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Self-sustained magnetron sputtering of evaporating metal targets and its influence on the properties of deposited coatings

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Introduction

- Our strategy for the development of coating technologies using magnetron sputtering systems (MSS) is to increase the deposition rate and to provide high quality of coatings simultaneously.
- A dramatic increase in the deposition rate is achieved due to the creation of evaporation (or sublimation) on the target surface in addition to sputtering.
- Experimentally, we get up to 200 nm/s during the deposition of copper coatings, for chromium films - up to 50 nm/s. These results are an order of magnitude or more higher than the deposition rates when using conventional magnetrons.

Self-sustained sputtering (SSS-mode)

A significantly increased particles flux from the target surface can maintain magnetron discharge on vapors of the target material only. Then there is no need for the presence of a working gas, the target is sputtered by its own atoms. **This is a self-sustained sputtering mode.**

Why is it interesting for coating deposition technologies? First of all, because:

- the deposition process will take place at a lower than usual pressure in the working chamber (below 0.1 Pa); then the atoms emitted from the surface of the target will be less scattered by the atoms of the working gas and lose energy when moving from the target to the substrate;
- a cleaner atmosphere will be in the vacuum chamber, since no gases flow into it; then the film will not be contaminated by unwanted atoms entering the chamber together with the working gas.

Research objectives

- Revealing the mechanisms and operating parameters of the MSS, ensuring the stable functioning of the magnetron discharge in the SSS mode; analysis of the factors that determine the operation of the magnetron exclusively on vapors of the target material.
- Diagnostics of the characteristics of the magnetron discharge plasma during the transition to the SSS mode.
- Obtaining and analyzing data on the effect of deposition conditions in the SSS mode on the properties of the deposited coatings.

Experimental equipment: cathode assemblies

Var.1. Liquid target mode

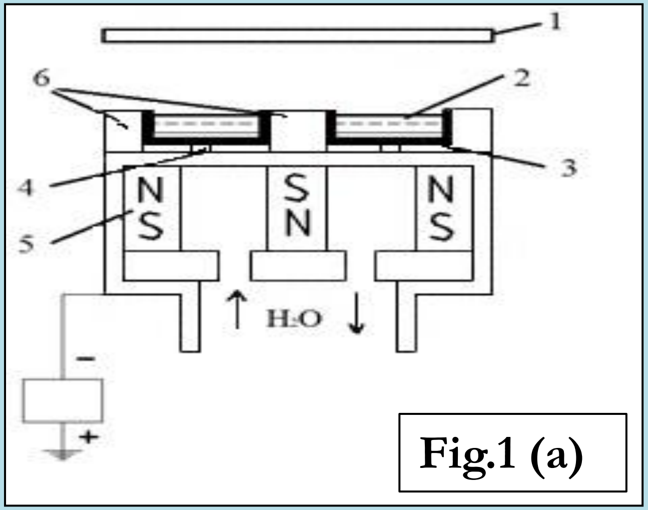


Fig.1 (a)

1 – substrate, 2 – target, 3 – crucible, 4 – ceramic inserts, 5 – magnetic system, 6 – pole pieces.

Var. 2. Hot solid target mode

Fig.1 (b)

Note: this mode is suitable for metals with a high sublimation rate (Cr, Ti, Mg..)

The main distinguishing feature of the cathode assemblies is a significant reduction in the heat-conducting contact of the target with the cooled magnetron body, which leads to strong heating of the target and the occurrence of evaporation or sublimation in addition to sputtering.

Experimental equipment and parameters

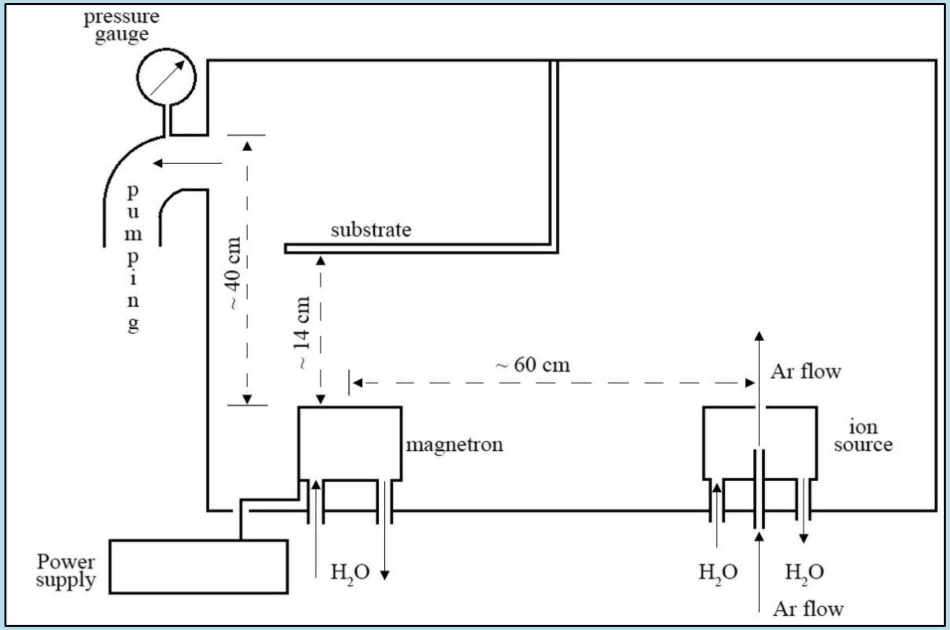


Fig. 2. Layout of equipment in the vacuum chamber

Power supplies:

- middle frequency power supply (IIS, Russia): ν=132 kHz, duty cycle is 80%.
- high-current power supply (APEL-M-5DOMS-1200, Applied Electronics, Russia) combined pulse frequency - 100 Hz, pulsed power – 25..30 kW.

MSS parameters:

1) Cu target in the crucible in the form of a ring of: a) graphite, b) Mo;
target surface area S_{surf} is 62 cm^2;
2) hot solid Cr target, disk form, S_{surf} is 64 cm^2;
3) solid cooled Cu and Cr targets (for comparison), disk form with S_{surf} is 63.5 and 64 cm^2;

- pressure in the working chamber: 0.4 Pa and lower;
- MSS power averaged over period Q_{per} is from 1 to 4 kW.

Calculations of thermal processes in the target

The thermal conductivity equation for calculating target temperature and the rate of evaporation (or sublimation) of atoms from its surface:

$$\frac{\partial E(\vec{r},t)}{\partial t} - V\frac{\partial E(\vec{r},t)}{\partial z} = div\lambda\nabla T(\vec{r},t)$$

Boundary conditions on the irradiated surface :

$$\lambda\frac{\partial T(\vec{r},t)}{\partial z}\bigg|_{z=0} = -q + Q_{ev} + Q_{rad} + Q_{sput}$$

q – plasma power density; Q_{ev}, Q_{sput} и Q_{rad} – energy consumption for evaporation (or sublimation), sputtering and thermal radiation, respectively

Calculations of particles fluxes and concentration in the “target – substrate” system

1) Fluxes densities of sputtered and evaporated atoms on the target surface:

$$F_{sput} = \frac{Y_{sput} \cdot I_{ion}}{e},$$

$$F_{ev/subl}(T_{surf}) = \frac{1}{\left(2\pi m k_B T_{surf}\right)^{1/2}} (P_{sat}(T_{surf}));$$

here *Y_{sput}* - sputtering yield, *I_{ion}* - ion current density, *P_{sat}* – pressure of saturation vapor at the surface temperature T_{surf};

2) Calculation of particle fluxes passing through any plane parallel to the target surface at a distance L:

$$F(x,y) = \frac{L^2}{\pi} \iint_{S_{targ}} \frac{(\mathrm{F}_{sput}(x_{targ}, y_{targ}) + F_{ev/subl}(x_{targ}, y_{targ}) - F_{ion}(x_{targ}, y_{targ})\, dx_{targ} dy_{targ}}{(L^2 + (x - x_{targ})^2 + (y - y_{targ})^2)^2}$$

3) Particles concentration near the target:

$$n_{sum} = n_{sput} + n_{ev/subl} = F_{sput} / \bar{V}_{sput} + F_{ev/subl} / \bar{V}_{ev/subl}$$

Analysis of the evolution of voltage and current in the MSS circuit

Cu target in Mo crucible, Q_{per}=3 kW, MF power supply

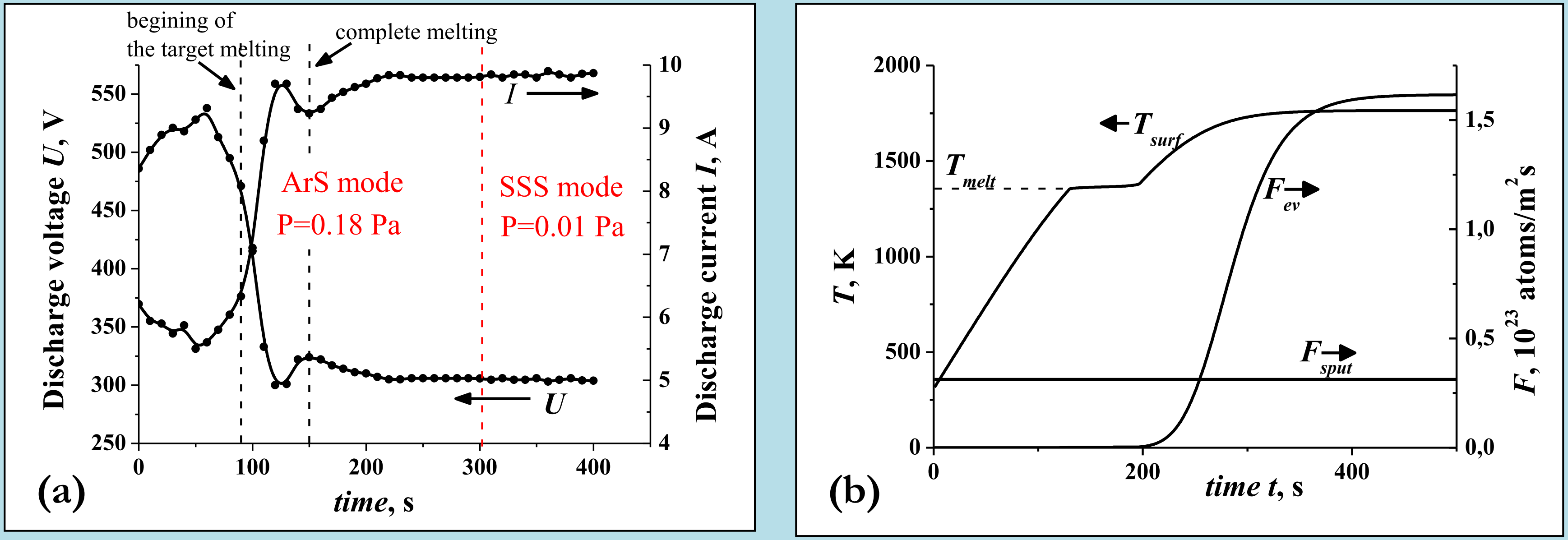


Fig. 3. Evolution of the discharge voltage and current (a), the temperatures on the target surface (T_{surf}) and flux densities of the emitted atoms (b).

The calculated T_{surf} (*time*) and F_{ev} (*time*) are in good agreement with the measured values of U (t) and I (t) ➡ evaporated copper atoms play an important role in maintaining the discharge.

Optical characteristics of plasma during the transition to the SSS mode

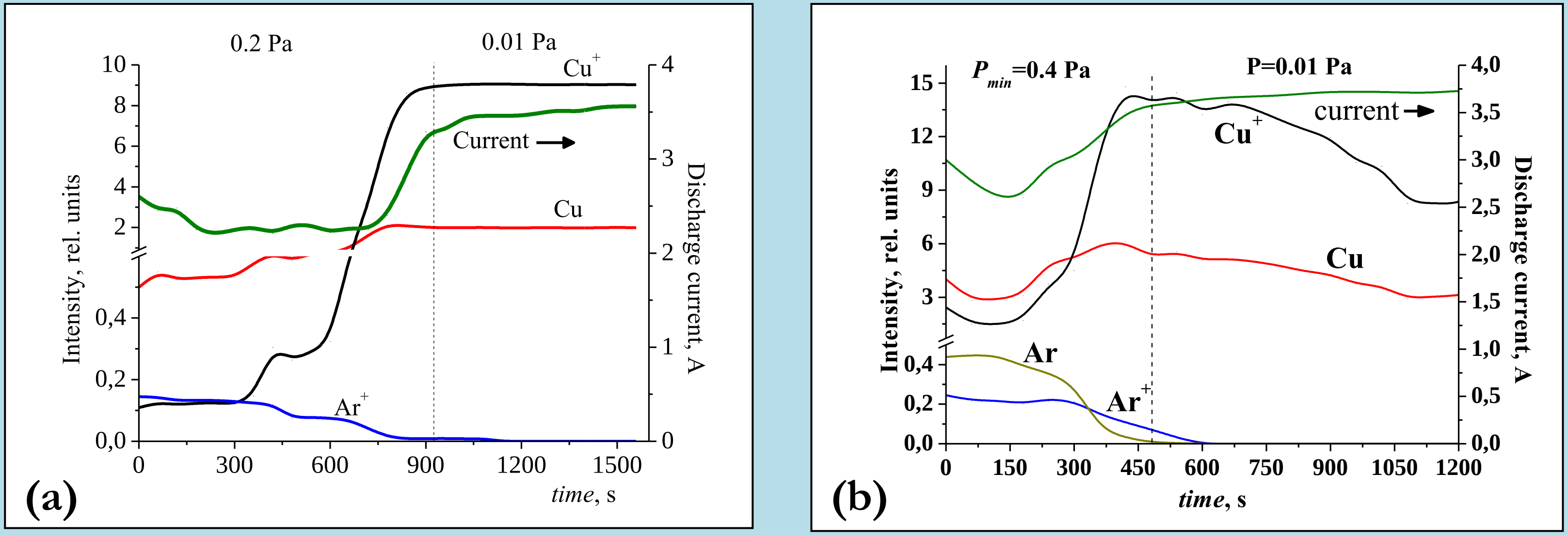
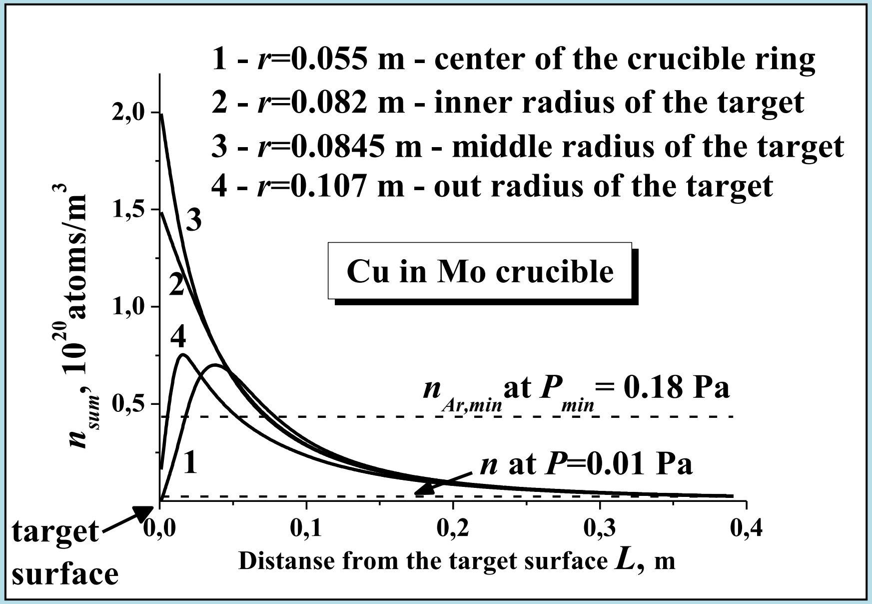


Fig. 4. Changes in optical signals of plasma components during sputtering of a Cu target in a Mo crucible with the power supply: a) MF, Q_{per}=1.35 kW and b) HiPIMS, Q_{per}=2.3 kW. Diagnostics performed using a spectrometer AvaSpec UL2048L2 (Avantes BV, Netherlands).

With the development of evaporation and an increase in the current in the MSS circuit, the intensity of lines of Cu atoms and ions increases, and the intensity of lines of Ar decreases. Ar atoms are displaced by Cu atoms near the target as the evaporation rate increases.

There is some difference in the evolution of signals from plasma components when using different power sources: MF and HiPIMS.

Significant factor contributing to stable SSS mode: the concentration of evaporated atoms near the target is sufficient to maintain the discharge



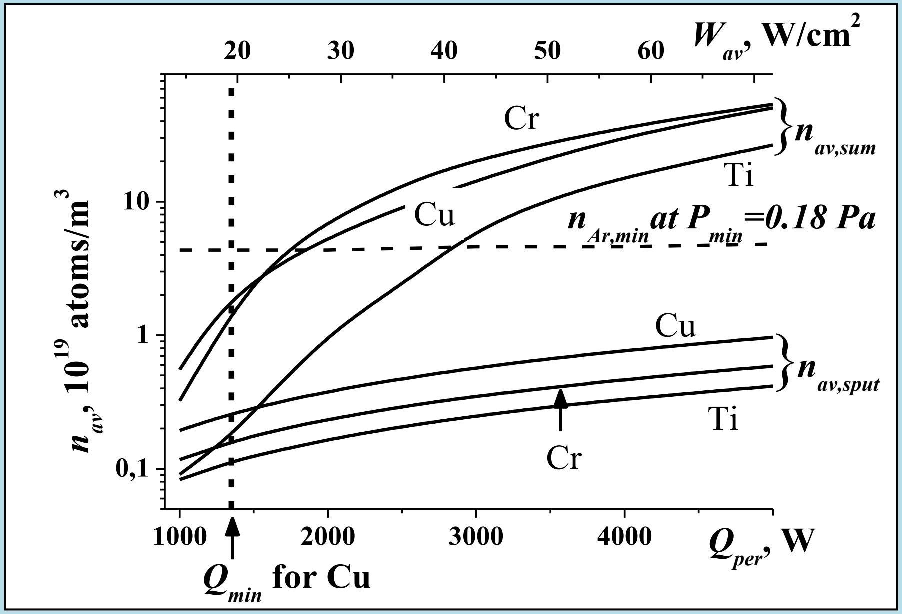


Fig. 5. Distribution of Cu atoms concentration in front of the target at Qper = 3 kW (MF supply).

Fig. 6. Averaged concentration of the target atoms depending on MSS power. Q_{min} is the minimal power fixed in the experiments with Cu target in SSS mode.

- A non-uniform spatial distribution of metal atoms concentration with a maximum near the target surface is established in the chamber.
- For the stable SSS mode with a Cu target, it is sufficient that the average concentration of Cu atoms near the target surface is about $0.5n_{Ar,min}$.

Other factors that contribute to SSS mode

- **the ionization potential of metal atoms is much lower than the ionization potential of argon (working gas);**
- **the velocity of evaporated atoms is much lower than that of sputtered ones, so they stay close to the target longer, → the probability of their involvement in ionization processes is higher compared to sputtered particles, so when there are many of them, the discharge burns stably;**
- **especially for the case of HiPIMS: evaporation helps maintain the SSS mode, as its intensity is nearly constant and metal atoms will always be present near the target.**

Note: thermionic emission is not required or essential for SSS mode.

The minimum power Q_{min} at which the magnetron is able to operate stably in SSS mode

Q_{min} depends on:

- thermophysical properties and geometrical characteristics of the target and crucible (if it necessary),
- type of power supply,
- magnetic field configuration.

Table 1. Q_{min} values found in our experiments

Cu in Mo crucible		Cu in graphite crucible	Al in ceramic crucible	Hot Cr target
MF supply	HiPIMS supply	MF supply	MF supply	HiPIMS supply
1350 W ~19.4 W/cm^2	2300 W ~33.0 W/cm^2	2500 W ~ 36.0 W/cm^2	3500 W ~ 50.4 W/cm^2	2250 W 35.2 W/cm^2

Coatings deposition rates and flows of deposited particles in conditions where SSS mode is possible

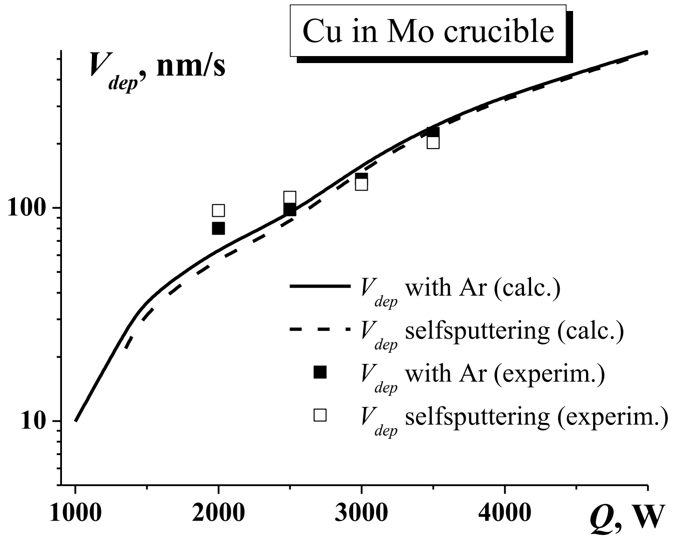


Fig. 7.

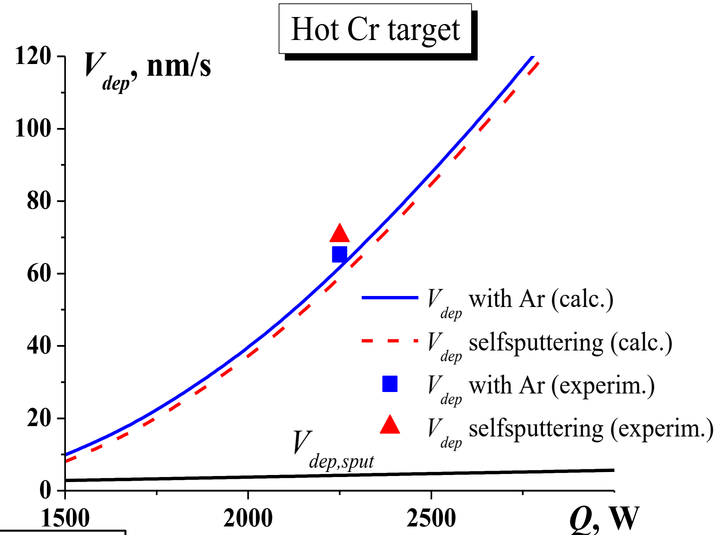


Fig. 8.

- The deposition rates of metal coatings under the consideration conditions are one to two orders of magnitude higher than in conventional sputtering, and are approximately the same both with a working gas inlet (ArS mode) and without it (SSS mode), because when evaporation (sublimation) occurs, the erosion yield due to evaporation increases by more than an order of magnitude compared to the sputtering yield.
- The flow of deposited particles consists of ~ 80-90% of evaporated (sublimated) atoms.

Crystal structure of coatings

Table 2. Data on XRD analysis of Cu and Cr films

Film deposition method	Power supply type	Sput. mode	Phase composition	Lattice parameter, Å	CSR, nm	Microstrains $\Delta d/d$, rel. units
Cu in Mo crucible, Q_{per}=3 kW, h~1 μm	HiPIMS	ArS	Cubic lattice, 100%; dominated peaks (111)	3.5968	245.6	0.160×10^{-2}
	HiPIMS	SSS		3.5970	307.7	0.272×10^{-2}
	MF	ArS		3.5963	306.8	0.195×10^{-2}
	MF	SSS		3.5965	272.8	0.156×10^{-2}
Cooled Cu target, Q_{per}=3 kW, h~1 μm	MF	ArS (only)		3.5976	94.3	0.180×10^{-2}
	HiPIMS	ArS (only)		3.6281	43.7	0.401×10^{-2}
Hot Cr target, Q_{per}=2.25 kW, h~8 μm	HiPIMS	ArS	dominated peaks (211)	2.8914	5.36	0.6410×10^{-2}
	HiPIMS	SSS	(110), (211)	2.8808	10.22	0.1604×10^{-2}

Note: SCR is coherent scattering region; $\Delta d=d_{[111]}-d_{0[111]}$, $d_{[111]}$ is the stressed interplane distance, $d_{0[111]}$ is the interplane distance of the reference sample, h is coating thickness.

- **Influence of SSS-mode does not manifest itself in the formation of the crystalline coatings structure.**
- **The films obtained by sputtering a solid Cu target have crystallites, the size of which is about 2 times smaller than in the case of liquid target with evaporation.**

The electrical resistance of Cu films

Table 3. Electrical resistivity (Ohm×cm) of Cu films ~ 1 μm thick deposited by the magnetron with different supplies of 3000 W power on glass substrates without preheating.

Cu in Mo crucible				Sputtering of cooled Cu target	
MF supply		HiPIMS supply			
ArS mode	SSS mode	ArS mode	SSS mode	MF supply	HiPIMS supply
2.22×10^{-6}	2.13×10^{-6}	2.61×10^{-6}	2.19×10^{-6}	3.59×10^{-6}	3.67×10^{-6}

● For both types of power supplies, the deposition with a liquid target produces films with a lower electrical resistivity as compared to sputtering a cooled solid target.

● Resistivity of the films obtained using MF supply are slightly lower compared to the case of HiPIMS.

● SSS mode has formed films with a lower electrical resistance compared to the discharge maintained by argon.

The electrical resistance of Cu films: the dependences on MSS power

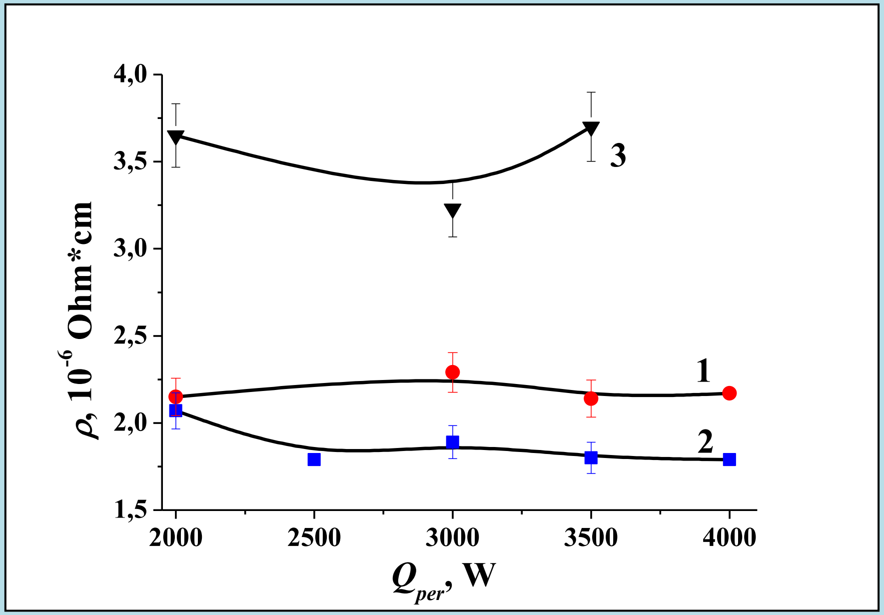


Fig. 9. Electrical resistivity ρ of Cu films with the thickness from 5 to 6 μm depending on MF supply power averaged over a period at sputtering: 1 – liquid target in ArS mode at P=0.18 Pa; 2 – liquid target in SSS mode; 3 – cooled target at P= 0.18 Pa.

- In the considered power range, the resistivity of the films deposited by sputtering a cooled solid target has turned out to be higher compared to the case of sputtering a liquid target.
- An increase in power from 2 to 4 kW practically does not affect the resistance of the films obtained by sputtering a liquid target.
- The value of ϱ is slightly lower (up to 20%) for films obtained in SSS mode.

Hardness of Cr coatings

Table 4. Hardness and Young's modulus of Cr coatings deposited using the MSS with HiPIMS supply on the surface of samples made of stainless steel using a hot Cr target.

Sputtering mode	MSS power (Qper), kW	Coatings thickness, μm	Indenter load, mN	Indentation depth, nm	Hardness, GPa	Young's modulus, GPa
SSS, $P=5\cdot10^{-3}$ Pa	2.25	8.2	40	444.3	12.73	195.22
ArS, P= 0.18 Pa	2.25	7.6	40	443.0	11.82	232.01
SSS, $P=5\cdot10^{-3}$ Pa	2.50	6.2	25	361.0	9.68±2.5	195.0±57
ArS, P= 0.18 Pa	2.50	5.1	25	428.0	6.38±0.9	175.64±31

● The hardness of all coatings are in the range typical of Cr films produced by magnetron sputtering.

●The hardness of the coatings deposited in the SSS mode turned out to be somewhat higher than when a hot target was sputtered in an Ar atmosphere.

Corrosion resistance of Cr coatings

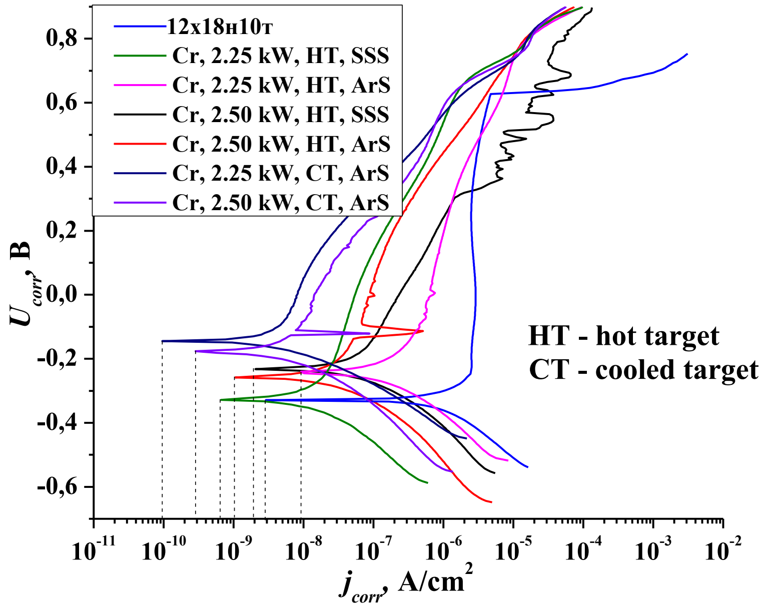


Fig. 10. Potentiodynamic dependences of current on voltage, obtained during corrosion tests of samples made of stainless steel 12X18H10T with Cr coatings, deposited during the operation of the MSS with the HiPIMS power supply and various modes of target sputtering

- ● All samples with Cr coatings have a higher corrosion resistance compared to the stainless steel sample.
- ● Samples with coatings deposited during sputtering of a cooled target have the highest resistance.
- ● The coating obtained in SSS mode at $Q_{per} = Q_{min} = 2.25$ kW showed higher corrosion resistance compared to the coating obtained in ArS mode.
- ● At a higher power, the anticorrosive properties of coatings obtained in SSS mode and with argon are approximately the same.

Conclusion

- A magnetron can operate in a self-sputtering mode without letting in a working gas, if, mainly due to evaporated (or sublimated) particles, a concentration of atoms is created near its surface, which is necessary to maintain the discharge.
- The threshold power value at which the magnetron is capable of operating in SSS mode depends largely on the material parameters of the target and the type of power supply.
- In the power range where the self-sputtering mode is possible without letting the working gas into the vacuum chamber, the flux density of the deposited particles and the growth rate of the coatings are one or two orders of magnitude higher as compared with conventional magnetron deposition at the same power. This circumstance has a great influence on various characteristics of the formed coatings.
- Under conditions of intense evaporation, a noticeably pronounced effect of the SSS mode and the type of power supply on the crystal and growth structure of the coatings is not traced. However, evidence has been obtained for an improvement in the electrical conductivity of Cu films, as well as an increase in the hardness and corrosion resistance of Cr coatings.