Effective sputtering yields of alloys chromel and kopel with argon ions in magnetron sputtering system

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Abstract. This article presents the results of research on sputtering of thermoelectric alloys chromel and kopel. Sputtering was performed in argon atmosphere with magnetron sputtering system. Results of this work can be used in creation of thin-film thermoelectric generators.

1. Introduction
Thermoelectric effects are widely used in various branches of industry, generally in temperature sensors, electricity generators and thermostabilizing modules [1]. Nowadays in connection with miniaturization of electronics increases the interest in various thin-film (thickness less than 1 micron) components.

For creation of thin-film thermoelectric generators (TEG) with use of traditional alloys is suggested to use magnetron sputtering [2]. This method allows to spray down thin layer structures of alloys with also saving of their stoichiometric composition in the coating. The key parameters in the process are sputtering yields. For pure metals they are well known in wide range of ion energies [3, 4]. For alloys, especially for complex ones, such data is absent in the modern literature.

This research is assigned to experimentally determining of effective sputtering yields of materials used in TEG (chromel and kopel).

2. Method substantiation
There is a lot of data regarding sputtering yields of various materials $S(\varepsilon)$ using monoenergetic ion beams with preset energy $\varepsilon$ [3, 4]. Ions that bombard the cathode of magnetron sputtering system (MSS) have non monoenergetic distribution function $f(\varepsilon)$, because of that coefficient $S_{eff}$ was determined:

$$S_{eff} = \int_0^{\infty} S(\varepsilon) f(\varepsilon) d\varepsilon$$

(1)

In sources [5, 6] retarding potential analyzer was used to determine distribution functions of ions by energies on the surface of cathodes of MSS. In result of that a conclusion was made that the type of distribution function barely depends on the material of the cathode, induction of magnetic field, surrounding gas or pressure. Average energy of ions depend on the voltage of discharge $U_d$ and is equal to:

$$\varepsilon_m = 0.8 \cdot eU_d$$

(2)

In paper [7] MSS was used to model effects of ion beams on the elements of Hall thrusters in which ion energy distribution function is almost equal to that of MSS. And thus effective sputtering yields were determined by the equation (1).
Sources [7, 8] describe effective sputtering yields of materials in MSS as proportional to that of sputtering yields by monoenergetic beam with energy that equals the average energy of ions

$$S_{\text{eff}}(\varepsilon_m) = k \cdot S(\varepsilon_m),$$

(3)

where $k$ – coefficient close to one.

Thus, the behavior of the sputtering yield of the substance during processing by a monoenergetic ion beam can be judged by the measured effective sputtering yield. At the same time, for the calculation of the technological process, the main value will be the dependence of the effective sputtering yield on the discharge voltage.

3. Experiment

Experiments to determine effective sputtering yields of kopel and chromel with MSS were performed at stand with vertical cylindrical vacuum chamber with diameter of 500 mm and height of 500 mm. MSS in the experiment had a cathode with diameter of 50 mm and thickness of 4 mm. Composition of alloys was controlled by X-ray fluorescent analyzer “Bruker S1 Titan”. Composition of Kopel consisted of copper (54.08%), nickel (44.11%), manganese (0.38%), molybdenum (1.11%), silicon (0.20%) and zirconium (0.13%). Chromel cathode consisted of nickel (87.53%), chromium (11.72%), copper (0.17%), rhodium (0.35%), hafnium (0.10%), bismuth (0.09%) and manganese (0.03%).

Effective sputtering yields with argon ions for researched materials were determined by difference of mass of cathode of MSS before and after the sputtering procedure with preset discharge voltage:

$$S_{\text{eff}} = \frac{e(M_1 - M_2)}{m_p M_d I t},$$

(4)

where $e = 1.6 \times 10^{-19}$ – elementary electric charge, C; $m_p = 1.6 \times 10^{-27}$ – mass of proton, kg; $M_a$ – atomic mass of researched alloy, u; $I$ – ion current, A; $t$ – duration of MSS performance, s; $M_{1,2}$ – cathode mass before and after the process, kg. Cathode masses were determined by the precision scales Sartorius CPA225D with precision up to $1 \times 10^{-5}$ g.

Sputtering yields were determined with different discharge voltage. MSS power supply was in current stabilizing mode. Discharge voltage was sustained on a preset level by adjusting the pressure of used gas (argon) and ranged from 350 Volts to 600 Volts. Argon pressure in vacuum chamber varied from $2 \times 10^{-2}$ to $3 \times 10^{-1}$ Pa.

![Figure 1. Effective sputtering yields of alloys chromel and kopel by argon ions with various average energies in discharge of MSS.](image-url)
Atomic mass of the alloys where determined from the mass parts of elements in the alloys:

\[ M_a = \sum M_i \cdot n_i, \]

where \( M_i \) – atomic mass of alloy element \( i \), \( n_i \) – mass fraction of alloy element \( i \).

By equation (4) calculated effective atom mass of kopel was resulted in 61.71 u, and for chromel – 57.91 u.

4. Results and discussion

Obtained sputtering yields for chromel and kopel with different average energies of ions on surface of MSS cathode are shown on figure 1.

**Figure 2.** Effective sputtering yields chromel alloy with argon ions in MSS and sputtering yields of basic alloy components by monoenergetic ion beam of argon.

**Figure 3.** Effective sputtering yields kopel alloy with argon ions in MSS and sputtering yields of basic alloy components by monoenergetic ion beam of argon.
On figures 2 and 3 for comparison are also shown sputtering coefficients of pure elements of the alloys by monoenergetic ion beam of argon. In both cases were selected three elements of alloy that had highest mass fraction in alloy’s composition.

As shown, obtained effective sputtering yields of both alloys are located in the area of coefficients for alloys’ basic elements and can be approximated as average sputtering coefficients of these basic elements.

5. Conclusion
Effective sputtering yields of alloys with the use of MSS for ion energies equal to $0.8eU_d$ are close to average value of sputtering yields for monoenergetic ion beam for alloys’ major components.

According to equation (3), obtained sputtering yields can be used for estimation of researched materials sputtering with monoenergetic ion beam with precision up to coefficient $k$.

Obtained data can be used for calculation of thin-film TEG spraying modes with magnetron sputtering system.

References
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