Peculiarities of metal coatings deposition using magnetron sputtering systems with hot and evaporative targets

G A Bleykher, D V Sidelev, V A Grudinin, V P Krivobokov and A V Yuryeva
National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk 634050, Russia

E-mail: bga@tpu.ru

Abstract. This article reports on the peculiarities of Cr and Cu coatings deposited by magnetron sputtering with hot and evaporative targets. There is shown the role of heat radiation from hot (evaporative) target and sublimated particle flux in energy flux density on the substrate and deposition rates. The Cr and Cu films were investigated by X-ray diffraction, scanning electron microscopy, nanoindentation, electrical conductivity and corrosion tests.

1. Introduction
Magnetron sputtering is a widely used and effective method of coatings deposition [1,2]. It has many advantages, such as high adhesion strength of deposited coatings, high uniformity of film thickness, wide range of operation parameters and etc. However, magnetron sputtering has a relatively low deposition rate in comparison with thermal and electron-beam evaporation [3].

This problem can be solved by using of evaporation or sublimation of target surface additionally to sputtering in plasma [4, 5]. The high temperature of the target material can be obtained in the case of complete or partial thermal insulation of the target from the cooled magnetron body. Apart from the increase of deposition rates, the additional factors of hot or evaporative target magnetron sputtering can influence on deposition process and parameters of the coatings. It is energy and particle fluxes on substrate due to heat radiation of the target and sublimation (evaporation) of their surface.

Thus, the aim of this study is to determine the role of parameters of magnetron sputtering system with hot or evaporative targets in structural and functional properties of the deposited coatings.

2. Hot and evaporative target magnetron sputtering
For conventional magnetrons, where cooled target is used, target surface is sputtered by gas ions [6]. In this case, only sputtered and ionized (from plasma) particles can be condensed on substrate and their flux and energy have a main impact in deposition rate and kinetic of film growth [7].

In the case of hot (evaporative) target magnetron sputtering there are additional energy and particle fluxes on substrate. The scheme of this process is shown in figure 1. Thus, energy flux density \( F \) on substrate for coatings deposition in the case of hot (evaporative) target sputtering can be calculated as:

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F = F_{\text{rad}} + F_{\text{cond}} + F_{\text{kin}},
\]

where \( F_{\text{rad}} \) – energy flux density due to hot target radiation; \( F_{\text{cond}} \) – energy flux density due to condensation of deposited (sputtered and sublimated) particles; \( F_{\text{kin}} \) – flux density due to kinetic energy of sputtered and sublimated atoms and ions reached the substrate.
Figure 2 shows the energy flux densities \( F \) on the substrate in dependence on discharge power density. There is shown that \( F \) significantly increases due to head radiation of hot (evaporative) target [8]. The notable role of sublimated particles flux in \( F \) appears only at high power densities.

3. Metal coatings and their properties

3.1. Deposition rates

The appearance of a large number of evaporated atoms in the erosive flux from target, in addition to the sputtered particles, leads to a significant increase of deposition rate (figure 2).

At low power density the target is only sputtered. In this case, as can be seen in figure 2a, the deposition rate \( V \) of the Cu coating is linear with the increase of discharge power density \( Q \) and does not exceed 10 nm/s. When target evaporation is occurred, nonlinear growth of \( V \) is observed with
the increase of $Q$ (curves 1 and 2 in figure 2). Due to surface evaporation of liquid target, the deposition rate can be increased by 1-2 orders of magnitude in the power density range from 10 to 100 W/cm$^2$.

A significantly high increase occurs when a molybdenum crucible is used. Such important role of the crucible material is due to the emissivity of its surface. When the emissivity factor is lower, the greater part of the energy entering the target from plasma can be used on heating and evaporation.

A similar change in the deposition rate of coatings with increase of discharge power density is characteristic not only of magnetrons with evaporative targets, but also to strongly heated solid targets from materials having a high sublimation rate (for example, Cr, Ti, figure 2b). The maximum increase of the deposition rate for Ti is approximately 2 times, for Cr – about 20 times.

3.2. Crystal structure

To estimate the size of structural elements, X-ray diffraction analysis (Debye-Scherrer formula) was used [9]. The results are shown in figure 3. The thickness of Cu coatings was approximately 6 μm.

The Cu coatings obtained by sputtering of liquid target in Mo crucible (curves 4-5 in figure 3) have the largest crystallite size. They are 3-4 times higher than in the case of cooled target sputtering (curve 1) or by deposition from molten Cu target in graphite crucible (curves 2-3).

![Figure 3. Crystallite size of Cu coatings deposited by magnetron sputtering with solid-state cooled (1 – 0.18 Pa) and liquid target in Mo (4 – 0.18 Pa, 5 – 0.01 Pa) and graphite (2 – 0.18 Pa, 3 – 0.01 Pa) crucible.](image)

3.3. Microstructure

There is a noticeable difference in microstructure of Cu coatings deposited by liquid target in Mo crucible and by using of graphite crucible or cooled solid target. Figure 4a-c show the results of scanning electron microscopy of the cross-section of Cu coatings deposited on Si substrates. The power density in all cases was ~40 W/cm$^2$. The investigations were carried out by means of scanning electron microscope TESCAN FERA3 GM.

The Cu coatings have a columnar structure, when cooled solid-state target and liquid Cu target in graphite crucible are sputtered. In the second case the coating has large number of pores (figure 4b). This difference in film microstructure is caused by lower energy flux density on the substrate for these cases in comparison with sputtering of Cu target in Mo crucible. In the last case, higher evaporated particle flux and heat radiation flux reached the substrate. These factors result in more intense substrate heating and mobility of atoms on its surface. Hence to this, the formation of denser film structure is.
3.4. Hardness

Figure 5 presents the dependence of hardness and toughness of the Cr coatings obtained by cooled and hot target sputtering on discharge power density ($Q$). As can be seen from the graph, the hardness of 2-μm-thickness Cr films increases with increasing $Q$. This kind of the dependence is typical for both types of the coatings. However, the hardness of the Cr samples deposited by hot target sputtering is lower on 1-2 GPa than in the case of cooled target sputtering.

For mechanical properties, the change of grain size has important role that was founded in X-ray diffraction analysis. It is good known [10] that the hardness of coatings increases for lower grain size ~20-50 nm (Hall-Patch effect). Thus, lower hardness is determined to hot target sputtering (figure 5a). This trend becomes more pronounced for higher film thickness.

The calculation of $H$ to $E$ ratio is to analysis toughness of films [11]. Figure 5b shows $H/E$ ratio to the Cr films deposited by hot and cooled target sputtering.

The toughness of the Cr coatings by hot target sputtering is reduced compared with the case of using a cooled target [8] and this dependence only enhanced for higher film thickness. This is due to the formation of more coarse-grained structure, which is less resistant to mechanical load.
3.5. Sheet resistance

Copper coatings should have a high electrical conductivity, they are widespread in microelectronic devices [12]. Thus, one of the important functional properties for them is the resistivity. We measured the resistivity of Cu coatings (thickness 6 μm), obtained with different deposition regimes by a four-point probe method. The results are shown in figure 6.

At the same power density the Cu coatings, obtained by using a graphite crucible, have the least electrical conductivity. In this case, the specific resistivity decreases by a factor of 1.5 with the working pressure varying from 0.18 to 0.01 Pa and the transition to the self-sputtering regime (curves 5 and 4 in figure 6).

![Figure 6](image)

Figure 6. Electrical resistivity of Cu coatings deposited by magnetron sputtering with solid cooled (3 – 0.18 Pa) and liquid target in Mo (1 – 0.01 Pa, 2 – 0.18 Pa) and graphite (4 – 0.01 Pa, 5 – 0.18 Pa) crucible.

In the case of sputtering Cu target in Mo crucible, the Cu coatings have a maximum electrical conductivity (curves 1 and 2 in figure 6), and the absence of argon in the deposition process also leads to a decrease in the resistivity from 2.4·10^{-6} to 1.8·10^{-6} Ω·cm. Such increase of electrical conductivity of Cu coatings deposited by liquid target sputtering (with Mo crucible) can be caused by lower concentration of structural defects and higher grain size.
Figure 7. (a) Potentiodynamic curves of Cr coatings in 3.5% NaCl. Photographs of Cr coatings deposited by (b) cooled and (c) hot magnetron sputtering after corrosion tests. The power density of plasma discharge is 27.5 W/cm². The film thickness is 6 µm.

3.6. Corrosion resistance

Figure 7 shows potentiodynamic curves of Cr coatings deposited by cooled and hot target sputtering in 3.5% NaCl and film surface after corrosion tests. It is obviously seen that deposition of Cr coating on steel substrate results in the decrease of corrosion current density approximately in one order (from $2 \times 10^{-7}$ to $2 \times 10^{-8}$ A/cm²). Moreover, the curve for Cr film obtained by hot target sputtering constantly increases. For the sample deposited by cooled target sputtering, the corrosion current density sharply rises. It indicates on worse corrosion resistance of the second sample.

The surface of the steel substrates with Cr coatings is significantly different. For cooled target magnetron sputtering, a lot of craters with average diameter of 1-3 µm and several large holes (up to 20 µm) in the film are founded. This indicates that electrochemical reaction on the surface of the coating was not uniform. The corrosion had more intensity in the regions of accumulation of structural defects. In the case of hot target sputtering, the chromium coating has a more uniform surface with formations of craters (up to 4-5 microns in size), which are evenly distributed over it. These results confirm the higher corrosion resistance in 3.5% NaCl.

Thus, Cr coatings can significantly improve the resistance of steel to aggressive environment and corrosion properties of the samples modified in a magnetron sputtering system with hot target in 3.5% NaCl are much better due to more uniform film microstructure and lower concentration of structural defects.

4. Conclusion

Hot or evaporative target sputtering is high-rate deposition method to thin film deposition. However, due to target heating or even melting of target material, the energy flux density to the substrate significantly increases. Both, higher deposition rate and energy flux to the substrate, result in changes of structural and functional properties of metal films. In common, they have higher grain size and more homogenous structure with lower concentration of defects, the film hardness reduces and sheet resistance can be equal to parameters of bulk material. Moreover, metal coatings deposited by hot or evaporative target sputtering can be used for corrosion resistance of steel.

Acknowledgments

This investigation was supported by Russian Science Foundation (project №15-19-00026). The research is carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program.

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