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Formation of targets and investigation of Mn₄Si₇ coatings produced by magnetron sputtering

The morphology, composition, electrical and optical properties of bulk samples and vacuum coatings of Mn₄Si₇ obtained by magnetron sputtering on a SiO₂/Si structure were studied. It is shown that manganese silicide coatings with a thickness of about 150 nm are close in properties to bulk Mn₄Si₇, have a uniform fine-grained structure of a semiconductor nature, which is characterized by thermal sensitivity up to 20–30 μV per degree. In addition, this article presents the electrophysical properties of high manganese silicide films produced by the authors by magnetron sputtering method. Heated films Mn₄Si₇ -146 nm coating has a uniform structure with fine grains, due to sufficient coating density. Since Mn₄Si₇ nanoclusters are semiconductor materials, it can be assumed that there will be energy barriers for charge carriers at the nanocluster–amorphous phase interface separating this phase. An increase in thermal sensitivity from 0 μV/K to 20 μV/K up to 800 K is explained by the disappearance of energy barriers for charge carriers at the nanocluster–amorphous phase interface due to the ordering of nanoclusters. The change from 20 μV/K to 28 μV/K upon cooling is explained by the appearance of structural relaxation in the amorphous phase.

Keywords: Hall constant, Mn₄Si₇, thin coating, nanocluster, electrical conductivity, nanostructure, resistivity, volume concentration.

Introduction

The main task facing scientists all over the world today is to search for environmentally friendly types of energy and increase the utilization rate of identified types. The main goal at the same time is to receive energy without harming the environment. Unfortunately, the efficiency of currently produced thermo- and photo batteries is very low. A key role in solving this problem is played by the creation of new materials and structures or the replacement of existing ones with cheap and high-quality ones.

Receiving and converting energy is one of the most important activities of modern civilization [1-7]. In this regard, much attention is paid to solid-state thermoelectric converters that do not have moving parts, operate silently, have high reliability and small size. An increase in the efficiency of using thermoelectric materials is associated with the formation of high quality layers [8-23]. Of all silicon compounds of thermoelectric interest, one can choose compounds representing a certain class of materials. These are, for example, solid solutions based on cobalt monosilicide (CoSi), high manganese silicide (MnSi_{1.7}), and Mn₂X (X=Si, Ge, Sn). Highmanganese silicide (HMS-MnSi_{1.7-1.75}), even in the unalloyed state, has a high thermoelectric efficiency and is a good basis for creating an efficient *p*-type thermoelectric. Therefore, thin vacuum coatings of Mn₄Si₇ were chosen as objects of study.

Experimental

To obtain thin-film samples of Mn₄Si₇, a disk target was first formed. Pure monocrystalline silicon and manganese were first pulverized in a mill (HERZOG HSM-100P), then 52.9 % Mn and 47.1 % Si (by mass) were mixed and sintered using electric spark plasma welding (SPS). The Mn₄Si₇ disk target was pressed in a setup under vacuum conditions with a residual gas pressure of 10⁻² Torr at a temperature of 1050 °C, with a pressing force of 6.5·10⁴ N for 2 hours (Fig. 1).

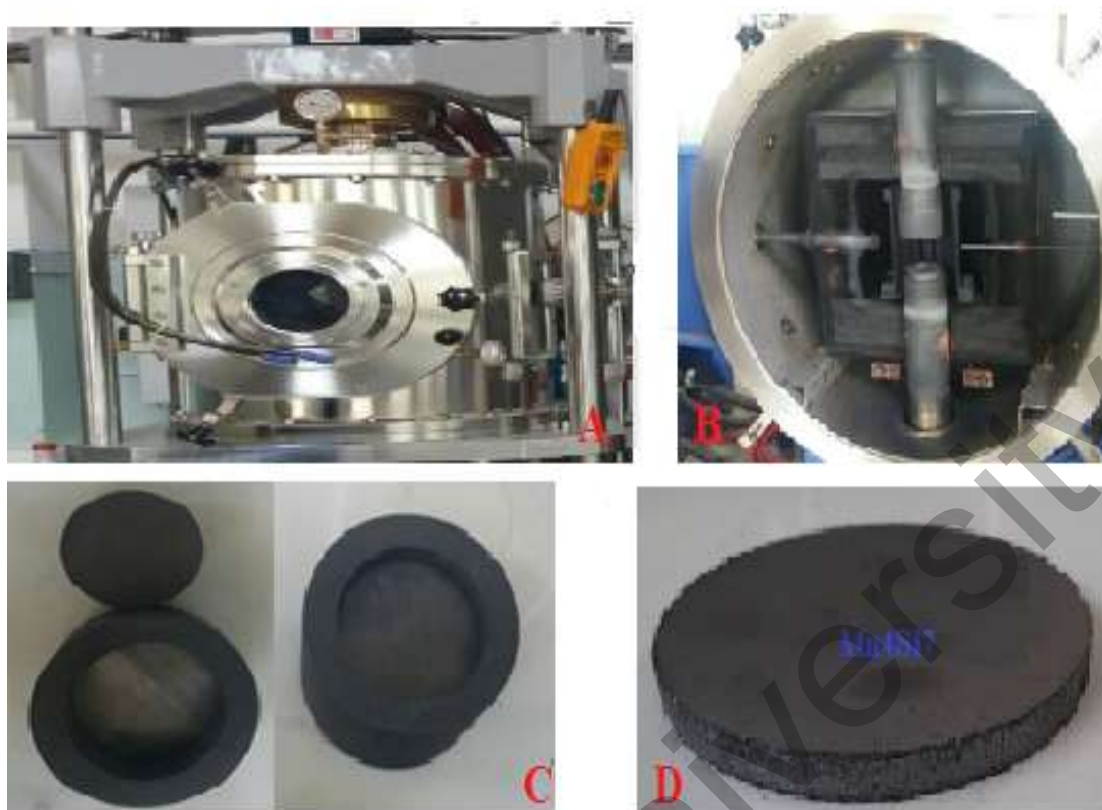


Figure 1. Preparation of the Mn_4Si_7 target by the (SPS) method

Polished silicon wafers of the Si(111) type with a diameter of 60 mm were used as a base (substrate) for deposition of thermally sensitive coatings. A group of plates after preliminary chemical cleaning in an ammonium peroxide solution, washing and drying were subjected to high-temperature treatment to create an oxide layer. Silicon dioxide layers of various thicknesses were grown on plates in an environment of dry oxygen at a temperature of 1200 ± 5 °C in a diffusion furnace of the SDO-125 type. The SiO_2/Si structures prepared in this way were processed in a vacuum working chamber. The surface of the Si(111) substrate was cleaned with an Ar plasma flow for 1 minute. The device and the process of processing plates is shown in Figure 2.

The SiO_2/Si structures were placed in a modified (EPOS-PVD-DESK-PRO) installation for magnetron sputtering of the Mn_4Si_7 target and coating formation. The coating formation process was carried out after reaching the starting vacuum degree of about 10^{-5} Torr. The SiO_2/Si structures were treated individually with heating up to 150 °C. The pressure of the working gas (pure argon) during spraying was $(2-4) \cdot 10^{-3}$ Torr. The discharge current was 200–300 mA at voltages of 450–550 V. The coating deposition time was 2–10 minutes. In one vacuum cycle, 3 structures were sequentially processed. The morphology, microstructure, and chemical composition of the coated samples were determined by scanning electron microscopy and energy-dispersive X-ray spectroscopy (Scios FEI; Quanta 200 3D setups). The electrical properties of the Mn_4Si_7 coating were studied by a four-probe method (JANDEL RM3000 setup), and the Hall constant was determined using an ECOPIA setup (HMS-3000 VER3.53).

Mn_4Si_7 samples obtained by sintering (SPS) and coated samples obtained by magnetron sputtering on the EPOS-PVD-DESK-PRO facility were studied.

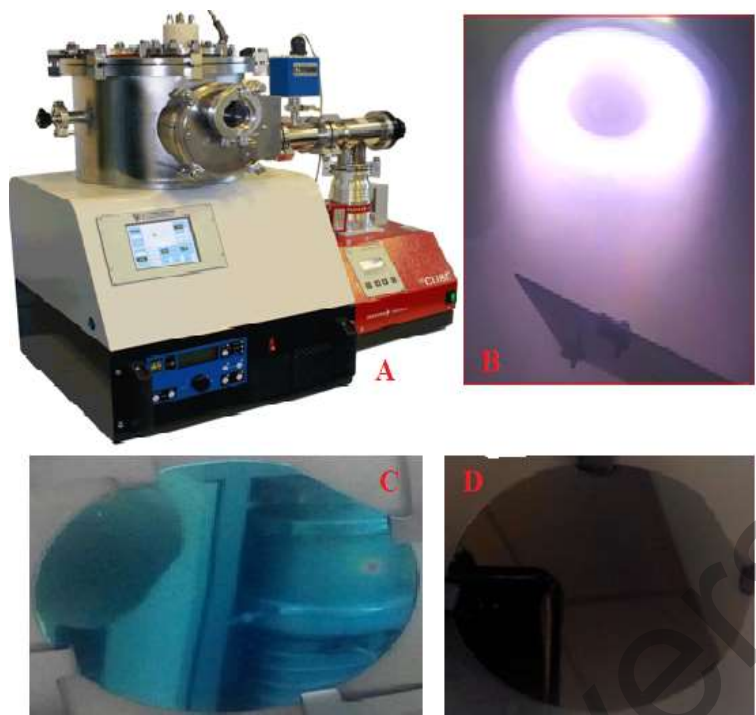


Figure 2. The process of forming the Mn_4Si_7 coating by the method of magnetron sputtering

Results and Discussion

Figure 3a, b shows images of the surface of the samples and the results of energy dispersive analysis: (a) — sample prepared by the (SPS) method, (b) — sample obtained by magnetron sputtering.

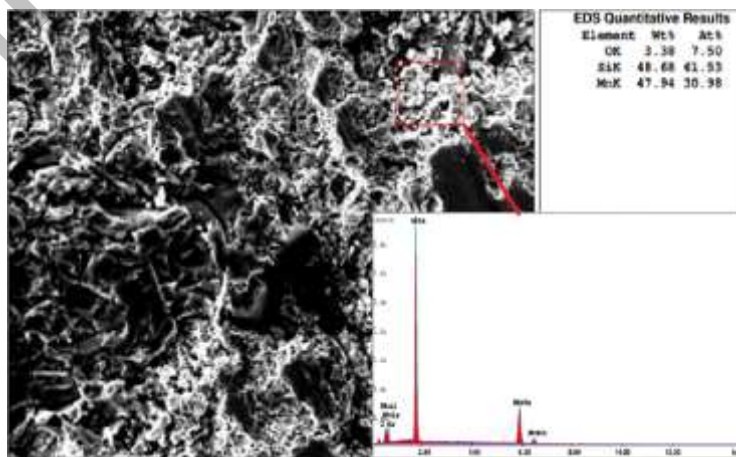
Figure 4 shows an electron microscope photograph of a cut of the Mn_4Si_7 coating on the $SiO_2/Si(111)$ structure. The measurements show a thickness of the silicon dioxide coating of about 249 nm, and the thickness of the Mn_4Si_7 coating is about 146 nm.

The results of averaged measurements by the four-probe method of the conductivity of Mn_4Si_7 (SPS) samples and the conductivity of Mn_4Si_7 coatings obtained by magnetron sputtering are shown in Table 1.

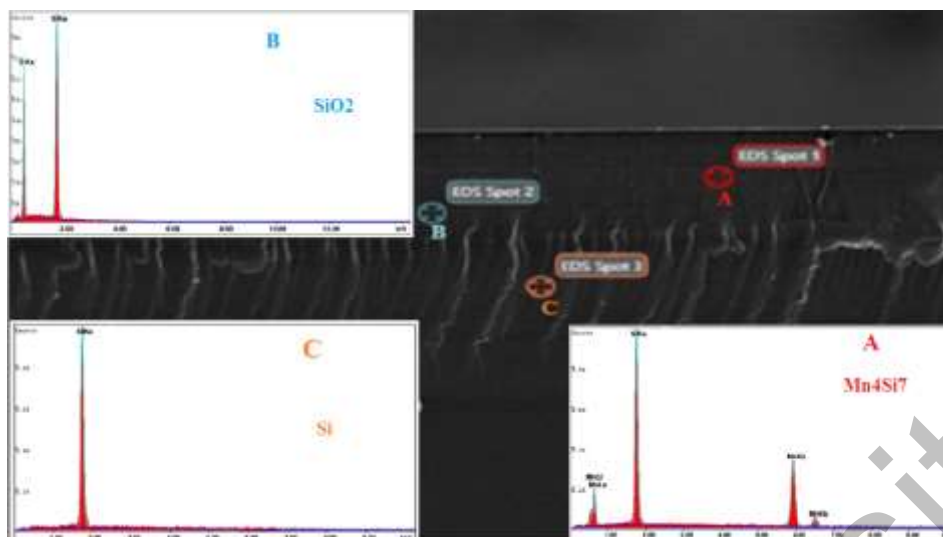
Table 1

Layer resistances of bulk samples Mn_4Si_7 and Mn_4Si_7 coatings on the SiO_2/Si structure

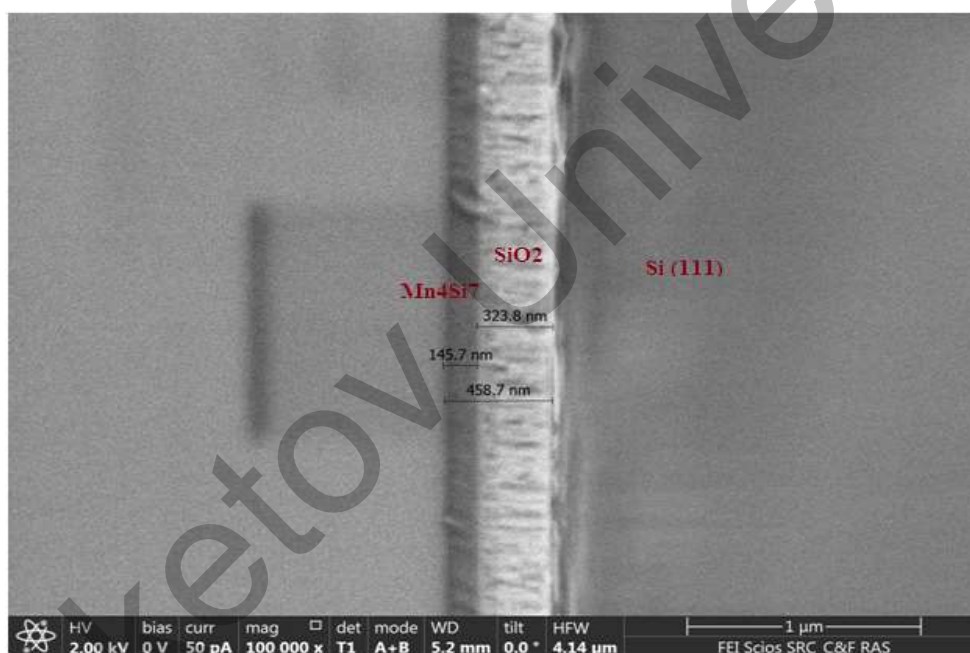
Sample type	Sheet resistance values, Ohm/square	Average value of sheet resistance, Ohm/square
Volume	508-602	556
Coating	4380-4460	4401



a



b

Figure 3. Image of Mn_4Si_7 sample (Scios FEI; Quanta 200 3D)Figure 4. Image of nanosized Mn_4Si_7 coating on SiO_2/Si structure

The measurement results show that the resistance of the samples (SPS) is different, which is possibly due to the different concentrations of Mn and Si in different zones of the samples. In Mn_4Si_7 vacuum coatings, the uniformity of the formed layer is higher, which indicates the same coating thickness. To determine the Hall constant on an ECOPIA(HMS-3000 VER3.53) instrument, a (SPS) Mn_4Si_7 sample with an area of 1 cm^2 and a thickness of 1 mm and a sample with a vacuum coating of Mn_4Si_7 with a thickness of 146 nm were used. In all measurements, the current strength was $100 \text{ } \mu\text{A}$, the magnetic field induction was 0.54 T, and the temperature was $27 \text{ } ^\circ\text{C}$.

The results of measurements obtained for these samples (Table 2), the dependences of the samples (VAX) and resistance on current (Fig. 5) are presented. There are the results of Hall measurements of bulk samples of Mn_4Si_7 and Mn_4Si_7 in the SiO_2/Si structure in Table 2.

Electrophysical properties of high manganese silicide structure formed by two different methods

Options	Volume Mn ₄ Si ₇	Coating Mn ₄ Si ₇
Resistivity, Ohm·cm	$7.826 \cdot 10^{-4}$	$6.409 \cdot 10^{-4}$
Hall constant, cm ³ /C	$1.285 \cdot 10^{-3}$	$1.597 \cdot 10^{-3}$
Conductivity, 1/Ohm·cm	$1.278 \cdot 10^3$	$1.560 \cdot 10^3$
Surface concentration, cm ⁻²	$1.215 \cdot 10^{17}$	$9.770 \cdot 10^{16}$
Volume concentration, cm ⁻³	$4.859 \cdot 10^{21}$	$3.908 \cdot 10^{21}$
Carrier mobility, cm ² /V·s	1.642	2.492

From the results obtained with the ECOPIA instrument (HMS-3000 VER3.53), it can be seen that the bulk sample (SPS) and the coating sample (EPOS-PVD-DESK-PRO) are close to each other.

Figure 6 shows the optical absorption and transmission spectra of the samples obtained on an IR Tracer-100-SHIMADZU instrument.

The measurement results show that the nanoscale Mn₄Si₇ coating (a) has an IR transmission of 35 %, (b) an IR absorption of about 1 %, from which it can be seen that the Mn₄Si₇ coating has a low IR absorption of the rays. Figure 6 shows the results of measurements of the Seebeck coefficient (*S*) and resistance (*R*) of the Mn₄Si₇ -146 nm coating during heating and cooling.

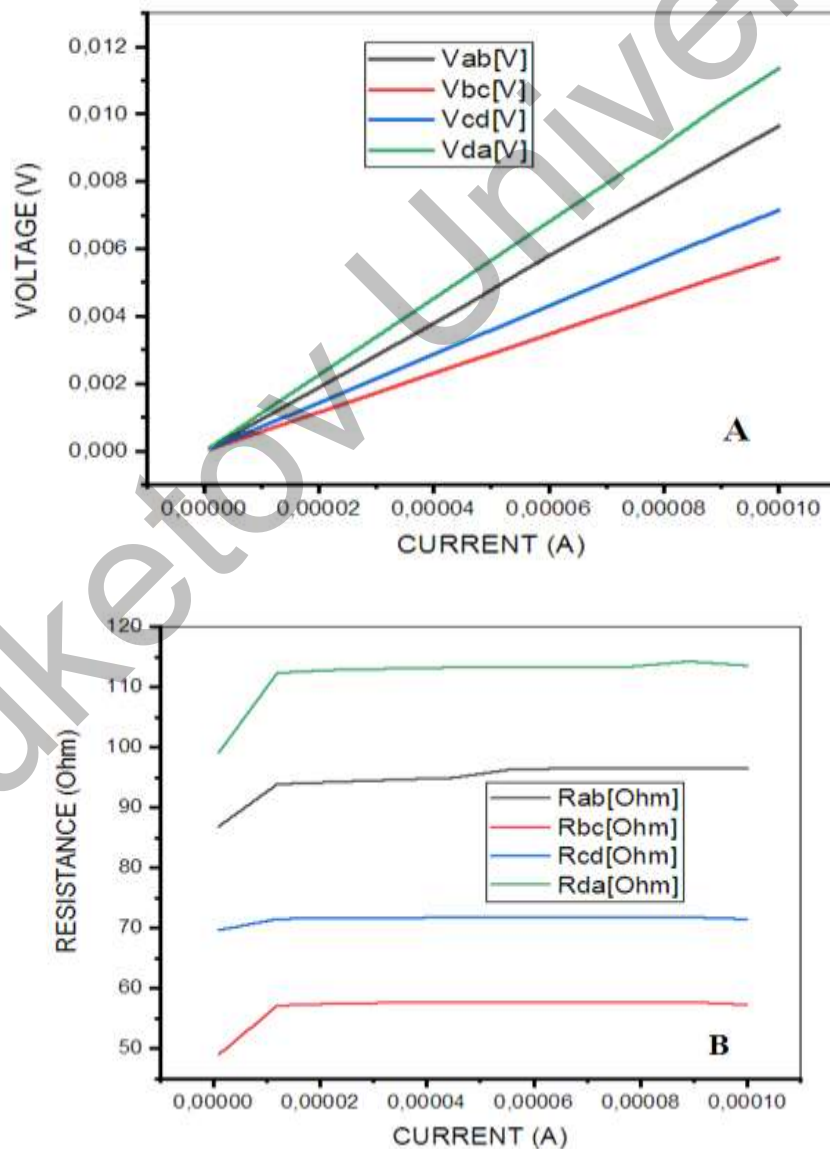


Figure 5. a) samples (I-V), b) relationship between (I-R)

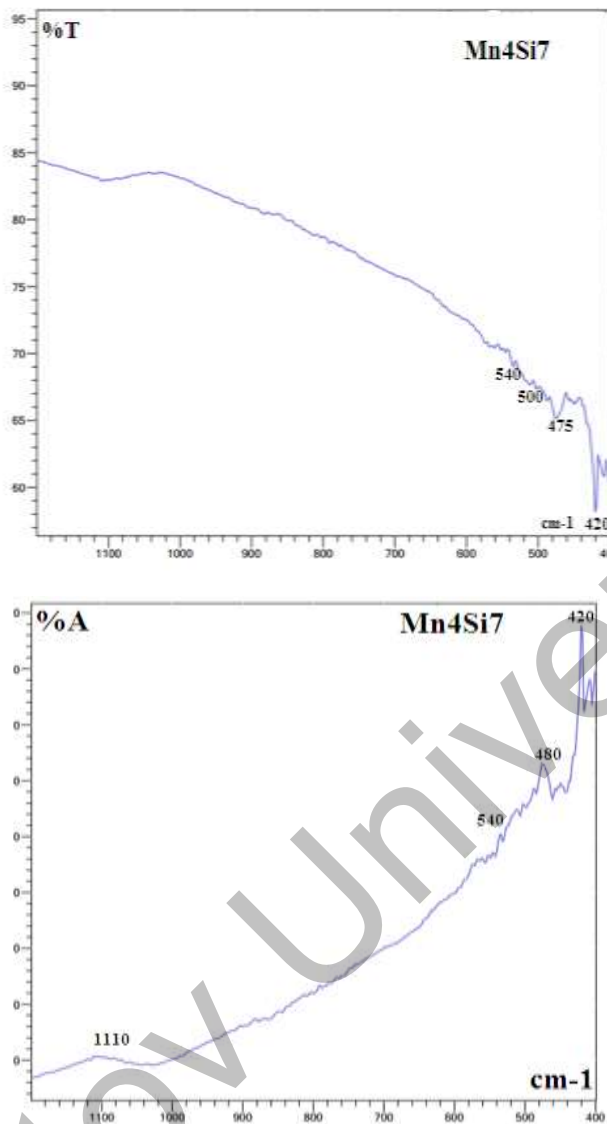


Figure 6. Spectra obtained with the IRTracer-100 — SHIMADZU instrument

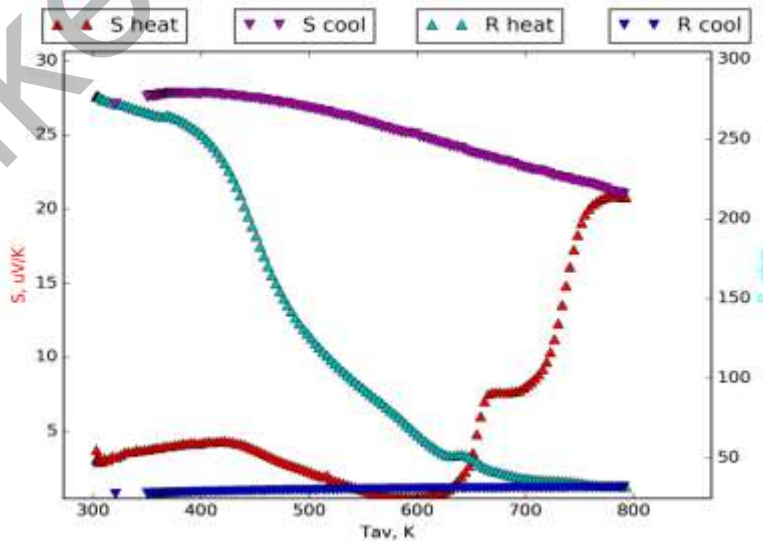


Figure 7. Temperature dependence of the Seebeck coefficient (S) and resistance (R) of a thin Mn₄Si₇ coating

When heated, Mn₄Si₇ -146 nm coating has a uniform structure with fine grains, due to sufficient coating density. With an increase in temperature from room temperature to 800 K, a decrease in resistance is observed from 250 Ohms to 25 Ohms, which in turn indicates a change in the characteristics of this material. The Seebeck coefficient decreases upon heating from room temperature from 300 K to 620 K. Since Mn₄Si₇ nanoclusters are semiconductor materials, it can be assumed that there will be energy barriers for charge carriers at the nanocluster–amorphous phase interface separating this phase (Fig. 7).

An increase in thermal sensitivity from 0 $\mu\text{V/K}$ to 20 $\mu\text{V/K}$ up to 800 K is explained by the disappearance of energy barriers for charge carriers at the nanocluster–amorphous phase interface due to the ordering of nanoclusters. The change from 20 $\mu\text{V/K}$ to 28 $\mu\text{V/K}$ upon cooling is explained by the appearance of structural relaxation in the amorphous phase. Seebeck coefficient (S) and resistance (R) vary with coating thickness.

Conclusions

Studies of the parameters of thin coatings of manganese silicide deposited on the SiO₂/Si structure by magnetron sputtering of a silicide target show that manganese silicide layers have a uniform fine-grained structure of a semiconductor nature, which is characterized by thermal sensitivity up to 20-30 μV per degree.

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Нысанды қалыптастыру және магнетронды шашырату арқылы алынған Mn₄Si₇ жабындарын зерттеу

SiO₂/Si құрылымында магнетронды шашырату арқылы алынған Mn₄Si₇ көлемді үлгілері мен вакуумдық жабындарының морфологиясы, құрамы және электрлік және оптикалық қасиеттері зерттелді. Қалыңдығы шамамен 150 нм болатын марганецті силицидті жабындар қасиеттері бойынша массалық Mn₄Si₇-ге жақын, жартылай өткізгіш сипаттағы біркелкі ұсақ түйіршікті құрылымы бар, ол бір градусқа 20-30 мкВ-қа дейінгі термиялық сезімталдықпен сипатталады. Сонымен қатар мақалада авторлар магнетронды шашырату әдісімен шығарған жоғары марганецті силицидті қабыршақтардың электрофизикалық қасиеттерін ұсынған. Қыздырылған пленкалар Mn₄Si₇-146 нм жабынның жеткілікті тығыздығына байланысты ұсақ түйіршіктері бар біркелкі құрылымға ие. Mn₄Si₇ нанокластерлері жартылай өткізгіш материалдар болғандықтан, осы фазаны бөлетін нанокластер-аморфты фаза интерфейсында заряд тасымалдаушылар үшін энергетикалық кедергілер болады деп болжауға болады. Термиялық сезімталдықтың 0 мкВ/К-ден 20 мкВ/К-ден 800 К-ге дейін жоғарылауына нанокластерлердің реттелгеніне байланысты нанокластер-аморфты фаза интерфейсындағы заряд тасымалдаушыларға арналған энергетикалық кедергілердің жойылуымен түсіндіріледі. Салқындату кезінде 20 мкВ/К-ден 28 мкВ/К-ге дейін өзгеруі аморфты фазадағы құрылымдық релаксацияның пайда болуымен түсіндіріледі.

Кілт сөздер: Холл тұрақтысы, Mn₄Si₇, жұқа жабын, нанокластер, электрөткізгіштік, нанокұрылым, меншікті кедергі, көлемді концентрациясы.

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Формирование мишеней и исследование покрытий Mn₄Si₇, полученных методом магнетронного распыления

Исследованы морфология, состав, электрические и оптические свойства объемных образцов и вакуумных покрытий Mn₄Si₇, полученных методом магнетронного напыления на структуру SiO₂/Si. Показано, что покрытия из силицида марганца толщиной около 150 нм близки по свойствам к объемному Mn₄Si₇, имеют однородную мелкозернистую структуру полупроводниковой природы, которая характеризуется термочувствительностью до 20–30 мкВ на градус. Кроме того, в настоящей статье представлены электрофизические свойства пленок высокомарганцевого силицида, полученных авторами методом магнетронного распыления. Нагретые пленки Mn₄Si₇ — 146 нм. Покрытие имеет однородную структуру с мелкими зёрнами, что обусловлено достаточной плотностью покрытия. Поскольку нанокластеры Mn₄Si₇ являются полупроводниковыми материалами, можно предположить, что на границе раздела «нанокластер–аморфная фаза», разделяющей эту фазу, будут существовать энергетические барьеры для носителей заряда. Увеличение термочувствительности от 0 до 20 мкВ/К вплоть до 800 К объясняется исчезновением энергетических барьеров для носителей заряда на границе «нанокластер–аморфная фаза» за счет упорядочения нанокластеров. Изменение от 20 до 28 мкВ/К при охлаждении объясняется появлением структурной релаксации в аморфной фазе.

Ключевые слова: постоянная Холла, Mn₄Si₇, тонкое покрытие, нанокластер, электропроводность, наноструктура, удельное сопротивление, объемная концентрация.