Deposition of solid solution films using reactive magnetron sputtering of a sandwich target

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Abstract. This work presents a magnetron with a sputtering unit (sandwich target). The novelty of the work is due to the three parallel plates of different metals included in the unit. They are mounted on the same axis with the magnetron and rigidly attached to it. The unit is located in a reactive environment consisting of plasma-forming argon and reactive gas (nitrogen, oxygen, etc.). The lower plate is cold, while the middle and outer ones operate in the hot target mode. In the erosion zone of the middle and outer plates, eight slits were made. They are located on the same axis and symmetrically relative to their center. The lower plate is sputtered through these slits. A magnetron with the above sandwich target can be used for the synthesis of composite films of the three-compound solid solutions. The possibility of synthesizing TiₓMoᵧCr₁₋ₓ₋ᵧN films with a continuous change in the stoichiometric coefficients x and y due to the change in the current density and relative areas of the slits, which provide a smooth change in the hardness of the films, is shown.

In this work, we consider films of the nitride solid solutions. The growing interest in films and coatings of single transition metal nitrides is illustrated in figure 1. The above interest arose in the second half of the last century. If in the last century, according to the Scopus database, on average 380 articles were published annually, then over the past 20 years this number has increased to about 2000. The data presented in figure 1 do not take into account solid solution films of different metals’ nitrides and heterostructures based on them.

1.5–2.0 times increase of attention to silicon nitride films (figure 2) is due to their extremely high mechanical properties, transparency in the visible and infrared ranges [1]. The most intensive development of silicon nitride films can be seen in radiophotonics [2].

The second place by the number of publications is taken by aluminum nitride films. This interest is mainly associated with their application in acoustoelectronics (resonators, delay lines, filters on surface acoustic waves, etc.) [3]. Another equally important application of films in the Al–N system is electronic components operating in the ultraviolet range (light and laser diodes, etc.) [4].

The last group of nitride films that attract high attention (see figure 2) are films in the Ti–N system. They have low resistivity, high hardness and chemical inertness [5]. As a result, they are used in electronics, as decorative, wear-resistant and corrosion-resistant coatings [6], etc. Films of nitrides of other transition metals have similar properties. They also have high hardness, are chemically inert and wear-resistant.

The properties of some films are rapidly degraded due to oxidation at high-speed processing and temperatures exceeding 500–700 °C. To overcome these problems and improve their properties, com-
Composites are created by introducing a third element into them. Examples of such composites are systems such as Cr–Al–N [7], Ti–Cr–N [8], Ti–Al–N [9], Ti–Ta–N [10], etc.

As a result of research aimed at increasing the lifetime of cutting tools, new types of composite coatings for the cutting edge have appeared. They include triple solid solutions of nitrides in the systems Cr–Ti–Al–N [11], Al–Ti–Si–N [12], Al–Cr–Si–N [13], etc.

The variety of films and coatings stimulated the research and development of many synthesis methods, which can be conditionally divided into two groups (figure 3): chemical and physical. Among the latter, magnetron sputtering methods are most often used. The numbers on the diagram indicate the share of publications.

For the synthesis of composite films containing two or three nitrides, several magnetrons with effectively cooled targets made of different metals are usually used [14]. Magnetrons are placed next to each other. A common disadvantage of this approach is the difficulty of synthesizing films with a continuous change in chemical composition, which provides a smooth change in hardness.

A new step in the development of reactive magnetron sputtering technology is the magnetron equipped with a sputtering unit. Several target plates [15–20] are fixed on one axis. A schematic representation of a sputtering unit intended for the deposition of composite films of solid solutions of three nitrides is shown in figure 4. The sputtering unit is rigidly bolted to the body of a balanced magnetron 1 with a diameter of 130 mm. The unit contains an inner plate 2 cooled by running water, a middle plate 3 and an outer plate 4. Washers 5 are installed between the plates, providing a gap of a given size. Each plate has an erosion zone created by the flux of ions.

The purpose of this work is to demonstrate the possibility of synthesizing the composite films containing a solid solution of three compounds by reactive magnetron sputtering of a sandwich target. Let us consider this problem further by the example of the deposition of a TiMoCr<sub>1-x</sub>N film. To prepare a film of this composition, the inner plate 2 was made of chromium, the middle plate 3 was made of molybdenum, and the outer plate 4 was made of titanium. The erosion zone 6 of the outer plate had the shape of a ring with an area s. In this area, there are slits 7 located symmetrically relative to its center.
They have a total area $s_{d, Ti}$. For the outer plate, the area of the zone from which the emission of titanium nitride particles occurs is $s_{Ti} = s - s_{d, Ti}$. Slits 7 define the area of zone 8 on the middle plate, which is bombarded by argon ions. Part of this zone is occupied by slits 9 with a total area of $s_{d, Mo}$; therefore, the area of the zone on the middle plate, which emits molybdenum nitride particles, is $s_{Mo} = s_{d, Ti} - s_{d, Mo}$. The total area of the slits 9 on the middle plate sets the area $s_{Cr} = s_{d, Mo}$ of zone 10, which emits chromium nitride particles from the bottom plate.

Along with the discharge current density and nitrogen consumption, the independent variables of the device are the relative total areas of the slits in the outer and middle plates:

$$\alpha = \frac{s_{d, Ti}}{s}; \quad (1)$$

$$\beta = \frac{s_{d, Mo}}{s}; \quad (2)$$

respectively.

The total flux of titanium nitride $J_{TiNtot}$ from the outer plate consists of atomized $J_{TiNsp}$ and evaporated $J_{TiNev}$ fluxes. The total flux from the middle $J_{MoNtot}$ plate can also consist of sputtered $J_{MoNsp}$ and evaporated $J_{MoNev}$ fluxes, since the molybdenum plate also operates in the hot target mode. To determine the $J_{TiNev}$ and $J_{MoNev}$ values, the temperature estimates of both plates in the form of exponentials were used:

$$T_{Ti}(j) = 293 + 2165\left(1 - e^{-0.00168j}\right); \quad (3)$$

$$T_{Mo}(j) = 293 + 1500\left(1 - e^{-0.00168j}\right). \quad (4)$$

In dependencies (3) and (4), the current density $j$ is given in amperes per square meter, the temperature $T_{Ti}$ and $T_{Mo}$ in kelvin. Since MoN has a significantly lower saturated vapor pressure and the temperature of the molybdenum plate is less than 1500 K, the $J_{MoNev}$ component is further neglected.

The ratio of the components in the film $Ti, Mo, Cr_{1-x}, N$ is set by the values:

$$x = \frac{J_{TiNtot}}{J_{TiNtot} + J_{MoNtot} + J_{Crsp}}, \quad (5)$$

$$y = \frac{J_{MoNtot}}{J_{TiNtot} + J_{MoNtot} + J_{CrNp}}. \quad (6)$$

At the same time, each of the components in (5) and (6) in a known manner depends on values (1) and (2). In this case, for example, the atomized flux of chromium nitride is:

$$J_{CrNsp} = \beta s \frac{S_{CN,j}}{e(1 + \gamma_{CN})}, \quad (7)$$

where for chromium nitride: $S_{CN} =$ sputtering yield; $\gamma_{CN} =$ coefficient of ion-electron emission; $j =$ discharge current density on the target, $A/cm^2$; $e = 1.6 \cdot 10^{-19}$ C is the electron charge. The flux of molybdenum nitride is given by the expression

$$J_{MoNsp} \approx J_{MoNsp} = (\alpha - \beta)s \frac{S_{MoN,j}}{e(1 + \gamma_{MoN})}, \quad (8)$$

where for molybdenum nitride: $S_{MoN} =$ sputtering yield; $\gamma_{MoN} =$ coefficient of ion-electron emission.

A titanium nitride flux of two components gives the expression

$$J_{TiNtot} = J_{TiNsp} + J_{TiNev} = (1 - \alpha)s \left( \frac{S_{TN,j}}{e(1 + \gamma_{TN})} + \frac{10^{A_{TN-B_{TN/Ti}}}T_{Ti}}{\sqrt{2m_{Ti}kT_{Ti}}} \right), \quad (9)$$

where for titanium nitride: $S_{TN} =$ sputtering yield; $\gamma_{TN} =$ the coefficient of ion-electron emission; $A_{TN}$
and $B_{\text{TiN}}$ - constants setting the saturated steam pressure; $m_{\text{TiN}}$ is the mass of the molecule; $T_{\text{Ti}}$ is the temperature of titanium platinum; $k = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant.

Figure 5 shows the dependences of the stoichiometric coefficients in the Ti$_x$Mo$_y$Cr$_{1-x-y}$N film on the current density and $\beta$ obtained using expressions (5)–(9). Figure 6 contains the dependences of the values $x$, $y$ and $1-x-y$ on the parameters of the sputtering unit $\alpha$ and $\beta$. As it follows from figures 5 and 6, the chemical composition of the Ti$_x$Mo$_y$Cr$_{1-x-y}$N film can be controlled by varying the discharge current density and parameters $\alpha$ and $\beta$. Moreover, the discharge current up to about 1000 A/m$^2$ has little effect on the values of $x$, $y$ and $1-x-y$. For $j > 1000$ A/m$^2$, the value of $x$ begins to increase at a rate that is higher than the rate of decrease in $y$. This conclusion is obvious, figure 5 shows that the fraction of chromium in the film at $j > 1000$ A/m$^2$ decreases in the same way as the fraction of molybdenum. The reason for this feature should be sought in a significant increase in the temperature of the outer titanium plate, at which the vaporized flux of $J_{\text{TiNeV}}$ becomes significant.

Figure 7 shows that at $\alpha = 0.5$, the $H = f(\beta)$ curve reaches a maximum of ~ 45 GPa at approximately $\beta = 0.05$, which in Figure 8 and 9 corresponds to the values $x = 0.62$ and $y = 0.28$.

Thus, a magnetron with a sputtering unit containing three plates of different metals makes it possible to deposit composite films during reactive sputtering. They can consist of solid solutions of three compounds (for example, nitrides or oxides). The chemical composition of the films can vary over a wide range due to changes in the current density and the relative areas of the slits $\alpha$ and $\beta$, which provide a smooth change in the defining parameter of the film. In particular, as shown above, the magnetron with the proposed unit allows the synthesis of superhard composite films Ti$_x$Mo$_y$Cr$_{1-x-y}$N with a continuous change in stoichiometric coefficients of $0.4 \leq x \leq 0.75$ and $0 \leq y \leq 0.4$. Their hardness can exceed 40 GPa.
It is characteristic that the current density less than 1000 A/m$^2$ practically does not affect the chemical composition of the Ti$_x$Mo$_y$Cr$_{1-x-y}$N film. At $j > 1000$ A/m$^2$, the TiN concentration in the film increases with an increase in the flux of the evaporated substance from the outer plate.

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