Study of the influence of bias voltage on the texture and residual stresses of Mo coatings deposited on a Cu substrate by magnetron sputtering deposition

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Abstract. The paper presents the results of studying the effect of the bias voltage on the structure, texture, and residual stresses of Mo coatings deposited on a copper substrate using an inverted magnetron. It is shown that variations in the bias voltage lead to changes in the texture and thickness of the Mo coatings. It was found that an increase in the bias voltage leads to an increase in the values of the compressive residual stresses.

1. Introduction

Currently, cylindrical magnetrons are widely used in industry along with planar magnetrons [1–4], which are a structure of coaxial metal electrodes. According to [5], cylindrical magnetrons are subdivided into post-cathode (the central electrode is the cathode, and the outer one is the anode) and inverted (reverse polarity of the electrodes). As a result of several decades of research, post-cathode magnetrons have been studied in great detail in the aspect of their application for the deposition of thin films [5]. Inverted cylindrical magnetrons for this application are much less studied. There are various designs of inverted magnetrons. One of such constructions was presented by us in [6, 7].

The service properties of coatings are determined by their structural state, which for magnetron coatings largely depends on the bias voltage. This also applies to coatings sputtered with inverted magnetrons. The structure of these coatings from various metals differs from those deposited by post magnetrons [5]. The influence of the bias voltage in the range from 0 to –300 V on the texture and the magnitude of residual macrostresses in Mo coatings on a Cu substrate was investigated in this paper.

2. Materials and research methods

The sputtering process was carried out on a specialized device for inverted magnetron sputtering. Argon with a purity of about 99.9 % was used as a working gas. The cathode was made of molybdenum (Mo) with a purity of ≈ 99.9 %. A copper tube M1 Ø 10 mm was used as a substrate. Before sputtering, the tube was polished and degreased in acetone and alcohol. Then the tube was installed on the rod for vertical movement of the samples and the working chamber of the device was evacuated to a residual pressure of 10^{-3} Pa. Before sputtering, the tube surface was cleaned by treatment in a glow discharge at an argon pressure of 5 Pa and a voltage on the substrate of 1100 V. Then, Mo was deposited onto the outer surface of the tubes at different substrate bias voltages. The
modes of coating deposition are presented in table 1, where \( U_m \) and \( I_m \) are the voltage and current of the magnetron discharge, \( U_{sub} \) and \( I_{sub} \) are respectively the bias voltage and current on the substrate.

**Table 1.** Modes of deposition of molybdenum on a copper substrate.

| Sam. № | \( U_m, \) В | \( I_m, \) А | \( U_{sub}, \) В | \( I_{sub}, \) А | \( P_{Ar}, \) Па | \( T, ^\circ C \) |
|--------|--------------|-------------|-----------------|--------------|----------------|-------------|
| 1      | 290          | 1           | -               | -            | 0,2            | 330         |
| 2      | 290          | 1           | 25              | 0,02         | 0,2            | 350         |
| 3      | 280          | 1           | 50              | 0,06         | 0,2            | 372         |
| 4      | 280          | 1           | 75              | 0,1          | 0,2            | 390         |
| 5      | 275          | 1           | 100             | 0,12         | 0,2            | 425         |
| 6      | 275          | 1           | 125             | 0,12         | 0,2            | 450         |
| 7      | 270          | 1           | 150             | 0,16         | 0,2            | 468         |
| 8      | 270          | 1           | 175             | 0,14         | 0,2            | 506         |
| 9      | 275          | 1           | 200             | 0,15         | 0,2            | 533         |
| 10     | 270          | 1           | 225             | 0,12         | 0,2            | 560         |
| 11     | 280          | 1           | 250             | 0,12         | 0,2            | 562         |
| 12     | 270          | 1           | 275             | 0,15         | 0,2            | 582         |
| 13     | 275          | 1           | 300             | 0,16         | 0,2            | 624         |

X-ray phase analysis, determination of texture and residual macrostresses were carried out on a DRON-4 X-ray diffractometer in filtered CuK\(\alpha\) radiation with wavelengths \( \lambda_{K\alpha \text{ave}} = 1.54178 \) Å.

The residual stresses were estimated by the X-ray method named "sin\(^2\)\(\psi\)". In the "sin\(^2\)\(\psi\)" method, the positions of reflections (222) and (321) were measured at angles \( 2\theta \approx 115^\circ \) and \( 2\theta \approx 132^\circ \), respectively, with a symmetrical position of the sample (\( \psi = 0^\circ \)) and its asymmetric position (\( \psi = 10^\circ \) and \( 40^\circ \)). From these data, the lattice parameters were calculated and the dependences between \( a_\psi \) on sin\(^2\)\(\psi\) were obtained. The slope of the straight line (tg\(\alpha\)), was determined by the method of least squares, and the value of the residual stress was calculated by equation:

\[
\sigma_\psi = \tg[\E/(1 + \nu)_{hkl}/a_0,]
\]

The values of \([\E/(1+\nu)]_{hkl}\) for Mo are 0.234x10\(^{-2}\) GPa\(^{-1}\) for the (222) reflex and 0.226x10\(^{-2}\) GPa\(^{-1}\) for the (321) reflex.

Inverse pole figures (IPF) were obtained by taking X-ray diffraction patterns in the angular range \( 2\theta = 30–150^\circ \). The pole density of 6 independent reflections \( hkl \) on the stereographic triangle: 001, 011, 013, 111, 112, 123, was determined from the equation:

\[
P_{hkl} = \frac{n (t_{ex} / t_{ref})_{hkl}}{\E \cdot (t_{ex} / t_{ref})_{hkl}}
\]

where \( t_{ex} \), \( t_{ref} \) are the integral intensities of the reflections \( hkl \) for the textured and textureless (reference) sample, respectively; \( n \) is the number of independent \( hkl \) reflections (\( n = 6 \)).

3. Experimental results

The X-ray diffraction patterns of all coatings contain reflections of the BCC Mo lattice, and starting from the coatings deposited at bias voltages \( > -125 \) V, the X-ray diffraction patterns show FCC reflections from the copper substrate, which intensity increases with increasing bias voltage. This indicates a decrease in the coating thickness due to an increase in the fraction of sputtered Mo atoms with an increase in the energy of deposited coating particles. X-ray diffraction patterns of a Cu
substrate (a) and a coating deposited at a bias voltage of \(-200\) V (b) are shown in figure 1. These results make it possible to evaluate the change in coating thickness with increasing bias voltage using the following equation:

\[
T = \ln\left(\frac{I_0}{I_t}\right) \sin \theta / 2\mu,
\]

where \(I_0\) and \(I_t\) are the intensities of the reflections of the uncoated and coated substrate; \(\mu\) is the X-ray absorption coefficient in Mo.

![X-ray diffraction patterns of Mo coatings on a Cu substrate: (a) Cu substrate; (b) Mo coating, Up = \(-200\) V.](image)

**Figure 1.** X-ray diffraction patterns of Mo coatings on a Cu substrate: (a) Cu substrate; (b) Mo coating, Up = \(-200\) V.

The dependence of the coating thickness on the bias voltage is shown in figure 2, which shows that the coating thickness is \(~13\)–\(15\) \(\mu\)m at bias voltages \(<100\) V and decreases to \(~1\) \(\mu\)m with an increase in this voltage to \(-300\) V. For coatings more than 12 \(\mu\)m thick, the X-ray method does not allow determining the thickness of the coating, since for these conditions (CuK\(_\alpha\) radiation, Cu substrate and Mo coating) the permissible depth is \(~12\) \(\mu\)m. Therefore, for coatings \#1–5, no substrate reflections were observed and their thickness was estimated on the sample’s cross sections, figure 3.

![Dependence of the thickness of Mo coatings on the substrate voltage.](image)

**Figure 2.** Dependence of the thickness of Mo coatings on the substrate voltage.

Variations in the bias voltage lead to a change in the texture of the Mo coatings. At bias voltages from 0 to \(-125\) V, the texture component (110) dominates (figures 4b and 4c), and at voltages from \(-150\) to \(-300\) V, the texture is one-component with the (111) plane parallel to the substrate plane (figure 4d). The dependences of the pole density of the (110) and (111) reflections on the bias voltage are shown in figure 5, which shows a clear pattern in the formation of the texture of Mo coatings, which is characterized by a transition from the (110) texture to the (111) texture with an increase in the bias voltage. This indicates that the mechanism of coating formation changes and this should affect the service properties of the coatings. It is important to note that the texture transition corresponds to the
bias voltage, at which the effect of sputtering of Mo atoms is enhanced and the thickness of the coating decreases (figure 2).

Figure 3. Cross sections of Mo coatings on a Cu substrate: (a) № 3 ($U_{sub} = -50$ V); (b) № 5 ($U_{sub} = -100$ V); (c) № 10 ($U_{sub} = -225$ V); (d) № 13 ($U_{sub} = -300$ V).

The dependence of the residual macrostresses on the bias voltage is shown in figure 6, which demonstrates an increase in the values of the compressive residual stresses with an increase in the bias stresses. However, at the maximum value of the bias voltage (~300 V), a sharp decrease in the value of residual stresses occurs, which can only be associated with a violation of the adhesion bond with the substrate due to high thermal stresses.

The dependences between voltage and the half-widths of the diffraction lines (222) and (321) are shown in figure 7. With an increase in the voltage on the substrate, the width of the diffraction lines increases, which is determined by the distortions of the crystal lattice and the refinement of the subgrain structure in the range of 10–100 nm. The most probable reason for the line broadening is an increase in the distortion of the molybdenum lattice, that is, an increase in the dislocation density. This is also evidenced by the significant value of the residual stresses, which reaches ~1.6 GPa at the maximum voltage on the substrate (figure 6). For voltages above ~250V, the coatings peel off from the substrate, which is caused by high compressive stresses. The nature of these stresses is thermal and is due to the difference in the thermal coefficient of linear expansion of molybdenum and copper. The magnitude of thermal stresses can be estimated from a simple equation:

$$\sigma_T = E \Delta T (\alpha_{coat} - \alpha_{sub}) = 320 \Delta T (5,1 - 17,2) 10^{-6} \text{ GPa/}K = -3,87 \Delta T \text{ MPa/}K,$$

Stress estimation for a temperature difference of 100 deg.
Based on this estimate, the maximum value of residual stresses (≈−1600 MPa) corresponds to a process temperature of ≈ 400 °C, which is close to the actual temperature of the substrate during the deposition process.

Figure 4. Standard stereographic triangle of a cubic lattice (a) and inverse pole figures for Mo coatings on a copper substrate, applied at different voltage values (U_{sub}): U_{sub} = −25 V (b); U_{sub} = −50 V (c); U_{sub} = −225 B (d).

Figure 5. Dependence of the pole density for orientations (111) and (110) on the substrate voltage.

Figure 6. Dependence of the magnitude of residual stresses on the substrate voltage.
Figure 7. Dependence of the half-widths of the diffraction lines (321) and (222) on the voltage on the substrate.

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