Magnetron with sandwich target for solid composite film deposition Mo$_x$Cr$_{1-x}$N

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Abstract. In this paper, we consider a technological magnetron equipped with a sandwich target designed for the synthesis of Mo$_x$Cr$_{1-x}$N composite films with a continuous change in the stoichiometric coefficient $x$, which provides a smooth change in hardness. In this paper, the relationship between the stoichiometric coefficient $x$ and the geometric factor equal to the relative total area of the slots in the external target is established. It is established that the proposed magnetron with a sandwich target makes it possible to synthesize Mo$_x$Cr$_{1-x}$N solid composite films with a continuous change in the stoichiometric coefficient $x$, which provides a smooth change in the hardness from 18 to 33 GPA. In this case, the stoichiometric coefficient can be controlled in the range $0 < x < 0.3$, varying the area of the slots in the range $0 < \alpha < 0.5$ for the specified values of the discharge current density and nitrogen consumption.

Currently, CrN chromium nitride films are widely studied and used [1]. Their practical significance is due to their high hardness (up to 15 GPA), thermal stability, good wear resistance, and excellent corrosion resistance. They are widely used to increase productivity and service life of processing tools [2]. However, the properties of CrN films quickly degrade due to oxidation during high-speed processing and temperatures exceeding 700 ℃ [3].

To overcome these problems, multilayer heterostructures of the MoN/CrN type are created, in which the integral hardness of the coating increases to 20–22 GPA [4]. While the hardness of single films of molybdenum nitride MoN does not exceed 18 GPA [5].

The most effective way to increase the hardness of CrN films is to create a solid solution of two nitrides on their basis. Such a composite containing CrN and a certain amount of nitride, for example, molybdenum (MoN) [6] is usually considered as a solid solution of substitution of two nitrides with the chemical composition Mo$_x$Cr$_{1-x}$N.

For the synthesis of solid composite films containing two nitrides, several magnetrons are usually used with effectively cooled targets made of different metals, which are located next to each other [7].

A common disadvantage of this approach is the difficulty of synthesizing films with a continuous change in the stoichiometric coefficient $x$, which provides a smooth change in hardness. A new step in the development of reactive magnetron sputtering technology is a magnetron with a sandwich target [8]. Consider a schematic representation of a sandwich target designed for deposition of composite films with the chemical composition Mo$_x$Cr$_{1-x}$N (figure 1). The magnetron model was implemented on the basis of a cylindrical balanced magnetron $I$ with a diameter of 130 mm, on which the authors performed experiments. The sputtered block contains on one axis an internal cooled plate 2 with a thickness of 4 mm, made of molybdenum, and an external plate 3 with a thickness of 2 mm, made of...
chromium. The entire structure is rigidly bolted 4 to the body of the magnetron 1 and placed in a reactive environment consisting of a gas mixture of argon and nitrogen. Washers 5 with a thickness of 1 mm are installed between the plates, providing a gap between the plates. The erosion zone 6 of the chrome plate has the shape of a ring with an area of $s$. In this zone, slots 7 are made, located symmetrically relative to its center. The slots are made in the form of holes. The total area of the slots $s_2$ sets the area of the erosion zone $s_1$ of the inner plate. For the outer plate, the area of the erosion zone is $s_1 = s - s_2$.

![Figure 1. Sendwich target.](image)

Target sputtering occurs at a total pressure of 2-8 mtorr. By controlling the discharge current density and nitrogen consumption, the plates are switched to the nitride mode of operation, in which their surfaces are covered with the corresponding nitrides. Argon ions formed in the discharge bombard these surfaces. The inner plate 2 is cooled, so the flow of molybdenum nitride $J_{MoN}^{sp}$ is formed only by sputtering its surface through the slots 7 in the chrome plate 3. Along with the discharge current density and nitrogen consumption, the device's independent variable is the relative total area of the slots:

$$\alpha = \frac{s_2}{s}.$$  \hspace{1cm} (1)

The outer plate 3 is heated by an ion current. In this case, the washers 5 provide an adjustable heat removal from it through the mounting elements (4 and 5) and due to radiation through the gap in the Central part of the structure. In this design, it is easy to establish experimentally the effect of the discharge current density on the temperature of the outer plate. This allows you to eliminate an uncontrolled error associated with its heating.

![Figure 2. Nitride fluxes (a) and stoichiometric coefficient $x$ (b).](image)

In figure 2, $a$ shows examples of the dependences of these fluxes on parameter (1), calculated at a discharge current density of 100 mA/cm$^2$ and a chrome plate temperature of 900 K.

This difference between the plates is due to the design feature of the block. Heat removal from the outer plate is two to three orders of magnitude less than from the inner plate. Therefore, the chrome plate can be heated to a high temperature at which the $J_{CrNeve}$ value can significantly exceed the $J_{CrNsp}$ value. If the first one has a dependence on the discharge power in the form of an exponential function $\sim 10^A$, then the second one is proportional to the discharge power (see figure 2, $a$). As a result, due to the symmetrical arrangement of the slots, axisymmetric flows of two nitrides arise, which are mixed in
the gas environment, creating a total flow with a uniform distribution of molecules in the sections at a distance of more than 40-60 mm from the target. A homogeneous film is synthesized on the substrate as a solid solution of two Mo\textsubscript{1-x}Cr\textsubscript{x}N nitrides.

The stoichiometric coefficient $x$ sets the ratio of flows:

$$x = \frac{J_{\text{MoNsp}}}{J_{\text{MoNsp}} + J_{\text{CrNtot}}}$$

(2)

At the same time, each of the flows in (2) depends on the value of (1) in a certain way. In our case, for example, the total flow of molybdenum nitride is only equal to the atomized flow:

$$J_{\text{MoNsp}} = \alpha S_{\text{MoN}} \frac{j}{e}$$

(3)

where $S_{\text{MoN}}$ is the sputtering coefficient of molybdenum nitride; $j$ is the discharge current density; $e = 1.6 \cdot 10^{-19}$ C – electron charge. A chromium nitride stream consisting of two components sets the expression:

$$J_{\text{CrNtot}} = J_{\text{CrNsp}} + J_{\text{CrNev}} = s(1-\alpha) \left( \frac{S_{\text{CrN}}j}{e} + \frac{10^{A-B/T}}{\sqrt{2\pi m_{\text{CrN}}kT}} \right)$$

(4)

where $S_{\text{CrN}}$ is the atomization coefficient of chromium nitride; $A$ and $B$ are constants that set the saturated vapor pressure of chromium nitride; $T$ is the temperature of chromium platinum; $m_{\text{CrN}}$ is the mass of the chromium nitride molecule; $k = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant.

In figure 2, $b$ the dependence $x = f (\alpha)$ obtained using expressions (2)– (4) is given, which is approximated by a second-order polynomial with a confidence greater than 0.99:

$$x = 0.480\alpha + 0.375\alpha^2$$

(5)

As follows from (5), the chemical composition of the Mo\textsubscript{1-x}Cr\textsubscript{x}N film can be uniquely controlled by varying the total area of the slots $\alpha$.

The described model of the proposed Device was used to evaluate the hardness $H$ of synthesized films. In figure 3 points show experimental results that were approximated by the dependence:

$$H = 15.3 + \frac{0.2}{(x-0.23)^2 + 0.011}$$

(6)

where $H$ is the film hardness in GPa. The dependence (6) is shown in the figure 3 as a solid line. From figure 3 it can be seen that as $x$ increases, the film hardness increases and reaches a maximum, as follows from (6), at $x = 0.23$. 

**Figure 3.** Dependence of the hardness on the chemical composition of the film.

**Figure 4.** Dependence of hardness on the geometric factor (1).
Using (6) and the relation between $x$ and $\alpha$ established by expression (5), we obtain the dependence of the film hardness on the value of $\alpha$ given in figure 4, which indicates that the proposed magnetron with a sandwich target allows the synthesis of solid composite films $\text{Mo}_x\text{Cr}_{1-x}\text{N}$ with a continuous change in the stoichiometric coefficient $x$, which provides a smooth change in hardness. In this case, the stoichiometric coefficient can be controlled in the range $0 < x < 0.3$, varying the area of the slots in the range $0 < \alpha < 0.5$ for the specified values of the discharge current density and nitrogen consumption.

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