Investigation of optical and electrophysical properties of Mn$_4$Si$_7$ coatings of different thickness

B.D. Igamov$^1$, I.R. Bekpulatov$^2$, G.T. Imanova$^{3,4,5}$, A.I. Kamardin$^1$, D.A. Normurodov$^2$

Studies of Mn$_4$Si$_7$ 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$_4$Si$_7$ coating, the reflection coefficient is practically the same at all wavelengths. It was found that the Seebeck coefficient varies from 16 µV/K to 22 µV/K, and the resistance decreases from 77 Ω to 20 Ω with increasing thickness of the thin Mn$_4$Si$_7$ coating.

Keywords: transmission, absorption and reflection coefficients of coatings, Seebeck coefficient, thin coating, nanostructure, resistivity.

Introduction

According to the world’s leading scientists, the best way to increase the efficiency of thermoelectric converters is to create nanostructured materials. The control of the electronic structure by nanostructuring makes it possible to noticeably change their thermoelectric and other parameters of materials. Currently, electricity is mainly obtained by burning hydrocarbons, hydropower and nuclear power. In recent years, much attention has been paid to the use of alternative sources of electricity. An important problem is to increase the energy efficiency of the economy and the social sphere, the introduction of energy-saving technologies and the development of renewable energy sources. Based on this, the creation of new nanostructured film materials, the study of their thermoelectric and transport properties is one of the urgent tasks of alternative energy and electronics.

At present, interest is growing in the problem of saving energy resources and the use of heat-sensitive materials (metal silicides, in particular, higher manganese silicide - Mn$_4$Si$_7$). Metal-silicide films have been extensively research and various methods of their formation are available, and there is a large literature on the subject [1-11]. Coatings and bulk crystals of Mn$_4$Si$_7$ are important for practical applications in micro- and nanoelectronics, optoelectronics, microsensors, as well as for the creation of thermogenerators and other thermoelements. The creation of new devices based on 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 silicides 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 MnSi system.

I. Method of processing and research

To form Mn$_3$Si$_7$ in the form of a disk, pure single-crystal silicon and manganese were ground to a powder in a special mill of the HERZOG HSM-100P type. Then a vacuum chamber for electric spark plasma welding (SPW) model PH 550-N700, SUS 304, special (graphite or tungsten carbide) molds was used. A mixture containing 52.89% Mn and 47.1% Si (by mass) after mixing was placed in a mold. Then the pressing process was carried out at a vacuum degree of about 10$^{-2}$ Torr for 2 hours, with a pressing force of up to 7·10$^4$ N at an average temperature of 1050°C. The generated pressure reached 0.15–0.65 MPa. The power of electric spark plasma welding varied in the range of 30–90 kVA (voltage about 15 V, current up to 5000 A). The DC pulse frequency was 20–40 kHz. During plasma heating of Mn and Si, the temperature in the mixture was uniformly distributed over the volume. The surfaces of the Mn and Si powders were cleaned of impurities and bonded to each other. The Mn and Si powders underwent plastic deformation under the action of a uniaxial force and condensed (Figure 1). Thus, a disk-shaped (diameter 76 mm thickness up to 5 mm) cathode-target for vacuum magnetron sputtering was formed.

![Fig. 1. (SPS) spark plasma welding process.](image)

Vacuum deposition of Mn$_3$Si$_7$ coatings was carried out in a vacuum working chamber of an EPOS-PVD-DESK-PRO installation with a Pfeiffer Vacuum Hi-Cube 80 Eco turbomolecular pump. The installation provided heating up to 200 °C and movement of several samples, preliminary plasma treatment of the surface and magnetron deposition of coatings with indication of their thickness using a quartz sensor. The target cathode was fixed on the magnetron sputtering source by a clamping ring. A heat-conducting paste based on zinc oxide or beryllium oxide was used for thermal contact of the target [12-25].

Mn$_3$Si$_7$ coatings were deposited on various dielectric substrates - special glass 24×24×0.17 mm in size, SiO$_2$/Si(111) structures 60 mm in diameter, obtained by thermal oxidation of silicon in oxygen at a temperature of 1200 °C. The thickness of the dioxide coating was 100–500 nm. The process of deposition of Mn$_3$Si$_7$ coatings on preliminarily cleaned samples of glass-ceramic ST-50-1, oxidized silicon, K-8 glass and mica was carried out after obtaining an initial degree of vacuum in the working chamber of about 10$^{-3}$ Pa and heating the treated samples to 100-150 °C. Then the working gas (pure technical argon) was supplied to the chamber at a stable pressure (2-4)·10$^{-3}$ Pa and the source of magnetron sputtering was turned on. The sputtering process was carried out at a cathode voltage of minus 450–550 V and a discharge current of 200–300 mA. The discharge current stabilized with an accuracy of 5%. After preliminary sputtering of the target cathode onto the shutter (screen), coatings were deposited on the substrates for a specified time. The coating time was 2–10 minutes. In one vacuum cycle, 3 samples were sequentially processed.

Figure 2 shows photographs of the vacuum setup, the target cathode, the sputtering process, and processed silicon and mica samples.

The magnetron sputtered coatings were examined using an HR-4000 high resolution spectrometer with a combination of optics and electronics that measured the absorption, transmission and reflection coefficients of light in the wavelength range from 300 to 1100 nm. The structure and properties of the substrate surface, as well as the structure and optical properties of the surface of a thin coating of manganese silicide, were studied using energy-dispersive X-ray analysis on a Scios FEI setup; Quanta 200-3D microscope and ECOPIA (HMS-5000).

II. Research results

As a result of energy dispersive analysis, the weight fractions of the oxygen and silicon components on the structures were determined SiO$_2$/Si(111) (O- Wt. 24.43%, At% 35.96), (Si-Wt. 75.77%, At% 64.04) (Figure 3).

Figure 4 shows microscopic studies of the coating, which show that the composition of the Mn$_3$Si$_7$ coating with a thickness of (200–500) nm, obtained by magnetron sputtering, practically coincides with the composition of the used Mn$_3$Si$_7$ target.

As can be seen in the image, the energy dispersive analysis shows strong Si peaks, weak Mn peaks in the range of 1–6 keV. Using an HR-4000 spectrometer, the light transmission and absorption coefficients of a Mn$_3$Si$_7$ coating with a thickness of (200–500) nm on the surface of a glass substrate were determined in the wavelength range from 300 to 1100 nm (Figure 5).

As a result of the research, the average light transmission coefficient of the glass substrate taken as a sample was determined, which amounted to 93–86% in the field of view. Transmittance of Mn$_3$Si$_7$ coating (14–26%), thicker Mn$_3$Si$_7$ coating (4–6%). It can be seen that with an increase in the thickness of the coating, the light transmission coefficient decreases, and the light absorption increases (Figure 6).
Investigation of optical and electrophysical properties of Mn₄Si₇ coatings of different thickness

As can be seen in the image, light absorption was observed in the field of view for glass (2.9–7.2%), for a thin coating (5.2–3.6%), and for a thick coating (1.93–1.20%). Light reflection coefficients were also compared (Figure 7).

As a result of comparative studies of the light reflection coefficients of several samples (Si/SiO₂ with a thickness of 270 nm, Mn₄Si₇ with a thickness of 270 nm, and Mn₄Si₇ with a thickness of 450 nm), it can be noted that light is differently reflected from the studied samples in the field of view at different wavelengths. CoSi has a reflection maximum in the range (331.7–409.1 nm), SiO₂ has a maximum in the range (371.6–704.68 nm), Mn₄Si₇ with a thickness of 270 nm in the range (308–437 nm), and Mn₄Si₇ with a thickness of 450 nm in the range (339.4–408 nm). Here one can observe the difference between thin and thicker Mn₄Si₇ coatings. The reflectance of the thin layer increases from 437 nm to 853.6 nm, while the reflectance of the thicker layer remains unchanged from 408 nm to 845 nm. The analysis shows that a relatively thin coating reflects different wavelengths in the visible range.

Fig. 2. Obtaining coatings by magnetron sputtering.

Fig. 3. Analysis of the composition of the SiO₂/Si(111) structure on Scios FEI; Quanta 200 3D.

As can be seen in the image, light absorption was observed in the field of view for glass (2.9–7.2%), for a thin coating (5.2–3.6%), and for a thick coating (1.93–1.20%). Light reflection coefficients were also compared (Figure 7).
field differently, while a thicker layer reflects almost uniformly.

The Hall constant and a number of electrophysical values of the coatings were determined on Mn$_4$Si$_7$ crystalline samples (ECOPIA HMS-5000). Mn$_4$Si$_7$ samples before and after magnetron sputtering and Mn$_4$Si$_7$ coating samples up to 450 nm thick were compared. In all measurements, the current was 100 μA, the induction magnetic field 0.54 T, temperature 27° C. The results of electrophysical measurements are given in Table 1. (Mn$_4$Si$_7$ target and Mn$_4$Si$_7$ thin coating).

When samples are heated at a temperature of 300–800 K, thin Mn$_4$Si$_7$ coatings show that the resistance of nanoclusters 150 to 500 nm thick decreases from 80 Ω to 20 Ω. It can be seen that the resistance of a thin coating varies depending on the thickness of the coating (Figure 8). A study of the conductivity (resistance) of Mn$_4$Si$_7$ layers showed that their layer resistance drops from 80 to
Investigation of optical and electrophysical properties of Mn$_4$Si$_7$ coatings of different thickness

20 Ohm/square with an increase in the coating thickness from 150 to 450 nm (Figure 8).

Table 1. Data of electrophysical measurements of Mn$_4$Si$_7$ coatings

<table>
<thead>
<tr>
<th>Measured parameters</th>
<th>Volume Mn$_4$Si$_7$</th>
<th>Coating Mn$_4$Si$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity, Ω·cm</td>
<td>7.826·10$^{-4}$</td>
<td>6.409·10$^{+4}$</td>
</tr>
<tr>
<td>Hall constant, cm$^2$/C</td>
<td>1.285·10$^{-3}$</td>
<td>1.597·10$^{+3}$</td>
</tr>
<tr>
<td>Conductivity, 1/Ω·cm</td>
<td>1.278·10$^{-3}$</td>
<td>1.560·10$^{+3}$</td>
</tr>
<tr>
<td>Surface concentration, cm$^{-2}$</td>
<td>1.215·10$^{+17}$</td>
<td>9.770·10$^{+16}$</td>
</tr>
<tr>
<td>Volume concentration, cm$^{-3}$</td>
<td>4.859·10$^{+21}$</td>
<td>3.908·10$^{+21}$</td>
</tr>
<tr>
<td>Carrier mobility, cm$^2$/V·s</td>
<td>1.642·10$^{+0}$</td>
<td>2.492·10$^{+0}$</td>
</tr>
</tbody>
</table>

Fig. 8. Dependence of Mn$_4$Si$_7$ sheet resistance on thickness.

Figure 9 shows the results of studies of the Seebeck coefficient and the resistance of the Mn$_4$Si$_7$ layer during the heat treatment of samples.

Fig. 9- Seebeck coefficient for thin Mn$_4$Si$_7$ coating

The Seebeck coefficient for a thin Mn$_4$Si$_7$ coating varies from 1 to 3 µV/K. At temperatures from 300 K to 685 K, the Seebeck coefficient changes, which indicates the presence of energy barriers for charge carriers at the interface between the Mn$_4$Si$_7$ nanocluster and the amorphous phase. Then, as the temperature changes from 685 K to 800 K, the Seebeck coefficient changes from 11 µV/K, which indicates the formation of ordering between nanoclusters. When the nanocluster is cooled, the Seebeck coefficient changes from 11 µV/K to 16 µV/K, depending on the location of the nanolayer and the coating thickness. With an increase in the thickness of the thin Mn$_4$Si$_7$ coating, an increase in the Seebeck coefficient is observed (Figure 10).

The Seebeck coefficient of the sample with a thicker coating is from 3.5 µV/K to 3 µV/K at temperatures from 300 to 610 K, which indicates the presence of energy barriers for charge carriers at the interface between the Mn$_4$Si$_7$ nanocluster and the amorphous phase. Then, as the temperature changes from 610 K to 700 K, the Seebeck coefficient changes from 6 µV/K to 18 µV/K, which indicates the formation of ordering between nanoclusters. When the nanocluster was cooled, the Seebeck coefficient changed from up to 22 µV/K depending on the location of the nanolayer and the coating thickness.

Fig. 10. Seebeck coefficient for thicker coating Mn$_4$Si$_7$.

Conclusions

Research of Mn$_4$Si$_7$ coatings of two different thicknesses have shown that magnetron deposition practically does not change the composition of the coating in comparison with the composition of the target. Studies of the transmission, absorption, and reflection coefficients of coatings in the visible region of the spectrum have shown that for the Mn$_4$Si$_7$ coating, the reflection coefficient is practically the same at all wavelengths. It was found that the Seebeck coefficient varies from 16 µV/K to 22 µV/K, and the resistance decreases from 77 Ω to 20 Ω with increasing thickness of the thin Mn$_4$Si$_7$ coating.

Igamov B.D. – PhD (Physics), Associate Professor, Leading Researcher, Uzbekistan;
Bekpulatov I.R. – (DSc), Associate professor, Vice-rector for scientific affairs and innovations, Uzbekistan;
Imanova G.T. – PhD (Physics), Associate Professor, Leading Researcher, Azerbaijan;
Kamardin A.I. – PhD (Physics), Associate Professor, Leading Researcher, Uzbekistan;
Normurodov D.A. – PhD (Physics), Associate Professor, Leading Researcher, Uzbekistan.

425


[12] T.S. Kamilov, A.S. Rysbaev, V.V. Klechkovskaya, A.S. Orekhov, B.D. Igamov, I.R. Bekpulatov, The Influence of Structural Defects in Silicon on the Formation of Photosensitive Mn\textsubscript{1}Si\textsubscript{2}Si\textsubscript{2}Mn\textsubscript{1}Si\textsubscript{2} and Mn\textsubscript{1}Si\textsubscript{2}Si\textsubscript{2}Mn\textsubscript{1}M Heterostructures, Solar engineering materials science, 55(6), 380 (2019); https://doi.org/10.3103/S0003701X19060057.


[20] Jabarov, S.H., Nabiyeva, A.K., Huseynov, E.M. et al. Dielectric and electrical properties of La0.5Ba0.5MnO\textsubscript{3} and La0.5Sr0.5MnO\textsubscript{3} perovskites. J Porous Mater (2024); https://doi.org/10.1007/s10934-024-01632-6.


[22] V.V. Klechkovskaya, A.S. Rysbaev, T.S. Kamilov, I.R. Bekpulatov, B.D. Igamov, I.Kh. Turapov, Formation of thin films of Mn\textsubscript{1}Si\textsubscript{2} on the surface of various substrates by the methods of magnetron sputtering and impulse laser precipitation, Uzbek J. Physics, 22(3), 43 (2021); https://doi.org/10.52304/v23i3.263.
Investigation of optical and electrophysical properties of Mn₄Si₇ coatings of different thickness


Б.Д. Ігамов¹, І.Р. Бекпулатов², Г.Т. Іманова³, А.І. Камардин¹, Д.А. Нормуродов²

Дослідження оптичних та електрофізичних властивостей покриттів Mn₄Si₇ різної товщини

¹Науково-технічний центр з конструкторським бюро та дослідним виробництвом Академії наук Республіки Узбекистан, м. Ташкент, Республіка Узбекистан;
²Каршинський державний університет, м. Карші, Узбекистан;
³Інститут радіаційних проблем Міністерства науки і освіти Азербайджанської Республіки, Баку, Азербайджан, imanovagunel77@gmail.com;
⁴Західно-Каспійський університет, Баку, Азербайджан;
⁵Хазарський університет, факультет фізики та електроніки, Баку, Азербайджан

Дослідження покриттів Mn₄Si₇ різної товщини показали, що магнетронне осадження практично не змінює складу покриття в порівнянні зі складом мішені. Представлена технологію та основні режими створення необхідних мішень для установки магнетронного розпилення. Мішени створювали шляхом додавання порошків кремнію та марганцю в необхідній кількості та їх нагрівання в умовах вакууму при високій температурі та тиску. На поверхні діоксиду кремнію із виготовлених мішеней методом магнетронного напилення формували тонкі силіцидні плівки (покриття) різної товщини. Дослідження коефіцієнтів пропускання, поглинання і відбиття покриттів у видимій області спектра показали, що для покриття Mn₄Si₇ коефіцієнт відбиття практично однаковий на всіх довжинах хвиль. Встановлено, що зі збільшенням товщини тонкого покриття Mn₄Si₇ коефіцієнт Зеебека змінюється від 16 мкВ/К до 22 мкВ/К, а опір зменшується від 77 Ом до 20 Ом.

Ключові слова: коефіцієнти пропускання, поглинання та відбиття покриттів, коефіцієнт Зеебека, тонкі покриття, наноструктура, питомий опір.