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ELECTROPHYSICAL AND THERMOELECTRIC PROPERTIES AND CRYSTAL STRUCTURE OF THE FORMED Mn_4Si_7 THIN VACUUM COATING

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Abstract. The necessary information on the formation of high manganese silicide (Mn_4Si_7) coating by magnetron sputtering method is presented in this work. The technology and basic modes of creating the necessary targets for a magnetron sputtering device are presented. Targets were created by adding silicon and manganese powders in the required amount and heating them under vacuum conditions at high temperature and pressure. Thin silicide films (thin coatings) of different thicknesses were formed on the surface of silicon dioxide from the produced targets using the method of magnetron sputtering. The electrophysical and thermoelectric properties of the produced films were studied using physical and optical methods. Due to the change in the structure of the coatings during subsequent heat treatment, the Seebeck coefficient noticeably increases. The composition and structure of vacuum coatings with a thickness of about 100-150 nm depend on the parameters of their formation, as well as subsequent treatments. Due to the change in the structure of the coatings during subsequent heat treatment, the Seebeck coefficient noticeably increases.

Keywords: Thin coating, Hall constant, electrical conductivity, nanostructure, volume concentration, resistivity be used for indexing purposes.

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1 Introduction

At present, interest is growing in the problem of saving energy resources and the use of heat-sensitive materials (metal silicide's, in particular, higher manganese silicide - Mn_4Si_7). Metal-silicide films have been extensively re-searched and various methods of their formation are available, and there is a large literature on the subject (Umirzakov et al., 2019; Isakhanov et al., 2015; Isakhanovet et al., 2020; Donaev et al., 2022; Bekpulatov et al., 2022; Normuradov et al., 2021; Rysbaev et al., 2017; Kamilov et al., 2015; Orekhov et al., 2022). Coatings and target of Mn_4Si_7 are important for practical applications in micro- and nano electronics, optoelectronics, micro sensors, as well as for the creation of thermo generators and other thermo elements. The creation of new devices based on thin coatings of higher manganese silicide with desired properties requires a detailed study of their micro- and nanostructure, phase and chemical composition, as well as solid-phase reactions occurring in the Mn-Si system at elevated temperatures. Data on the structural diversity of higher manganese silicide's have come to light only recently. Small changes in the composition and structure quite noticeably affect their crystal structure, which was not taken into account when studying the physical properties of the Mn–Si system. At the moment, according to leading scientists of the world, one of the most promising ways to improve the efficiency of thermoelectric converters is the creation of nanostructured materials. Nano structuring opens up new possibilities for modifying the transport properties of materials by changing their structure. The parameters of manganese silicide's were studied in a number of works (Bekpulatov et al., 2023, 2024; Umirzakov et al., 2024; Jabarov et al., 2015; Khallokov et al., 2024), which show their dependence on physical and technological factors of coating formation.

Studies of Mn_4Si_7 coatings of different thicknesses have shown that magnetron deposition practically does not change the composition of the coating in comparison with the composition of the target. The technology and basic modes of creating the necessary targets for a magnetron sputtering device are presented. Targets were created by adding silicon and manganese powders in the required amount and heating them under vacuum conditions at high temperature and pressure. Thin silicide films (coatings) of different thicknesses were formed on the surface of silicon dioxide from the produced targets using the method of magnetron sputtering. Studies of the transmission, absorption, and reflection coefficients of coatings in the visible region of the spectrum have shown that for the Mn_4Si_7 coating, the reflection coefficient is practically the same at all wavelengths (Imanova et al., 2021; Aliyev et al., 2021; Aliyeva et al., 2022; Normuradov et al., 2022).

2 Materials and methods

Two methods of Mn_4Si_7 silicide sample preparation were considered.In the first method, pure single-crystal silicon and manganese were ground into a powder with a size of about 100 μm in a mill (HERZOG HSM-100P) for subsequent electric Spark Plasma Sintering (SPS) of the samples.The crushed materials were mixed in the ratio of Mn - 52.89% and Si - 47.1% (by mass), after which a Mn_4Si_7 silicide sample (SPS silicide) was made in the form of a disk up to 76 mm in size on the SPS. For this, a pressing force of $6.5{\cdot}10^4$ N was used for 2 hours in a vacuum of 10^{-2} Torr at a temperature of 1050 °C (Fig. 1a).

The second methodfor fabrication Mn_4Si_7 silicide sample consist of two stages. The first is included silicide synthesizing by means of high-temperature diffusion Si(111) furnace to obtain Mn_4Si_7 crystal samples with linear dimensions 10×10×5 mm (Si(111) crystal). Manganese atoms settled on the substrate from the vapor-gas phase and interacted with silicon atoms, forming nuclei and islands of manganese silicide. Subsequently, small islands increased due to the migration of molecules along the substrate and formed large islands. As a result of the diffusion transition of silicon and Mn_4Si_7 molecules into islands, stepped craters appear in some places of the base, which increase and form a continuous coating. When manganese and silicon interact at a temperature of 1100°C, it was possible to observe the formation of small Mn_4Si_7 islands 20-50 nm in size. Subsequently, these islands became larger (up to 1.0 μm), had an oval or crystalline shape, and passed into a single-crystal structure. As a result of combining large silicon-based islands, a single Mn_4Si_7 layer $1 - 5\mu m$ thick was formed (Fig. 1b). In the second step, Mn_4Si_7/Si(111) crystals synthesized by diffusion were placed on the disk target in such a way that the entire front surface of the target with a diameter of 110 mm was covered with 10×10 mm crystals.

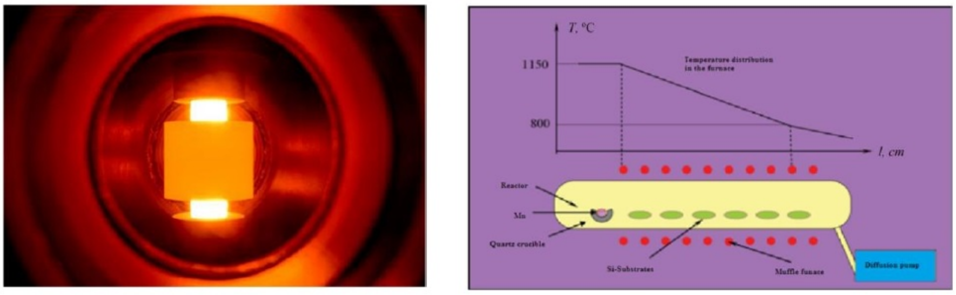


Figure 1: Preparation processes of Mn_4Si_7 samples. a) SPS method, b) Diffusion method

SiO_2/Si structures were chosen as the basis for the study. Magnetron sputtering was used to prepare two series of Mn_4Si_7 coating samples. The first sample was created based on SPS. A disk-shaped Mn_4Si_7 silicide was installed on the cathode of the magnetron sputtering device of the EPOS-PVD-DESK-PRO vacuum device. The process of magnetron sputtering was carried out after reaching the initial vacuum level of the order of 10^{-5} Torr. The SiO_2/Si substrates were treated by heating up to 300°C in order to remove organic substances from the substrate surface.Sputtering was carried out at an argon pressure of the order of (3-4)·10^{-3} Torr, a voltage of 450-550 V, and a discharge current of 200-300 mA. The thin coating time was 2-10 minutes. In one vacuum cycle, 3 structures were sequentially processed.

The second sample was created on the basis of Diffusion under high temperature conditions. The sample created on the basis of diffusion was mounted on a magnetron sputtering device in a modernized working chamber of the UVN-75R-1 device. Sputtering was carried out at a pressure of pure argon on the order of (3-4)·10^{-3} Torr, a voltage of 550-900 V, and a discharge current of up to 200 mA. The time for coating the movable disk equipment with samples was 2-5 minutes.

3 Results and discussion

Define abbreviations and acronyms the first time they are The morphology, microstructure, and chemical composition of thin coatings grown on the EPOS-PVD-DESK-PRO vacuum setupand the upgraded UVN-75R-1 setupwere studied using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The electrical properties of the Mn_4Si_7 coating and the Hall constant were determined on an HMS-3000. The chemical composition of the thin layer and the formation of bonds were monitored using a Raman spectrometer (Igamov et al., 2024).

Figure 2 is shown the morphology and chemical analysis results of the samples obtained magnetron sputtering method. Analysis of Mn_4Si_7coating samples diffraction images comparing their distances between planes and angles between inverted lattice vectors with the parameters of the known Mn_4Si_7 coating, revealed that the resulting coatings have a tetragonal structure (P4-c2) with unit cell constants $a = 0.552$ nm, $c = 1.751$ nm (fig. 3). The thickness of the Mn_4Si_7 coating obtained by the SPS method is 146 nm, Fig. 4a. When examining the composition of the SPS sample before magnetron sputtering and the coating obtained by SEM, the results were consistent (Fig. 4b).

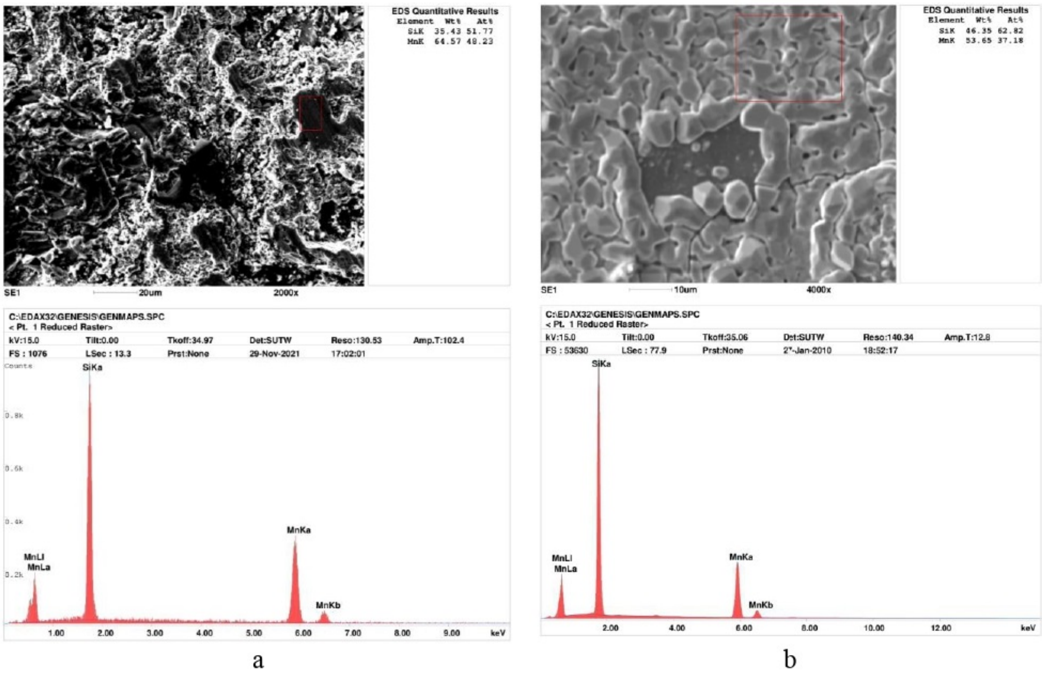


Figure 2: (a) Mn_4Si_7 Morphology and composition of SPS (b) diffusion prepared sample

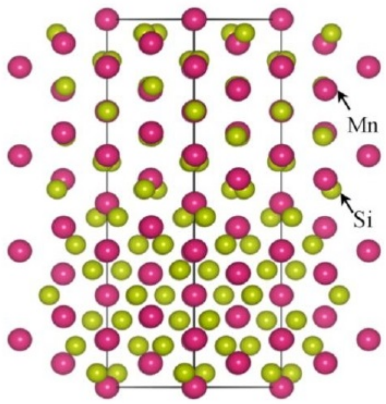


Figure 3: Atomic structure Mn_4Si_7

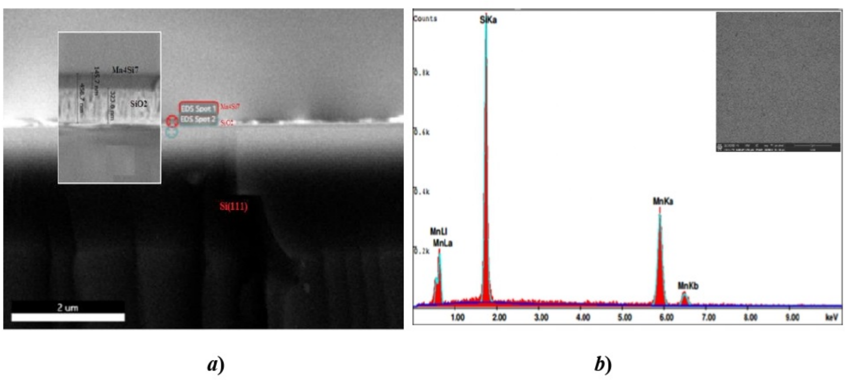
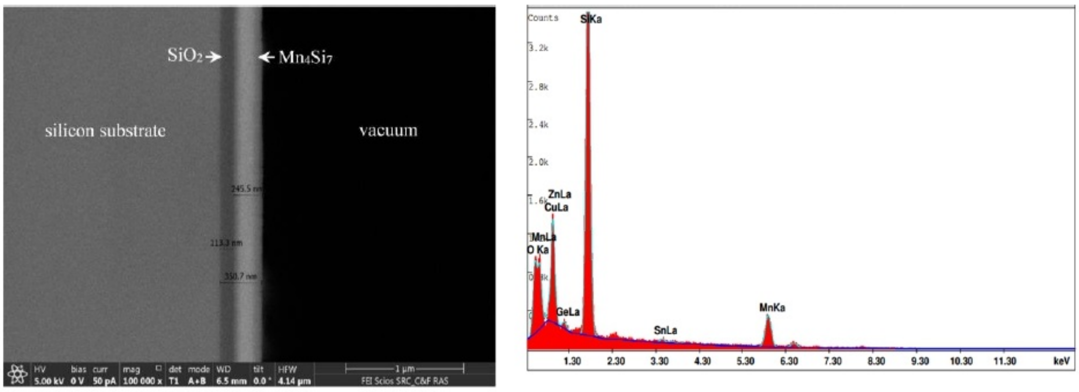


Figure 4: Structure (a) and composition (b) of a 146 nm thick Mn_4Si_7 coating

Table 1: Mn_4Si_7 crystal and vacuum thin coating composition prepared by diffusion method

EDS Mn_4Si_7 diffusion method crystal Quantitative Results			EDS Mn_4Si_7 thin coating Quantitative results		
Element	weight %	at. %	Element	weight %	at. %
SiK	46.35	62.82	CK	95	86
MnK	3.65	37.18	OK	4.59	37
			CuL	16.94	9.63
			GeL	1.07	0.53
			SiK	35.72	45.92
			SnL	2.16	0.66
			MnK	36.57	24.03

Figure 5 shows the structure and composition of the Mn_4Si_7 coating obtained by the diffusion method. The thickness of the Mn_4Si_7 coating obtained by the diffusion method is 245.5 nm, Fig. 5a. The chemical composition of the Mn_4Si_7 target and comparative data on the thin coating obtained from this target are shown in table 1.



a) *b)*

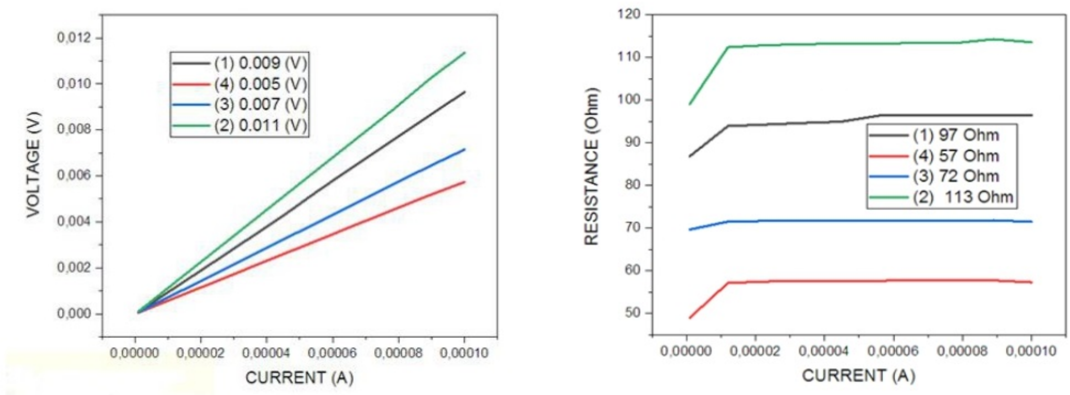
Figure 5: Structure (a) and composition (b) of the Mn_4Si_7 coating with a thickness of 245.5 nm obtained by the diffusion method

As can be seen from table 1, the target coatings obtained by the diffusion method contain compounds derived from the alloys used to connect the Mn_4Si_7 crystal to the disc. When Mn_4Si_7 crystals are attached to the surface of a brass disk 110 mm in diameter, cracks are observed between the crystals, and Ar^+ ions sputter these impurities. In addition, local heating and additional thermal evaporation of impurities are possible. From the energy dispersive X-ray diffraction analysis, it can be seen that the elements Sn, Cu, O, C, Zn, Ge are present in the formed coating (Fig. 5b).

The electrophysical properties and the Hall constant were determined for the Mn_4Si_7 coating grown on the EPOS-PVD-DESK-PRO setup from a crystal prepared by the SPS method (Table 2). The results showed that the electrophysical properties of target samples and thin coatings formed by magnetron sputtering correlate with each other, although they differ quantitatively. Figure 6 shows the U/I and R/I graphs of the samples described in table 2 obtained using the HMS-3000 device.

Table 2: Electrophysical parameters of target samples and Mn_4Si_7 coatings

Samples	(Sample 1) target Mn_4Si_7	(Sample 1) Mn_4Si_7	(Sample 2) target Mn_4Si_7	(Sample 2) Mn_4Si_7
Parameters	Samples of Mn_4Si_7 obtained by the SPS method		Samples of Mn_4Si_7 obtained by the diffusion method	
	before sputtering in the magnetron	Thin coating	before sputtering in the magnetron	Thin coating
Resistivity, Ohm·cm	$7.826{\cdot}10^{-4}$	$6.409{\cdot}10^{-4}$	$2.075{\cdot}10^{-3}$	$7.803{\cdot}10^{-4}$
Constant Hall, cm^3/C	$1.285{\cdot}10^{-3}$	$1.597{\cdot}10^{-3}$	$1.370{\cdot}10^{1}$	$5.035{\cdot}10^{-4}$
Conductivity, 1/Ohm·cm	$1.278{\cdot}10^{3}$	$1.560{\cdot}10^{3}$	$4.819{\cdot}10^{2}$	$1.282{\cdot}10^{3}$
Surface concentration, cm^{-2}	$1.215{\cdot}10^{17}$	$9.770{\cdot}10^{16}$	$4.556{\cdot}10^{16}$	$3.1{\cdot}10^{17}$
Volume concentration, cm^{-3}	$4.859{\cdot}10^{21}$	$3.908{\cdot}10^{21}$	$4.556{\cdot}10^{17}$	$1.24{\cdot}10^{22}$
Carrier mobility, cm^2/V·c	$1.642{\cdot}10^{0}$	$2.492{\cdot}10^{0}$	$6.620{\cdot}10^{3}$	$6.453{\cdot}10^{-1}$



a) *b)*

Figure 6: Shows the U/I and R/I graphs of the samples described in table 2 obtained using the HMS-5000 device

Of interest is the dependence of the electrophysical parameters of coatings on additional heat treatment. The Mn_4Si_7 coating obtained by the SPS method with a thickness of 146 nm was heated in the temperature range from 300 K to 800 K and then cooled to room temperature. In this case, the resistance decreased from 250 Ω to 25 Ω and remained stable during cooling, which, in turn, indicates a change in the properties of this Mn_4Si_7 coating. The Seebeck coefficient was state about 1-4 $\mu V/K$ during heated from 300 K to 620 K. As the temperature changes from 620 K to 800 K, an increase in the Seebeck coefficient to 22 $\mu V/K$ was observed. It was found that during cooling, the Seebeck coefficient increase from 22 $\mu V/K$ to 30 $\mu V/K$. (Fig. 7).

The chemical composition of the thin coating and the formation of a chemical bond was observed using Raman scattering (Raman spectra). As a result of the research, it was determined that there is a chemical change between Mn and Si, possibly due to the appearance of coating nanoclusters. Figure 8 shows the emerging Raman peaks in the region 963.1 cm^{-1}, 1342.17 cm^{-1}, 1592.15 cm^{-1}. When comparing the Raman peaks from the thin Mn_4Si_7 coating (284.549 cm^{-1} 1.347.174 cm^{-1}, 633.455 cm^{-1}), the peaks obtained from the SiO_2/Si substrate (1342.17 cm^{-1}, 1592.15 cm^{-1}).

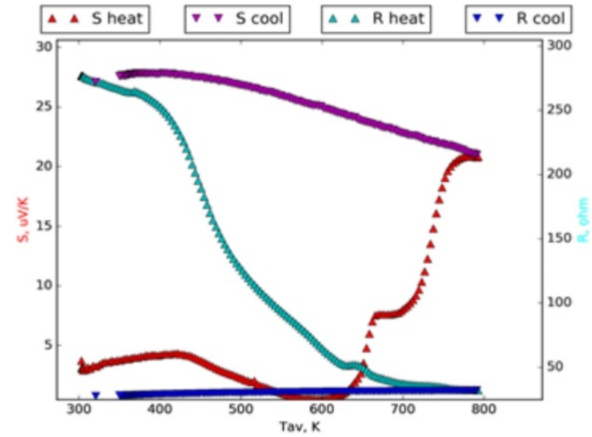


Figure 7: Seebeck coefficient (S) and resistance (R) for Mn_4Si_7 coating obtained by SPS method depend on temperature

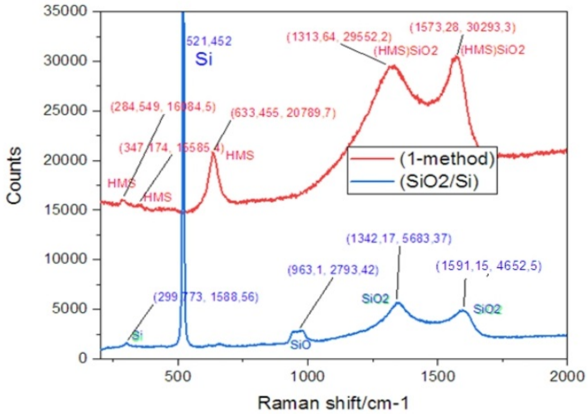


Figure 8: Comparison of Raman peaks of the first sample and SiO_2/Si substrates

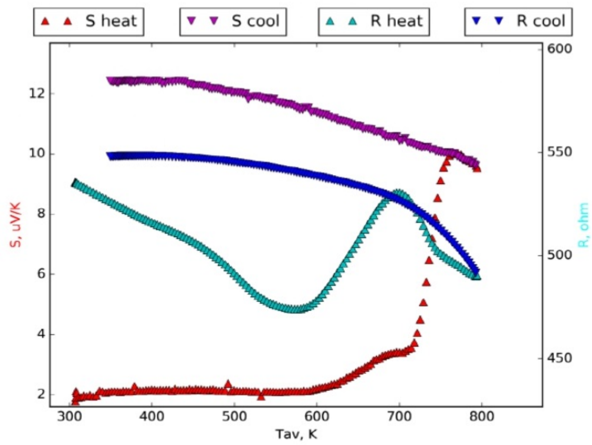


Figure 9: Seebeck coefficient (S) and resistance (R) of the sample 2 as a function of temperature

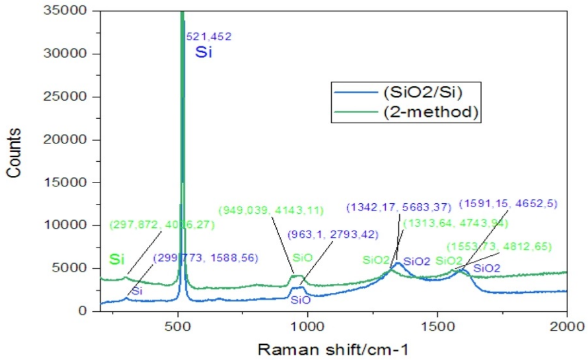


Figure 10: Raman peaks of the sample 2 and SiO_2/Si substrate

The Mn_4Si_7 coating with a thickness of 113.3 nm, obtained according to the sampl 2, when heated from 300 K to 800 K, changes the resistance from 500 Ohm (± 5%) to 525 Ohm (± 5%). An increase in the Seebeck coefficient from 2 μV/K to 4 μV/K upon heating from 300 K to 710 K and an increase in the Seebeck coefficient from 4 μV/K to 11 μV/K upon a change in temperature from 710 K to 800 K are explained by the ordering of nanoclusters. It was found that during cooling, the Seebeck coefficient changes from 11 $\mu V/K$ to 12.5 $\mu V/K$ (Fig. 8)

As a result of the analysis obtained using a spectrometer, it was found that due to the multicomponent composition of the coating with a thickness of 113.3 nm (Sn, Cu, O, C, Zn, Ge), a coating typical of metals is formed. When comparing the Raman peaks obtained from the SiO_2/Si substrate (299.773 cm^{-1} 521.452 cm^{-1}, 963.1 cm^{-1},1342.17 cm^{-1}, 1592.15 cm^{-1}) (second sample), there are no significant changes discovered. The composition of the obtained sample is typical for metals, which indicates that chemical bonds are not formed due to the composition of different metals in the thin layer. Therefore, the Raman peaks of the SiO_2/Si substrate are observed in this figures 9-10.

4 Conclusions

Comparative studies of the electrophysical parameters of samples 2 of Mn_4Si_7 crystals obtained by plasma welding and sintering in a furnace with the parameters of thin vacuum coatings samples 1 of these materials show similar physical characteristics and have thermal sensitivity. The composition and structure of vacuum coatings with a thickness of about 100-150 nm depend on the parameters of their formation, as well as subsequent treatments. Due to the change in the structure of the coatings during subsequent heat treatment, the Seebeck coefficient noticeably increases.

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