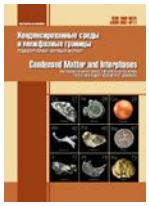

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Synthesis of bulk crystals and thin films of the ferromagnetic MnSb

M. Jaloliddinzoda✉[1], S. F. Marenkin[1,2], A. I. Ril'[2], M. G. Vasil'ev[2], A. D. Izotov[2], D. E. Korkin[2]

[1]National University of Science and Technology MISIS,
4 Leninskiy prospekt, Moscow 119049, Russian Federation

[2]Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences,
31 Leninsky prospekt, Moscow 119991, Russian Federation

Abstract

High-temperature ferromagnets are widely used on a practical level. Based on them, magnetic memory for computers and various types of magnetic field sensors are created. Therefore, bulk ingots and thin-film samples of ferromagnet manganese antimonide (MnSb) with a high Curie point are of great interest, both from the practical and fundamental sides. Manganese antimonide films are obtained in hybrid structures using molecular-beam epitaxy. The thickness of the films does not exceed tens of nanometers. Despite their high sensitivity to magnetic fields, their small thickness prevents them from being used as magnetic field sensors. The aim of this work was to synthesise thick bulk ingots of manganese antimonide crystals and films with a thickness of ~ 400 nm on sitall and silicon substrates.

MnSb crystals were synthesised using the vacuum-ampoule method and identified using XRD, DTA, and microstructural analysis. The results of studies of bulk samples indicated the presence of an insignificant amount of antimony in addition to the MnSb phase. According to the DTA thermogram of the MnSb alloy, a small endothermic effect was observed at 572 °C, which corresponds to the melting of the eutectic on the part of antimony in the Mn-Sb system. Such composition, according to previous studies, guaranteed the production of manganese antimonide with the maximum Curie temperature. A study of the magnetic properties showed that the synthesised MnSb crystals were a soft ferromagnet with the Curie point ~ 587 K. Thin MnSb films were obtained by an original method using separate sequential deposition in a high vacuum of the Mn and Sb metals with their subsequent annealing. To optimise the process of obtaining films with stoichiometric composition, the dependences of the thickness of metal films on the parameters of the deposition process were calculated.

The temperature range of annealing at which the metals interact with the formation of ferromagnetic MnSb films was established, the films were identified, and their electrical and magnetic properties were measured.

Keywords: High-temperature soft ferromagnets, XRD, DTA, Thin films, Microstructure analysis, Manganese antimonide (MnSb)

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✉ Jaloliddinzoda Muhammadyusuf, e-mail: muhammad.9095@mail.ru

1. Introduction

According to the phase diagram, manganese antimonide has a wide range of homogeneity and forms two polymorphic modifications, a hexagonal and a tetragonal one [1–5]. The first modification is a soft ferromagnet with the high Curie temperature (T_C). The Curie temperature of manganese antimonide changes significantly in the range of homogeneity from 300 to 587 K and depends on the content of manganese in a crystal lattice ($P6_3/mmc$) from 55 to 50 at% Mn [6–7]. The compositions of 50 at% Mn and Sb have the highest Curie point [8,9]. As for the melting point of MnSb, which is ~ 840 °C, there is no decisive answer as to whether MnSb melts peritectically or not [10–12].

Different areas of application of manganese antimonide were studied, both as bulk crystals and thin films [13, 14]. Manganese antimonide in the form of bulk crystals is considered to be a promising material for creating high-temperature microrefrigerators based on the magnetocaloric effect [15, 16]. MnSb films obtained on semiconductor substrates of the $A^{III}B^{V}$ group are considered to be promising materials for spintronics devices. Thus, it was of interest to synthesise bulk crystals and obtain thin films of manganese antimonide.

Molecular-beam epitaxy is a traditional way to obtain thin MnSb films [17, 18]. However, this method is complex and it does not allow obtaining films that are thicker than 20 nm. Due to the low concentration of manganese antimonide, the films have low magnetic field sensitivity. It was of interest to synthesise films with greater thickness using vacuum thermal sputtering [19–22]. However, the use of this method was limited due to the incongruent nature of the evaporation of manganese antimonide. To solve this problem, the separate sequential production of Mn and Sb films of a certain thickness was used with further thermal annealing, which ensured their stoichiometric composition. The aim of this work was to synthesise thick bulk ingots of manganese antimonide crystals and films with a thickness of ~ 400 nm on sitall and silicon substrates.

2. Experimental

Bulk single crystals were synthesised from high-purity elements. We used antimony N5 and manganese N3. Mn was subjected to resublimation in a high vacuum for additional purification. The crystals were obtained using the vacuum-ampoule method at a temperature 5 °C lower than the melting point of MnSb. To obtain samples with the maximum Curie point, a small excess of antimony was introduced to the stoichiometric composition of antimony. To protect the walls of the quartz ampoule from exposure to manganese, they were graphitised.

We used quartz ampoules with the thickness of the walls from 1.5 to 2 mm. The ampoules were purified using the solution of aqua regia, washed with distilled water, and dried. Mn and Sb were placed in the ampoules that were then pumped out to 10^{-1} Pa and unsoldered. We synthesised MnSb in the furnace at a temperature of 835 °C with a heating rate of 60 deg/hour. The temperature was controlled and regulated with an accuracy of ± 1 °C using a Termodat-16E3. For the purpose of homogenisation, the melt was kept at a temperature of 835 °C for at least 25 hours with further cooling in the switched-off furnace. As a result, thick ingots were obtained and identified using XRD, DTA, microstructural analysis, and other methods.

XRD was conducted in the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, using a Bruker D8 Advance powder diffractometer. The obtained diffraction patterns confirmed the formation of MnSb phase of the space group $P6_3/mmc$, corresponding to the composition 50 at% Mn (Fig. 1). The X-ray patterns also showed reflections of an insignificant amount of Sb.

The synthesised samples were examined using DTA on the equipment with the software for heating and cooling processes. Fig. 2 shows a thermogram of the heating and cooling of a bulk sample of MnSb. Two thermal effects were noted on the thermogram. The high-temperature effect was related to the melting of MnSb, while the low-temperature effect was due to the melting of the eutectic of MnSb + Sb.

According to the thermogram, endothermic effects were observed: the first one at 572 °C was related to the melting of the eutectic (MnSb + Sb), the second one at 792 °C was due to the melting of MnSb, which corresponds to the XRD data on the presence of a small excess of

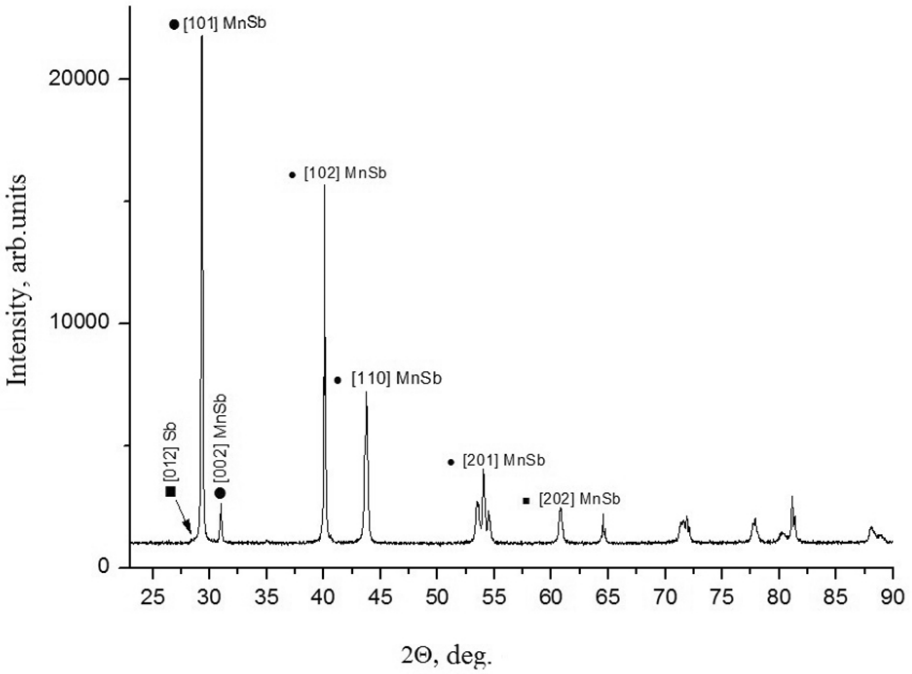

Fig. 1. Diffraction pattern of the synthesised MnSb sample

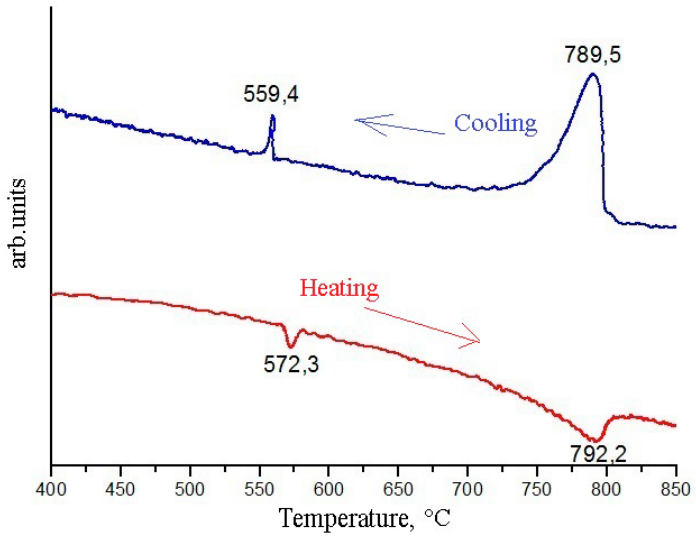

Fig. 2. Thermogram of the heating and cooling of MnSb

antimony in the samples. The examination of temperature dependences of the magnetisation (Fig. 3) showed that the synthesised samples were soft ferromagnets with the Curie point of 587 K, which corresponds well with the previous studies. The study of changes in the magnetisation due to the value of the magnetic field showed that coercive force was H_c = 5.9 Oe (Fig. 4). The magnetisation value in the magnetic saturation field was *Ms* = 84 emu/g with the value of residual magnetisation being 0.9 emu/g.

Manganese antimonide films were synthesised using sequential separate vacuum-thermal deposition of Mn and Sb films on sitall and silicon substrates with their further thermal annealing. To optimise obtaining the stoichiometric composition of MnSb films, we calculated the flux density and the rate of condensation of vapours of Mn and Sb metals. The calculations were made under conditions of molecular evaporation using the Langmuir equation [23]. Based on the results of temperature dependences of the evaporation

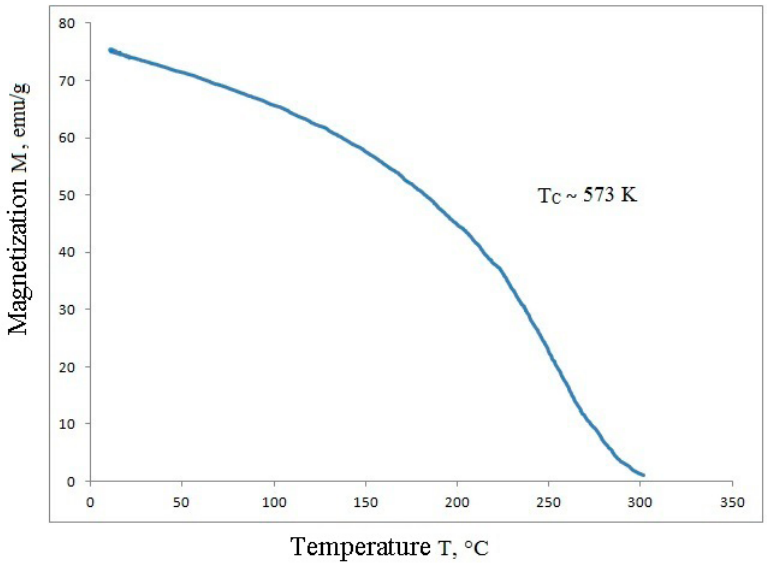

Fig. 3. Temperature dependences of the magnetisation of MnSb samples

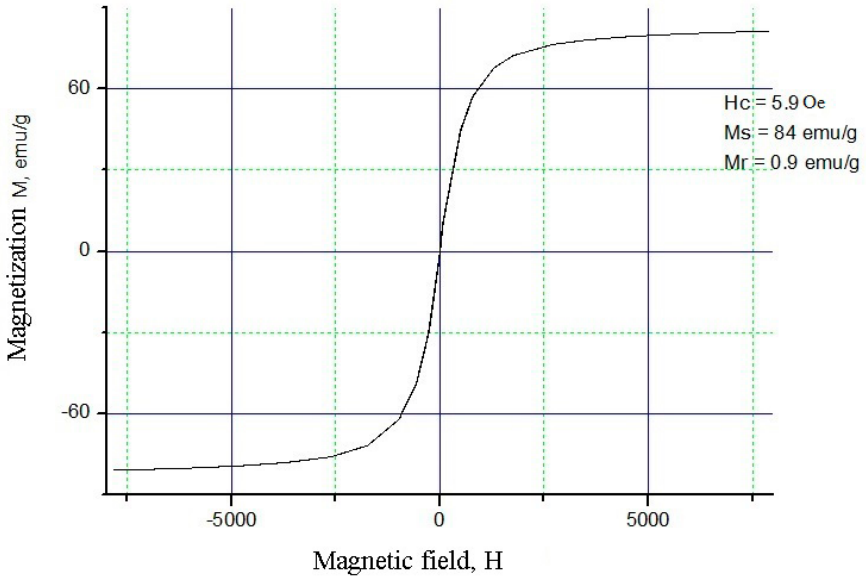

Fig. 4. Dependence of the magnetisation of bulk samples on the value of the magnetic field at T = 300 K

rates of antimony and manganese in the range of 900–1700 K, the distance from the evaporator to the substrate varied from 3 to 15 cm. The calculation results are presented in Figs. 5, 6.

The metals were evaporated in vacuum ($5 \cdot 10^{-4}$ Pa) on a substrate made of single-crystal silicon. We used high-purity metals Mn (5N) and Sb (5N). Conical resistive heaters, pre-annealed in a high vacuum, were used as the source of evaporation. We chose the temperature of the evaporator and the distance between the evaporator and the substrate based on the calculated densities of fluxes and the rate of evaporation. The time of evaporation was chosen so that the thickness of the films was ~ 200 nm.

The samples of metals for the synthesis of manganese antimonide with a stoichiometric composition contained 0.020 g of manganese and 0.032 g of antimony respectively. The films were deposited using a vacuum universal post (VUP-5). The sputtering was conducted with a ~ 10^{-4} Pa vacuum. Conical resistive heaters were

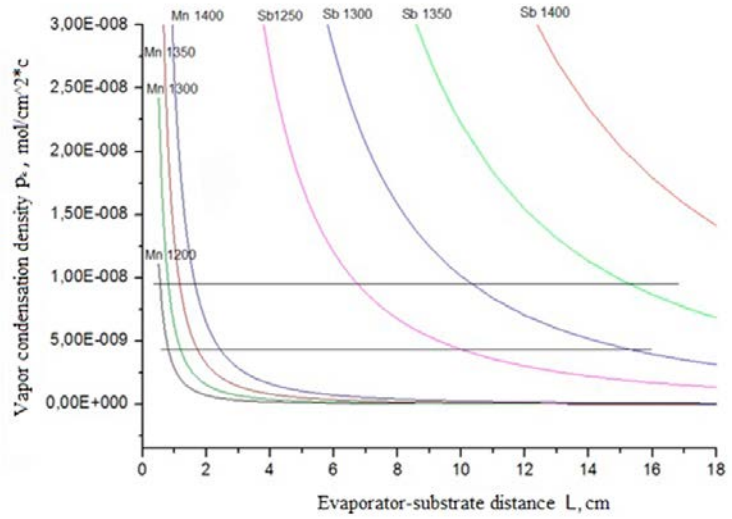

Fig. 5. Dependence of the condensation flux density on the evaporator-substrate distance

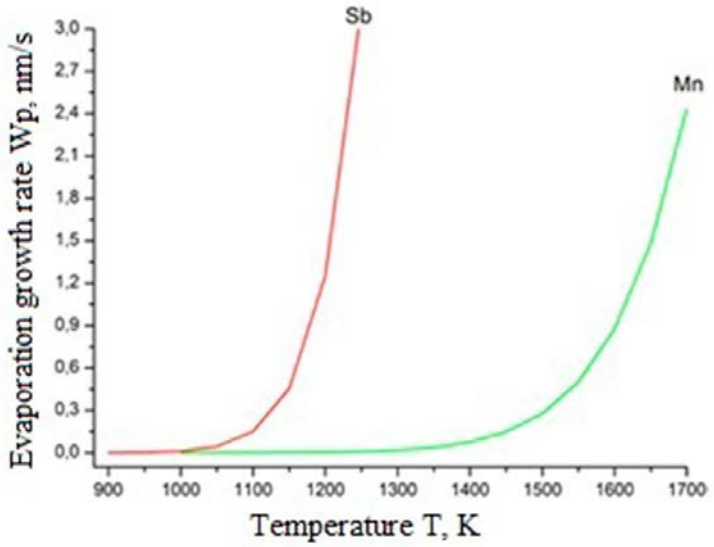

Fig. 6. Temperature dependence of the rate of condensation of Mn and Sb on the substrate 2θ

used as the evaporator. The distance between the evaporator and the substrate was at least 10 cm. The size of the substrates was 10x5x0.5 mm. The composition of the films was studied using XRD and scanning electron microscopy (SEM). Fig. 7a shows a diffraction pattern of the Sb film on a sitall substrate where only reflections related to antimony and sitall were observed. Fig. 7b shows the diffraction pattern of the Sb film on silicon substrates.

Manganese films were sputtered on antimony films. The MnSb films were synthesised by thermal annealing in vacuumed ampoules placed in the isothermic section of an electrical furnace. According to XRD data (Fig. 8) and microstructural analysis (Fig. 9), phase synthesis of MnSb started at a temperature of 380 °C.

The optimal temperature of synthesis was ~ 400 ± 20 °C with an annealing time of 2 hours. A further increase of the temperature resulted in the disruption of the mechanical strength and detachment of the films from the substrate. Fig. 10 shows the temperature dependence of the resistivity within the temperature range of 100 – 300 K, according to which the films had metal conductivity. It should also be noted that the resistivity of the annealed films was 3-4 times higher as compared to the unannealed ones. This

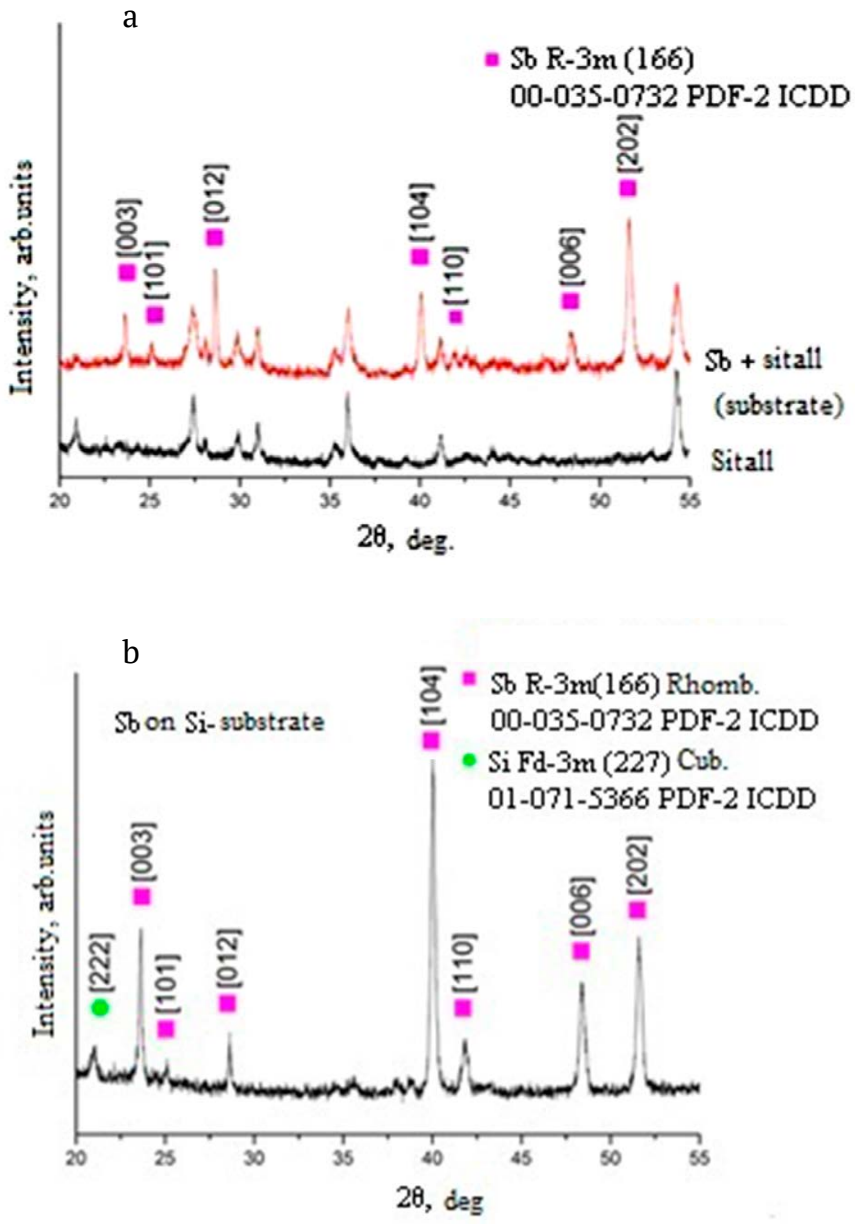

Fig. 7. X-ray diffraction patterns of Sb films on substrates made of sitall (a) and single-crystal silicon (b)

also proves the interaction between manganese and antimony metals with the formation of a manganese antimonide film (MnSb).

4. Conclusion

Using the vacuum-ampoule method, we synthesised thick bulk samples of manganese antimonide, which are soft ferromagnets with T_C = 587 K. The high chemical activity of nanostructured Mn and Sb metal films allows synthesising the MnSb compound at low temperatures by annealing in a high vacuum. We found optimal conditions for the synthesis of MnSb from Mn and Sb films.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

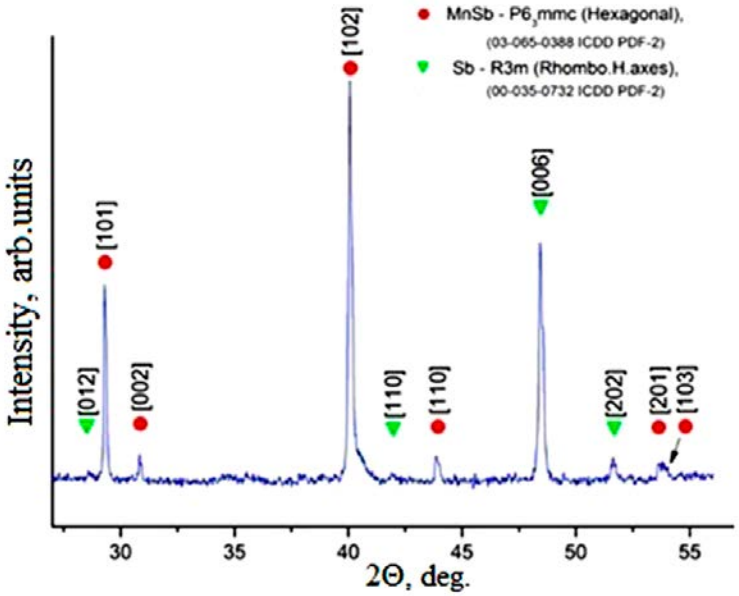

Fig. 8. Diffraction patterns of Mn + Sb films after annealing at T = 400 ° C

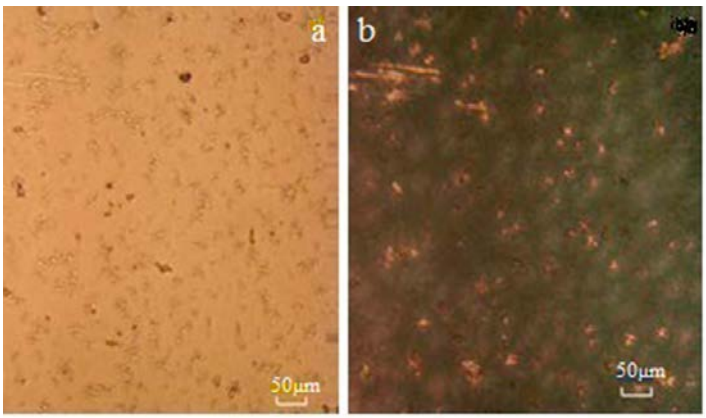

Fig. 9. Microstructure of a film with Mn and Sb layers, before annealing (a), after annealing at 400 °C (b)

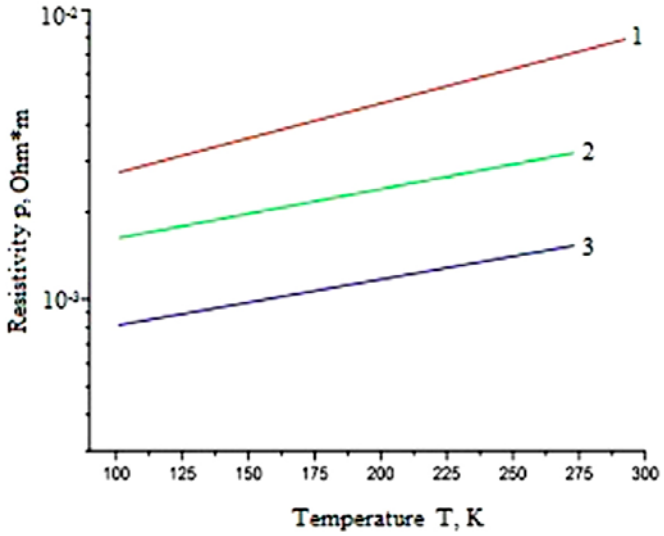

Fig. 10. Temperature dependence of the resistivity of films with a temperature range of 100-300 K: *1* – annealed MnSb film on sitall; *2* – Mn + Sb, unannealed on sitall; *3* – unannealed Mn + Sb on silicon

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Information about the authors

Muhammadyusuf Jaloliddinzoda, PhD student, Department of Electronic materials technology, National University of Science and Technology "MISIS", Moscow, Russian Federation; e-mail: muhammad.9095@mail.ru. ORCID iD: https://orcid.org/0000-0002-5187-5136.

Sergey F. Marenkin, DSc in Chemistry, Professor, Chief Researcher of the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; email: marenkin@rambler.ru. ORCID iD: https://orcid.org/0000-0003-2577-6481.

Alexey I. Ril', Junior Researcher at the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: ril_alexey@mail.ru. ORCID iD: https://orcid.org/0000-0002-7745-2529.

Mikhail G. Vasil'ev, DSc in Technical Sciences, Professor, Head of the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: mgvas@igic.ras.ru. ORCID iD: https://orcid.org/0000-0002-4279-1707.

Alexander D. Izotov, DSc in Chemistry, Corresponding Member of Russian Academy of Sciences, Chief Researcher at the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: izotov@igic.ras.ru. ORCID iD: https://orcid.org/0000-0002-4639-3415.

Denis E. Korkin, Technologist at the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: disa5566@yandex.ru. ORCID iD: https://orcid.org/0000-0001-6838-3974.

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