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Obtaining higher manganese silicide films with high thermoelectric properties

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Abstract. This article provides information about the process of obtaining a Mn_4Si_7 film by magnetron sputtering, its high thermoelectric properties, and the possibility of using the resulting film in instrument-making production. Using the magnetron sputtering method, a thin Mn_4Si_7 film was obtained, and the composition and structure were studied by a scanning electron microscope. Two-stage cleaning of the silicon surface was used in work. Resistivity was determined by the four-probe method, thermoelectric properties, by the two-probe method. The bandwidth of the Mn_4Si_7/SiO_2 film was measured on a high-precision spectrometer according to the law of light reflection. It is shown that the thermoelectric power of the Mn_4Si_7 film increases during the transition from the amorphous state to the nanocrystalline one, which is associated with the selective scattering of charge carriers at the boundaries of nanoclusters and Mn_4Si_7 on SiO_2/Si have high speed and high sensitivity. It is shown that this film can be used in thermal detectors radiation waves in the visible and IR ranges.

1 Introduction

Many research centers worldwide are currently researching the creation of environmentally friendly and low-cost energy sources. Recently, scientists worldwide have focused on developing effective methods for producing environmentally friendly and more cost-effective energy sources. In this regard, great results have been achieved in converting wind, light, and heat energy into electrical energy, which has increased the efficiency of the generated photovoltaic and thermoelectric elements [1-10].

This, in turn, led to very important scientific discoveries in the field of physical electronics, but some issues remain a pressing problem to this day. This is due to the film's low efficiency and high cost of the film-forming process. Among such materials, a film of higher manganese silicide is the most promising. (HSM), the thermoelectric figure of merit can reach 0.4 in the temperature range of 20 – 700°C [11-16].

A thin Mn_4Si_7 film can be used as a high-quality thermoelement and shows the possibility of creating nanostructures with high thermal properties based on fundamental research on various physical properties, quantum effects, and size factors. Photocells from such structures are promising when using highly sensitive receivers of electromagnetic

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waves in optical and IR fields. Photocells of such structures are promising when using highly sensitive receivers of electromagnetic waves in the optical and IR areas.

This article provides information about the Mn_4Si_7 film formed by magnetron sputtering and its high thermoelectric properties.

2 Methods

Before the formation of the HCM film, the SiO_2/Si substrate was cleaned in two ways:

1. Cleaning the surface of silicon wafers SiO_2/Si (d=60 mm) in an ammonia-peroxide mixture at a temperature of 60-70°C, washing in deionized water, drying in a centrifuge;

2. Vacuum treatment (cleaning) of the surface of a group plate (2-4 pieces) with an argon plasma flow on EPOS-PVD-DESK-PRO. The plasma flow creates a source of ions with a cold cathode at a voltage of 2-3 kV and a current of up to 100 mA in the flow for 3-5 minutes on a rotating tool with plates.

HSM films were formed using an EPOS-PVD-DESK-PRO magnetron sputtering apparatus at a pressure of 10^{-4} Pa and at room temperature. The purity of Mn_4Si_7 used as a target was 99.5%, the diameter was 76 mm, and the thickness was 6 mm. [17, 18]. Before placing the target on the magnetron, their composition and structure were studied with a Quanta 200 3D scanning electron microscope from the Dutch company FEI (Fig. 1).

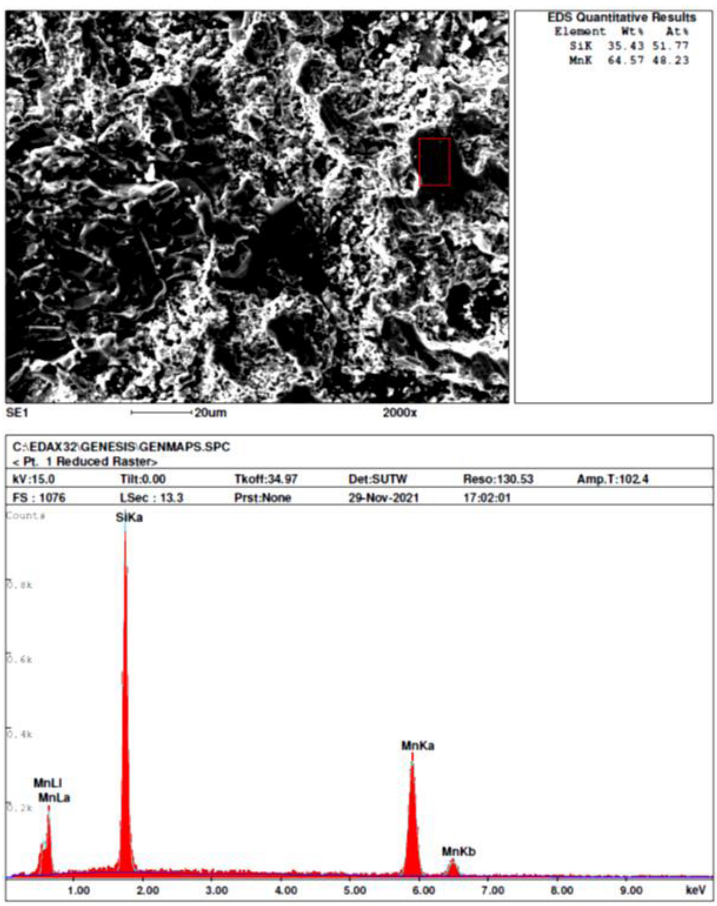

Fig. 1. Scanning electron microscope image of the Mn_4Si_7 target.

The specific resistance of the formed Mn_4Si_7 film with a thickness of ~0.7 μm was determined by the four-probe method, and the thermoelectric properties were determined in a vacuum of 10 Pa by the two-probe method [19]. The bandwidth of the Mn_4Si_7/SiO_2 film was measured on an HR-4000 high-precision spectrometer according to the law of light reflection. It is known that the thermoelectric figure of merit of a material is a dimensionless quantity and is determined by the formula

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

where α is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, T is temperature [20-22].

3 Results and Discussion

The Mn_4Si_7 film formed by magnetron sputtering is in an amorphous state before thermal heating, which we can identify by (Fig. 2-a). Silicon and manganese atoms deposited on silicon oxide almost completely covered the substrate. As a result of experiments with an amorphous film, we (see--saw) observed that the film has metallic properties. In the amorphous state, the film's resistance is greater than the resistance in the polycrystalline state. This is because the bond between the manganese and silicon atoms is very weak, and there are point defects on the surface areas that are not completely covered. After the film is annealed, point defects on the surface disappear, the manganese and silicon atoms form a bond, and the resulting structure has semiconductor properties.

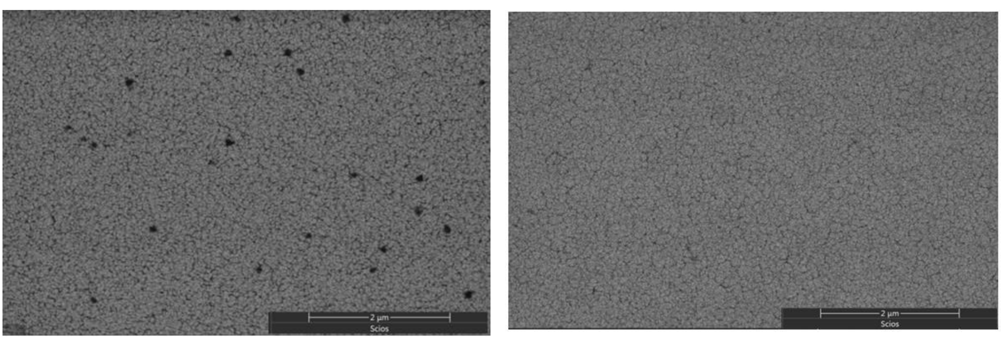

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Fig. 2. Mn_4Si_7 film before heating a) and after heating at a pressure of 10^{-3} Pa at a temperature of $T = 650\ K$ b).

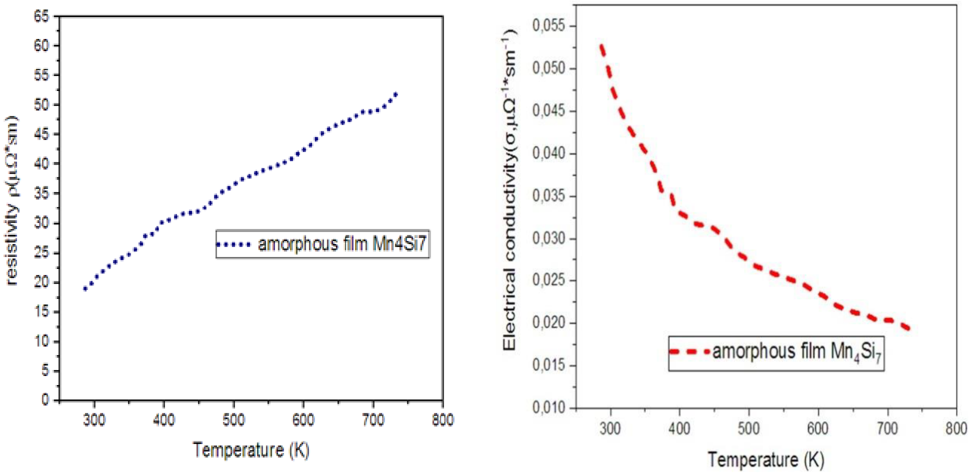

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Fig. 3. Temperature dependence of the resistivity and electrical conductivity of the resistance of the Mn_4Si_7 film in the amorphous state

The specific resistance of the formed Mn_4Si_7 film is $20 \cdot 10^{-6}$ Ω·cm at room temperature; when heated to a temperature of 750 K, its resistivity increases to $50 \cdot 10^{-6}$ Ω·cm (Fig. 3-a). The specific electrical conductivity of this film is $5 \cdot 10^4$ $\Omega^{-1} \cdot cm^{-1}$ at room temperature. When heated to 750 K, it can be seen that its electrical conductivity decreases to $1.2 \cdot 10^4$ $\Omega^{-1} \cdot cm^{-1}$ (Fig. 3-b). After annealing the Mn_4Si_7 silicide film at 650 K for 1 hour at a pressure of 10^{-3} Pa using a special device, the film was cooled in a vacuum until room temperature was reached. The graph of the temperature dependence of the resistivity and electrical conductivity of the Mn_4Si_7 silicon film is shown in fig. 4. At room temperature, it is $7.86 \cdot 10^{-6}$ Ohm·cm, and when heated to a temperature of 700 K, it resistivity decreases to $3.9 \cdot 10^{-6}$ Ohm·cm (Fig. 4-a). The specific electrical conductivity of this film is $0.12 \cdot 10^6$ $\Omega^{-1} \cdot cm^{-1}$ at room temperature. When heated to 700 K, it can be seen that its electrical conductivity increased to $0.27 \cdot 10^6$ Ω^{-1} cm^{-1} (Fig. 4-b).

It can be seen from the graph the decrease in resistivity with increasing temperature (Fig. 4-a) and the increase in electrical resistivity (Fig. 4-b) confirm that the film has a polycrystalline structure.

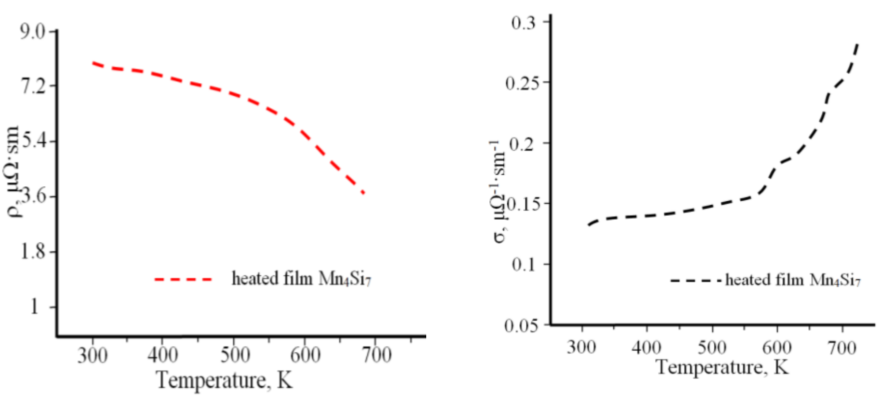

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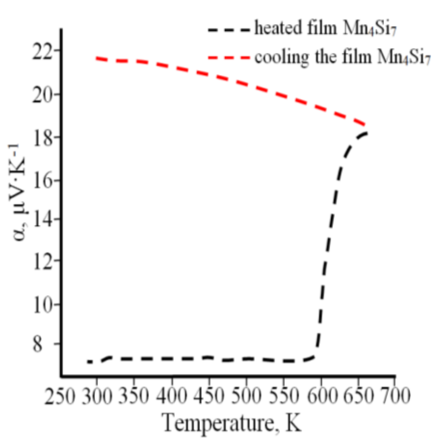
Fig. 4. Graph of the dependence of the resistivity of the Mn_4Si_7 silicon film in the polycrystalline state a) and the electrical conductivity b) on temperature.

Figure.5 shows graphs of the temperature dependence of the Seebeck coefficient of the Mn_4Si_7 film in the amorphous state (Fig. 5-a) and in the polycrystalline state (Fig. 5-b). The Seebeck coefficient of the film in the polycrystalline state turned out to be approximately 6 times higher than in the amorphous state.
These experiments lead us to conclude that an increase in the temperature of the Mn_4Si_7 silicon film in the polycrystalline state leads to an increase in the concentration of electrons and holes in the film.



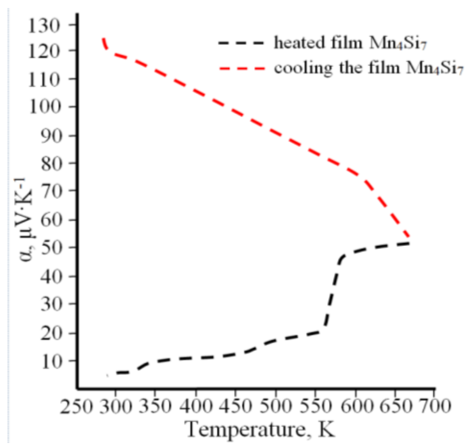


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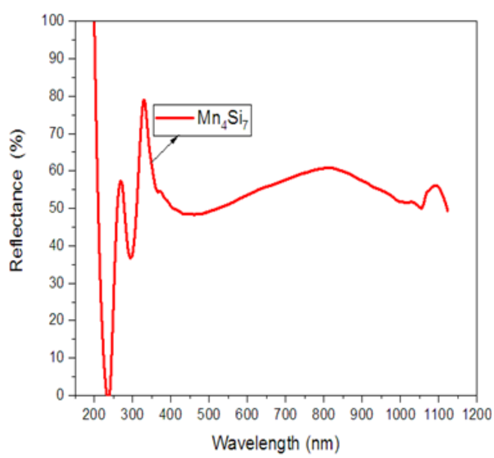
Fig. 5. a) - temperature dependence of amorphous film thermopower and b) - temperature dependence of polycrystalline silicon film thermopower Mn_4Si_7.



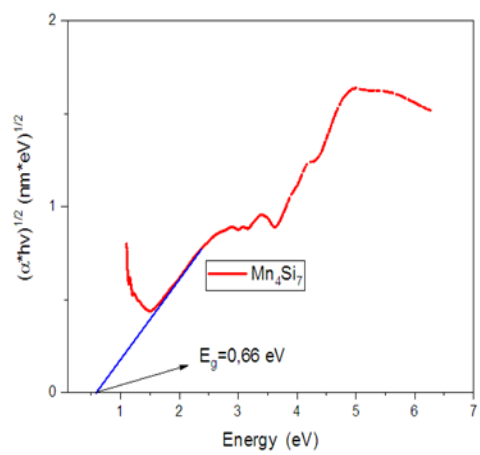


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Fig. 6. a) dependence in % of the light reflection coefficient of the Mn_4Si_7/SiO_2 film on the wavelength; b) dependence of the energy of the absorbed photon on the energy of the incident photon.

Based on the laws of reflection from the graphs shown in fig. 6, it can be seen that the Mn_4Si_7 silicide film has a high sensitivity in the visible and IR regions for the corresponding wavelengths. In addition, from these data, using the "Kubelka - Munk" function, it is possible to determine the band gap of the Mn_4Si_7 silicide film. Where α is the absorption coefficient, hν is the photon energy, R is the reflection coefficient, λ is the light wavelength [23, 24].

4 Conclusion

It has been found that the thermoelectric power of the Mn_4Si_7 film increases during the transition from the amorphous state to the nanocrystalline state, which is associated with the selective scattering of charge carriers at the boundaries of nanoclusters.

It is shown that Mn_4Si_7 films grown (grew) on a SiO_2/Si substrate have the highest conversion coefficient, which is explained by the low specific thermal conductivity of SiO_2/Si k = 149 W/m·K. Films of Mn_4Si_7 on SiO_2/Si have a high response speed and high sensitivity and can be used in thermal wave radiation detectors in the visible and IR ranges.

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