconductors*, 2002, v. 36, V. 6, p. 641-649.
6. Bakhadirkhanov M.K., Abdurakhmonov B.A. physical and technological foundations for the formation of clusters of impurity atoms in silicon. Report of the Academy of Sciences of the Republic of Uzbekistan, 2013, No. 3, p. 29-33.
7. Zikrillayev N.F., Ayupov K.S., Shoabdurahimova M.M. Kurbonaliev K.K. Program for calculating the distribution of diffusion of manganese atoms into silicon from boron atoms on its surface. Intellectual Property Agency under the Ministry of Justice of the Republic of Uzbekistan. No. DGU 16201, 2022 y.
8. Risbaev A.S., Normuradov M.T., Nasriddinov S.S., Adamboev K.A. Properties of silicide films created by low-energy implantation of metal ions into silicon. *Radio engineering and electronics* 1997, v. 42, No. 1, pp. 125-128.
9. Risbaev A.S. Thin nanoscale silicide films: preparation and properties. Monograph, Tashkent 2013
10. A. S. Risbaev, A. A. Risbaev, Zh. B. Khuzhanieyev, A. M. Rakhimov, and L. Kh. On the formation of new surface superstructures during the formation of thin nanoscale films of silicides. *Uzbek Journal of Physics*. 2013 Vol. 15, N1-2, pp. 16-32.
11. Samsonov G.V., Dvorina L.A., Dud B.M. Silicides. Moscow, Metallurgy, 1979, p. 272.
12. Bakhadirkhanov M.K., Kamilov T.S., Khusanov A.Zh. et al. Investigation of the influence of the layer surface on the photoelectric properties in the structures of higher manganese silicide (HSM) Si-<Mn>-M. Surface. X-ray synchronous and neutron studies. 2002, No. 6. p. 100-103.
13. Risbaev A.S., Kamilov T.S., Klechkovskaya V.V., Orekhov Igamov B.D., Bekpulatov I.R. The Influence of Structural Defects in Silicon on Formation of Photosensitive Mn_4Si_7 -Si<Mn>- Mn_4Si_7 and Mn_4Si_7 -Si<Mn>-Mn Heterostructures. *Applied Solar Energy*, 2019. Vol. 55, № 6 pp. 380-384.
14. Risbaev A.S., Bekpulatov I.R. Thermoelectric converters of infrared radiation based on films of higher manganese silicide. Monograph: "Ziyo print" 2020 140p.
15. V.V. Klechkovskaya, A.S. Risbaev, T.S. Kamilov, I.R. Bekpulatov, B.D. Igamov, I.Kh. Turapov. Formation of thin Mn_4Si_7 films on various substrates by magnetron sputtering and pulsed laser deposition. *Uzbek Physics Journal*, 2021 Vol. 22, no. 3, pp. 43-48.
16. Risbaev A.S., Bekpulatov I.R., Khairiddinov B.Z., Khuzhanieyev Zh.B. Structure and physical properties of nanosized films of metal silicides. Monograph. Tashkent. "Adad plus" 2017, 230 pp.
17. N. F. Zikrillayev., S.A. Tachilin. E.B.Saitov. "Problems of modern engineering" Andijan May 16- 17, 2013
18. E.B. Saitov, O.O. Ponomareva, H. Turaev. International scientific conference. Karshi April 15 – 17, 2016.
19. Zikrillayev N.F., Abdurakhmonov B.A., E.B. Saitov. "Innovations in materials science" (Tashkent-2014).
20. Kovalev F.I., Usachev V.A. M.: Radio and Communication, 2012 Chen Jiaheand etc., (RRL)-5, no. 8 (2011): 277-279.
21. Sapaev, I., Saitov, E., Zoxidov, N., Kamanov, B. IOP Conference Series: Materials Science and Engineering, 2020, 883(1), 012116
22. Javoxir Toshov, Elyor Saitov. E3S Web of Conferences RSES 139, 01087 (2019) pp. 1-4, 2019.
23. M.K.Bakhadyrkhanov, S.A.Valiev, N.F.Zikrillayev, S.V.Koveshnikov, E.B.Saitov, S.A.Tachilin. *Applied solar energy* 52 (4), pp.278-281, 2016.
24. Sh.A.Faiziev and Yu.B.Sobirov. *Applied Solar Energy*, 2017, Vol. 53, No. 1, pp. 57–60.
25. Krivtsov V. S., Oleynikov a.m. et al. Textbook. Inst."Sevast: Sevast. NATs. tehn. Univ., 2003. -400 p.
26. Elyor Saitov. *IJARSET* Vol. 3, Issue 5, May 2016.
27. Elyor Bahriddinovich Saitov. *JMSChE*, 2016, 4, 30- 35.
28. M.K.Bakhadyrkhanov., S.A.Valiev., N.F.Zikrillayev., S.V.Koveshnikov., E.B.Saitov., S.A.Tachilin. *Geliotekhnika* No. 4 pp. 28-32, 2016.26.
29. I.Sapaev, E.B.Saitov, N.Zoxidov and B.Kamanov. *Conmechhydro – 2020 IOP Conf. Series: Mat. Sci. Eng.* 883(2020) 012116.
30. Saitov E.B, Toshov J.B, Umarov Sh.B., Fayzullayev B.H., Abdullabekov I.A, Nasriddinov B.A. *JCR*, ISSN - 2394-5125VOL 7, ISSUE 15, 2020.
31. Saitov Elyor Bahriddinovich, Pulatov Abror Obidovich. *JCR*, ISSN - 2394-5125 VOL 7, ISSUE 15, 2020.
32. Zikrillayev Nurilla, Saitov Elyor. Monograph - LAP LAMBERT Academic Publishing. 2019, ISBN:987-620-0-50311-4.
33. Nurullo Zikrillayev, Elyor Saitov. *Sbor. Mat. Mej. Nau. –ret. Onl. Konf.*, 28-may 2020 g, st. 53-60.
34. Elyor Saitov, Javoxir Toshov, Shuxrat Umarov, Boxodir Nasriddinov. *Sbor. Mat. Mej. Nau. – ret. Onl. Konf.*, 28-may 2020 g, st. 329-339.
35. Zikrillayev N.F., Saitov E.B. *Vestnik TashGTU*, 2018; №1. S. 51-56.
36. B. A. Abdurakhmanov, M. K. Bakhadirkhanov, H. M. Iliyev, Saitov E.B. and etc. *Nanoscience and Nanotechnology* 2014, 4(3): 41-43.
37. Abdurakhmanov B.A., Bakhadirkhanov M.K., Saitov E.B. and etc. *Nanoscience and Nanotechnology*, Vol. 4, No. 2, 2014. pp. 23-26.
38. Iliyev X.M., Saitov E.B., Saydaliyev S.X., Tachilin S.A. *Prob. ener- i res. TashGTU*, 2014, №1-2. s. 183- 185.
39. Sapaev, I., Saitov, E., Zoxidov, N., Kamanov, B. IOP Conference Series: Materials Science and Engineering, 2020, 883(1), 012116

40. Toshov, J., Saitov, E. E3S Web of Conferences, 2019, 139, 01087
41. Bakhadyrkhanov, M.K., Valiev, S.A., Zikrillayev, N.F., Saitov, E.B., Tachilin, S.A. Applied Solar Energy (English translation of *Geliotekhnika*), 2016, 52(4), c. 278-281
42. Saitov, E.B., Kodirov, Sh., Beknazarova, Z.F., Nortojiyev, A., Siddikov, N. AIP Conference Proceedings, 2022, 2432, 020015
43. Saitov, E.B., Sodiqov, T.B. AIP Conference Proceedings, 2022, 2432, 020022
44. Saitov, E.B., Kodirov, Sh., Kamanov, B.M., Imomkulov, N., Kudenov, I. AIP Conference Proceedings, 2022, 2432, 040036
45. Zikrillayev, F., Saitov, E.B., Toshov, J.B., Ilyasov, B.K., Zubaydullayev, M.B. AIP Conference Proceedings, 2022, 2432, 020021
46. Ergashov, Y.S., Donaev, S.B. (2022) Journal of Nano- and Electronic Physics, 14 (4)
47. Sergeevna, V.Y., Stefan Lilia, S., Nikolaevna, V.S., Yokub Suvonovich, E. Conference on Energy Efficiency and Agricultural Engineering, EE and AE 2022 - Proceedings.
48. Zoryna, T.G., Aliaksandrovich, S.A., Valeeva, Y.S., Kalinina, M.V., Ilikova, L.E., Suvonovich, E.Y. (2022) 2022 8th International Conference on Energy Efficiency and Agricultural Engineering, EE and AE 2022 - Proceedings.
49. Ergashov, Y., Donaev, B., Khudainazarov, S., Normuminov, J. (2021) E3S Web of Conferences, 264.
50. Yokub, E., Boltakhodja, U. (2020) E3S Web of Conferences, 178.
51. Umirzakov, B.E., Tashmukhamedova, D.A., Tursunov, M.A., Ergashov, Y.S., Allayarova, G.K. (2019) Technical Physics, 64 (7), pp. 1051-1054.
52. Ergashov, Y.S., Umirzakov, B.E. (2018) Technical Physics, 63 (12), pp. 1820-1823.
53. Ergashov, Y.S., Umirzakov, B.E. Journal of Surface Investigation, 12 (4), pp. 816-818.
54. Ergashov, Y.S., Umirzakov, B.E. Journal of Communications Technology and Electronics, 62 (6), pp. 612-615.
55. Ergashov, Y.S. Technical Physics, 62 (5), pp. 777- 780.
56. Ergashov, Y.S., Tashmukhamedova, D.A., Umirzakov, B.E. Journal of Surface Investigation, 11 (2), pp. 480-484.
57. Ergashov, E.S., Isakhanov, Z.A., Umirzakov, B.E. Technical Physics, 61 (6), pp. 953-955.
58. Ergashov, Y.S., Tashmukhamedova, D.A., Djurabekova, F.G., Umirzakov, B.E. Bulletin of the Russian Academy of Sciences: Physics, 80 (2), pp. 138-140.
59. Mukhtarov, Z.E., Isakhanov, Z.A., Umirzakov, B.E., Kodirov, T., Ergashev, E.S. Technical Physics, 60 (12), pp. 1880-1883.
60. Ergashov, Y.S., Tashmukhamedova, D.A., Rabbimov, E. Journal of Surface Investigation, 9 (2), pp. 350-354.