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Thermoelectric coefficient of nanoscale transition metals films

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We study the thermoelectric coefficient of island transition metal films as a function of temperature and film thickness. We show that the thermoelectric coefficient value is determined by the properties of the film metal element and is different for different metals at dimensionless conductance value $g > 1$ and $g < 1$. The main factor in the behavior difference of the thermoelectric coefficient as a function of temperature is the individual characteristics of the Fermi surface of each metal. Dependence of the thermoelectric coefficient on the film thickness is also determined by the Fermi surface shape change.

Keywords: Island film, Thin film, Thermopower, Thermoelectric coefficient, Conductivity.

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1. Introduction

The most widespread method for the making of nano-sized metal films at present is the magnetron sputtering method. Films made by this method, having thicknesses less than $d < 3$ nm, are usually island films. Such films are characterized by tunneling conductivity and, at a thickness of $d \approx 2$ nm, they transition from the metal type of conductivity ($g > 1$) to the dielectric type of conductivity ($g < 1$). Here $g = (e^2/\hbar)^{-1}\sigma$ is the dimensionless conductance of structure, \hbar — Planck constant, σ — conductivity per unit area [1–4]. The following phenomena were found in island metal films: radiation in the external electric field [5], photoconductivity in the visible and infrared spectrum regions [6], anomalous conductivity [7,8] etc. Thermoelectric properties in island and granulated metal systems are studied in several papers, e.g. [9–13]. The interest in thermoelectric properties of metal nanoisland structures is due to the fact that, on the one hand, they can have a high electrical conductivity, and on the other hand — a low thermal conductivity. These factors make it possible to hope that thermoelectric figure of merit in metal island films can be higher than in bulk materials.

One of the main parameters which determines the material's thermoelectric properties is its thermoelectric coefficient (Seebeck coefficient). The theory of thermopower of granulated and island systems was developed taking into account mainly the temperature factor, hopping nature of conductivity in structures and granule sizes (D) or granule charge energy ($E_C \approx e^2/2D$, $D \propto C$, C — island capacity, e — electron charge) [10–12]. The role of the granules' elemental composition was neglected in the given papers. Paper [13] describes measurements of the thermoelectric coefficient of island films while taking into account the metal film thickness, nature of film conductivity (metal $g > 1$ or dielectric $g < 1$) and film chemical composition. It was

demonstrated that the thermoelectric coefficient value for all the studied films is determined by properties of the film's metal element and is different for different materials. Influence of the tunnel component of film conductivity on the value of the island structure thermoelectric coefficient was not found even at the conductance of $g \ll 1$. Mechanisms of change of the value of the island structure thermoelectric coefficient with change of film thickness and chemical composition were not discussed previously.

The present paper is aimed at studying the processes of change of the thermoelectric coefficient of island metal films with change in the thickness of films made of different metals and alloys.

2. Problem statement and measurement results

The results of studies of island films with the tunneling conductivity $g \ll 1$ turn out to be unexpected [13]. On the one hand, it was demonstrated that the thermoelectric coefficient value for all the studied films is determined by properties of the film's metal element and is different for different materials. On the other hand, the thermoelectric coefficient in a Co film with the thickness of $d = 0.8$ nm with temperature decrease to $T \approx 150$ K passes through $S = 0$, i.e., while the main role is determination of the thermoelectric coefficient value and sign at $T > 150$ K was played by electrons, at $T < 150$ K the thermoelectric coefficient value and sign are determined by holes. This dependence of the cobalt film thermoelectric coefficient on temperature cannot be explained from the viewpoint of change of conductivity in metal islands with change of the charge carriers' free path length. The authors of [13] emphasized the fact that both electrons and holes are involved in metal conductivity. Taking into account the

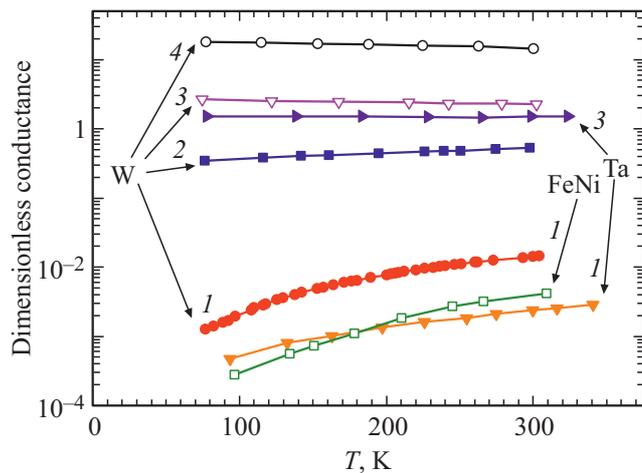


Figure 1. Conductance vs. temperature for structures having different metal film thicknesses (Tungsten: 1 — 0.8 nm; 2 — 1.2 nm; 3 — 1.8 nm; 4 — 4 nm; Tantalum: 1 — 0.8 nm; 3 — 1.8 nm; FeNi: 1 — 0.8 nm).

aforsaid, we have measured the thermoelectric coefficients of island films of Ta and W transition metals, as well as the FeNi alloy, in order to study the processes which are responsible for changes of the thermoelectric coefficient value with change of film thickness. The selection of the Ta and W metals is due to the fact that tantalum has an odd number of valence electrons, while tungsten has an even number.

We made island metal films of FeNi, Ta and W for studies; their effective thicknesses were as follows: № 1 — $d = 0.8$ nm; № 2 — $d = 1.2$ nm; № 3 — $d = 1.8$ nm; № 4 — $d = 4$ nm. A detailed description of the film manufacture process is given in papers [4,13,14]. Differential conductivity and thermo-emf of the films were measured in the temperature region of 77 to 400 K, the measurement method is described in detail in [13].

Fig. 1 shows the conductances of the W, Ta and FeNi films vs. temperature for structures having different metal film thicknesses. In terms of dependence pattern, the film conductances virtually do not differ from each other when film thickness is the same. As seen in Fig. 1, conductivity of the W, Ta and FeNi films, made in identical conditions on identical dielectric substrates, changes by four orders of magnitude with approximately a twofold change of film thickness (from 0.8 to 1.8 nm). Film conductivity increases with temperature increase. When metal film thickness is 1.8 and 4 nm, film conductivity does not greatly depend on temperature in the studied range. In this case we observe a slight decrease of conductivity with temperature rise.

The thermoelectric coefficients vs. temperature for the W, Ta and FeNi films of different thicknesses are shown in Fig. 2,3 and 4 respectively. Fig. 3 shows (for reference) the dependence of the thermoelectric coefficient of bulk tantalum [15] (curve 5).

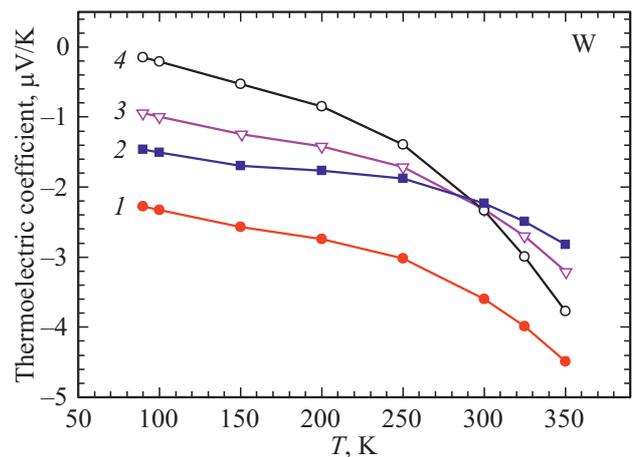


Figure 2. Thermoelectric coefficient of tungsten vs. temperature for four structures having different metal film thicknesses (1 — 0.8 nm; 2 — 1.2 nm; 3 — 1.8 nm; 4 — 4 nm).

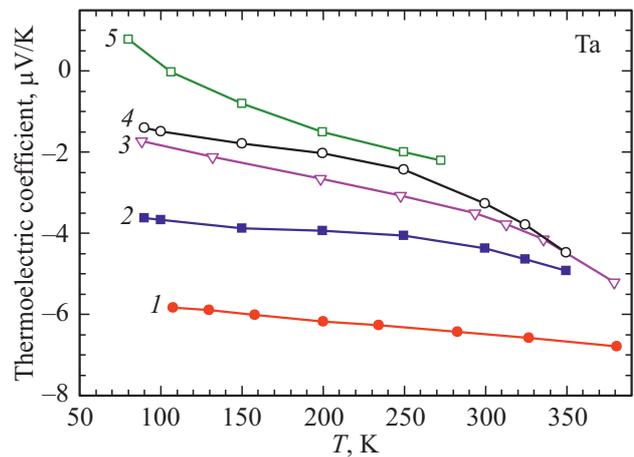


Figure 3. Thermoelectric coefficient of tantalum vs. temperature for four structures having different metal film thicknesses 1 — 0.8 nm; 2 — 1.2 nm; 3 — 1.8 nm; 4 — 4 nm; 5 — thermoelectric coefficient of bulk tantalum [5]).

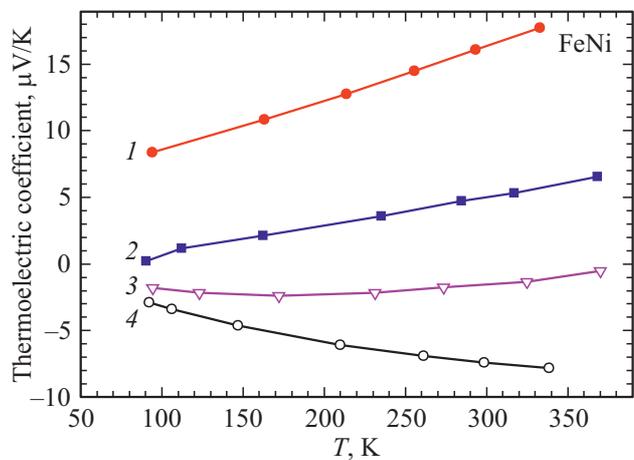


Figure 4. Thermoelectric coefficient of FeNi vs. temperature for four structures having different metal film thicknesses (1 — 0.8 nm; 2 — 1.2 nm; 3 — 1.8 nm; 4 — 4 nm).

3. Discussion

The value of dimensionless conductance (g) varies from 0.001 to 30 for all the types of films made of different metals from 0.8 to 4 nm thick. Films with the thickness of $d \approx 1.8$ nm have the dimensionless conductance value $g = 1$. In this case, conductivity in films having thicknesses $d > 1.8$ nm can be considered as metal-type, while tunnel conductivity must be observed in films having thicknesses $d < 1.6$ nm. Films with thicknesses $d < 1.6$ nm are island films. The average sizes of nanoislands in a film having thickness $d = 1.2$ nm are equal to approximately 10–20 nm. The average sizes of nanoislands in a film having thickness $d = 0.8$ nm are approximately 3–4 nm [13].

Our research of conductivity of granulated and island systems [4,14] have made it possible to determine the processes that define the charge carrier transfer in these structures. These processes at $g \ll 1$, on the one hand, define the concentration of excess charge carriers in islands, on the other hand characterize the rate of transfer of excess charge carriers from one island to another (mobility). Thereat, these processes occur irrespective of each other [14]. The process which defines the concentration of excess charge carriers in islands is chiefly related to electron tunneling from one neutral island to another neutral island and is an activation one. Activation energy is mainly determined by the value of charge energy E_C . Deviation of conductivity dependence from the Arrhenius law is determined by the spread of the activation energy in magnitude due to the spread of island sizes. As temperature rises, the activation process will involve islands with all the higher activation energy (with a lower value of quantity D) and, consequently, the average value of activation energy will increase as temperature rises [6]. The rate of transfer of excess charge carriers from one island to another is related to electron or hole tunneling from a charged island to a neutral island. Thereat, excess charge carriers tunnel to the nearest neutral island virtually without an energy change.

The thermoelectric coefficient is described by the following formula in case of the tunnel pattern of conductivity in inhomogeneous structures [12,16]:

$$S = \frac{k^2}{2e} (T_0 T)^{0.5} \frac{\partial \ln g(\epsilon_F)}{\partial E},$$

where T_0 — parameter, $T_0 \propto E_C \approx e^2/2D$, E_C — charge energy, k — Boltzmann constant, T — sample temperature, e — electron charge, $g(\epsilon_F)$ — density of states at Fermi level, ϵ_F — Fermi energy. However, the paper [13] demonstrated that the thermoelectric coefficient value in island films based on Co and W is determined by properties of the film's metal island and is different for different materials. Influence of the tunnel component of film conductivity on the value of the island structure thermoelectric coefficient was not found even at the conductance of $g \ll 1$. Moreover, the experimental data on dependence of the thermoelectric coefficient on temperature in transition metals (Fig. 2, 3

and 4), given in the present paper, confirm the conclusions made in [13].

Indeed, films of W, Ta and FeNi transition metals, made in identical conditions with identical effective thicknesses of metal and dielectric layers, have completely different dependences of thermoelectric coefficients on temperature. Thermoelectric coefficient values decrease in W films with thickness decrease. The decrease of the thermoelectric coefficient value with film thickness decrease is associated in paper [13] with decrease of the total area of nanoislands on the substrate. Temperature dependence of the thermoelectric coefficient in metal nanoislands of tungsten (like in bulk metals) is associated with change of the average charge carrier energy with temperature change.

However, the pattern of dependence of Ta and FeNi thermoelectric coefficients on film thickness and on temperature differs markedly from the dependences of tungsten film thermo-emf (Fig. 3 and 4). Tantalum films are characterized not by decrease but by increase of the absolute value of thermoelectric coefficient with thickness decrease (Fig. 3). Since the thermoelectric coefficient is negative, the main role in determination of tantalum thermoelectric properties is played by electrons, regardless of film thickness and in the whole region of measured temperatures.

The dependences of the thermoelectric coefficient on temperature and film thickness for FeNi films are also different. It can be seen from Fig. 4 (curve 3 and 4) that the thermoelectric coefficient for thick films (4 and 1.8 nm) is negative. With decrease of film thickness, the thermoelectric coefficient decreases in absolute magnitude. With further decrease of film thickness (1.2 and 0.8 nm), the thermoelectric coefficient passes through 0 and takes on a positive value. The W, Ta and FeNi metal films (made using the same technology), as it follows from the discussion above, demonstrate completely different thermoelectric properties depending on film thickness and element composition of metal nanoislands. This ambiguous behavior of island films cannot be explained within the framework of the free electron model and from the viewpoint of change of conductivity in metal islands with change of the charge carriers' free path length.

The absolute value of the thermoelectric coefficient of transition metals is usually determined by charge carriers of several energy bands located near the Fermi level, each of which contains only electron or hole orbits. The configurations of the outermost electron shells of the W, Ta and FeNi metals and, consequently, the Fermi surfaces of the said metals differ from each other. A peculiarity of the Fermi surface for each metal is the main factor of different behavior of the thermoelectric coefficient for these metals.

Thicknesses of the studied films are comparable to the interatomic distance of the metal lattice. It can be assumed that a film thickness change significantly affects the configuration and pattern of the metal Fermi surface. The following factors can influence a configuration change of the Fermi surface with change of the metal film thickness

- disruption of long-range order in atom arrangement in a metal in the film growth direction;
- influence of the substrate on the interatomic distance of a metal layer near the metal–substrate interface.

It is known [17,18] that interatomic distances can change in metals due to external actions, and the whole energy structure of the metal and the Fermi surface also change. Metals' electronic properties change simultaneously with the Fermi surface change. In the momentum space in each electron energy band there are points where the topology of isoenergetic surfaces changes: either a cavity of a constant energy surface appears (disappears) or a jumper breaks (forms) (Fig. 5). Transition of a system of corrugated toroids to ellipsoids is possible [17,18]. As a result of such changes, the open Fermi surface turns into a closed surface, while the position of individual energy band in relation to the Fermi level can transform the metal into a hole or an electron one. A particularly considerable change of the Fermi surface configuration can be observed in transition metals where hybridization of *d*- and *s*-states is present.

At the initial stage, the substrate greatly affects the formation of the metal crystalline lattice. We used a crown glass on the basis of SiO₂ oxide as a substrate. Interatomic distance in the SiO₂ oxide, depending on modification, varies within 0.5 nm, while all the metals deposited on the substrate (W, Ta and FeNi) have a lattice constant of approximately 0.3–0.35 nm. This mismatch of interatomic distances of the substrate and metal causes a considerable distortion of the crystalline lattice of metal layers near the metal–substrate interface. With further increase of the metal film thickness, the substrate influence on the metal crystalline lattice weakens, and the film crystalline structure approaches the bulk structure of metals.

A change of interatomic distances in the crystalline lattice of metal films with change of their thickness, as already mentioned above, results in a change of the Fermi surface in films. This assertion is confirmed by the results of measurement of dependences of metal film thermoelectric coefficients on thickness and temperature, shown in Fig. 2, 3 and 4.

Since the dependences of thermoelectric coefficients on temperature and film thickness for different metals differ considerably from each other, the behavior of W, Ta and FeNi metal films should be considered separately for each metal.

Tungsten is a group 4 element. The configuration of outermost electron shells is 5s²p⁶d⁴6s². The metal with a cubic bulk-centered lattice the parameter of which is $a = 0.31647$ nm. The Fermi surface is closed. In the Fermi surface center there is an electron „pocket“, while „pockets“ in its corners contain holes. The metal is „compensated“. The number of electrons is equal to the number of holes ($n = p$) [19]. Fig. 2 shows the thermoelectric coefficient of tungsten vs. temperature for four structures having different metal film thicknesses.



Figure 5. Change in Fermi surface cohesion with change of interatomic distances in the metal crystalline lattice. *a* — break of jumpers (an open Fermi surface becomes a closed surface); *b* — formation of a new Fermi cavity [17,18].

The crystalline structure in a thin film with thickness $d = 4$ nm is close to the crystalline structure of bulk tungsten. The Fermi surface in this film and the Fermi surface of bulk tungsten do not greatly differ from each other. In films of smaller thickness, a mismatch of interatomic distances of the substrate and the metal changes the parameters of the crystalline lattice of the thin metal film. When film thickness is $d = 0.8$ nm, influence of the substrate on the interatomic distance in the metal for the structures under study will be the maximum. It should be noted here that thickness in a film with $d = 0.8$ nm insignificantly exceeds the tungsten lattice parameter ($a = 0.31647$ nm), i.e. the long-range order is not present in the film. The whole energy structure of the metal changes in this case and the Fermi surface changes. The Fermi surface of tungsten is closed. In this case additional cavities of the constant energy surface can appear (Fig. 5, *b*) [17,18]. Additional cavities of the Fermi constant energy surface, apparently, do not affect the closed pattern of the Fermi surface in a tungsten film, then the metal remains „compensated“ [19].

The same as in bulk metals, the average charge carrier energy in metal nanoislands decreases with temperature decrease. The thermoelectric coefficient value in tungsten also decreases proportionally with decrease of the average charge carrier energy (Fig. 2). On the other hand, film thickness considerably affects the thermoelectric coefficient value. Thus, nanoisland dimensions decrease with film thickness decrease [13], and the total area of nanoislands on the substrate will decrease. Indeed, the average sizes of nanoislands in a film having thickness $d = 1.2$ nm are equal to approximately 10–20 nm. The average sizes of nanoislands in a film having thickness $d = 0.8$ nm are

approximately 3–4 nm. Consequently, the temperature difference, applied to the structure, is redistributed among metal islands and dielectric barriers in favor of the barriers while nanoisland sizes decrease.

It should be emphasized that the temperature gradient in a metal island is generated not due to heat propagation along the film, but due to heat coming through the surface between the island and the substrate, and heat coming to the metal nanoisland through the side surface from the barrier metal. Such a heat propagation in films leads to the equality of the temperature gradient in the substrate, the barrier and metal layers.

Tantalum is a group 5 element. The electron configuration of outermost shells is $5s^2p^6d^36s^2$. The metal with a cubic body-centered lattice the parameter of which is $a = 0.330$ nm. The Fermi surface is open and is a spatial grid of corrugated cylinders along axes (001). The number of electrons is not equal to the number of holes ($n \neq p$) [19].

Dependences of tantalum thermoelectric coefficients on film thickness and on temperature differ markedly from the dependences of tungsten film thermoelectric coefficient (Fig. 3). Tantalum films are characterized not by decrease but by increase of the absolute value of thermoelectric coefficient with thickness decrease. Such behavior of tantalum-based films can be explained only from the viewpoint of a significant change of the tantalum Fermi surface with a decrease of film thickness. Thermoelectric coefficient value and sign in tantalum are determined both by electrons and by holes. The thermoelectric coefficient at $T = 300$ K is negative and determined by electrons. The thermoelectric coefficient value at $T \approx 110$ K is $S = 0$ and becomes a positive value with further temperature decrease; this value is determined by holes (Fig. 3, curve 5). The sign and value of the tantalum thermoelectric coefficient in intermediate temperatures is determined by the joint influence of electrons and holes.

In films of smaller thickness, the same as in tungsten, a mismatch of interatomic distances of the substrate and the metal changes the parameters of the crystalline lattice of the thin metal film, which results in a change of the Fermi surface. In particular, the spatial grid of corrugated cylinders of the tantalum Fermi surface may transform into an ellipsoidal Fermi surface, and this surface will be closed [17,18]. The position of individual energy bands in relation to the Fermi level may cause predominance of an electron energy band in the metal. The effect of influence of the electron component on the thermoelectric coefficient value is seen in Fig. 3, which shows an increase of the negative thermoelectric coefficient in the tantalum-based structure with decrease of film thickness.

The FeNi alloy contains approximately 80% of nickel and 20% of iron and is classified as crystalline alloys [20]. The crystalline structure of FeNi differs from that of the alloy components, therefore the alloys' electron structure is very complex, while the alloy Fermi surface differs from the iron and nickel Fermi surfaces.

Thermoelectric coefficient of FeNi vs. temperature for four structures having different metal film thicknesses is shown in Fig. 4. We have already mentioned the distinctive feature of the FeNi alloy-based film, where a transition from a negative to a positive thermoelectric coefficient was observed with change of film thickness. The main role in determination of the thermoelectric coefficient value and sign in thick films ($d = 4$ nm and $d = 1.8$ nm) is played by electrons, while the thermoelectric coefficient value and sign in thin films ($d = 1.2$ nm and $d = 0.8$ nm) are determined by holes. A change of charge carrier type in the film can be due, like in tantalum, to the peculiarities of the modification of the FeNi alloy Fermi surface with change of its thickness.

4. Conclusion

The conducted studies of electrophysical properties of metal nanoisland structures, created on the basis of W, Ta and FeNi transition metals, have revealed several interesting peculiarities of island films' behavior under the electric field action and under the temperature gradient action. Thus, transfer of charge carriers from one island to another in thin films with thickness $d = 1.2$ nm, with the metal island sizes of 10–20 nm, and films with thickness $d = 0.8$ nm, with the metal island sizes of approximately 3–4 nm, is related to electron or hole tunneling from one island to another. The barrier in all island metal films was the same dielectric (Al_2O_3). As a result (Fig. 1), the conductances of the W, Ta and FeNi films are almost the same in case of an identical film thickness, while the tunnel current value is determined by distance between islands and height of the potential barrier of the dielectric located between the metal islands.

The situation is completely different when studying the dependences of thermoelectric coefficients on temperature of films of W, Ta and FeNi transition metals, made in identical conditions with identical effective thicknesses of metal and dielectric layers. Thermoelectric coefficients of films of different metals have different temperature dependences. It was demonstrated that the thermoelectric coefficient value for all the studied films is determined by properties of the film's metal element. Influence of the tunnel component of film conductivity on the value of the island structure thermoelectric coefficient was not found even at the conductance of $g \ll 1$. It should be taken into account, however, that tunneling of charge carriers in the structure provides electric coupling between metal islands.

The main factors of the different behavior of the film thermoelectric coefficient depending on temperature are the individual peculiarities of the Fermi surface of each metal. Change of the thermoelectric coefficient value depending on film thickness is also determined by change of the metal Fermi surface shape regardless of whether the Fermi surface of the metal of the studied film is open or closed. Modification of Fermi surface shape is related to change of interatomic distances of metal islands. At the initial stage

of film growth, the substrate greatly affects the formation of the metal crystalline lattice. A mismatch of interatomic distances of the substrate and metal results in a considerable distortion of the crystalline lattice of metal layers near the metal–substrate interface. A metal Fermi surface, where the distorted lattice determines its shape, forms near the metal–substrate interface. With increase of the film thickness (film thicknesses being $d = 4$ nm), the crystalline structure in the metal island approaches the bulk structure. The film Fermi surface in this case has a shape resembling that of the bulk material's Fermi surface. This assertion is confirmed, for instance, by the insignificant deviation of the temperature dependence of the thermoelectric coefficient in a tantalum film with thickness $d = 4$ nm and in bulk metal (Fig. 3, curves 4 and 5).

The conducted studies of metal nanoisland structures, thanks to their various properties and capability to affect the Fermi surface shape in different metals, open the prospects of engineering thermoelectric devices with improved characteristics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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