Modeling of reactive sputtering of hot titanium target in nitrogen and oxygen

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Abstract. A model for reactive sputtering of a hot titanium target in the environment of oxygen and nitrogen is considered. The target temperature is defined as a function of the ion current density. For the mathematical description of the process, the basic postulate of chemical kinetics including the equation of the Langmuir isotherm and the Arrhenius equation under nonisothermal conditions is used. In addition, the model takes into account thermionic emission and evaporation of the target surface.

Titanium oxynitride films with the composition expressed by the chemical formula TiO$_x$N$_y$ form a continuous series of compounds with different concentrations of nitrogen and oxygen (from TiO$_2$ to TiN) [1].

In order to deposit TiO$_x$N$_y$ films, the methods of reactive magnetron sputtering are most often used [2]. During reactive sputtering, a cold titanium target can operate in reactive or metallic modes [3]. The transition between the modes is controlled by the discharge current and reactive gas flow rate [3]. In a magnetron with a hot target, the physicochemical processes taking place on its surface change [4]. For a correct description of the problem, it is necessary to take into account the effect of the target temperature $T$.

In the first works devoted to the modeling of the reactive sputtering of a metal target in a mixture of argon, nitrogen, and oxygen, an isothermal chemisorption model for a single reactive gas was developed. A review of this theme is given in [3]. An alternative non-isothermal physicochemical model was originally developed for a single gas environment [5], and later for an environment of two reactive gases [3]. Then this model was developed and used for reactive sputtering of a hot target in an oxygen environment [4].

In this paper, we consider a more complicated problem. Modeling of sputtering of a hot titanium target in argon, nitrogen and oxygen was performed. Due to the limited size of the publication, below we describe the major assumptions, provide a system of algebraic equations in a general form, and present selected results of the solution.

We assume that the reactive sputtering system contains a hot titanium target, an unspecified substrate and a vacuum chamber wall with areas $A_t$, $A_s$ and $A_w$, respectively. Elements of the system are located in the gas mixture Ar + O$_2$ +N$_2$. In this system:

1) the substrate and the wall have constant temperatures $T_s$ and $T_w$, respectively. The target temperature $T_t = f(j_+)$ depends on the ion current density $j_+$;

2) we assume that titanium oxynitride is formed on all surfaces in the form of a solid solution of TiO$_2$ oxide and TiN nitride arising from surface chemical reactions:
where \( k_1(T) \) and \( k_2(T) \) are reaction rate constants \( \text{(1)} \). Hereinafter indices 1 and 2 refer to oxide (or oxygen) and nitride (or nitrogen), respectively;

1) two processes compete on the target surface:
- formation of a solid solution layer by reactions \( \text{(1)} \);
- removal of this layer by sputtering and evaporation. The flux density of the evaporated particles \( J_{ev} \) from a homogeneous surface gives the Hertz-Knudsen equation:

\[
J_{ev} = \frac{p_0}{\sqrt{2\pi m_0 k T_t}},
\]

where \( p_0 \) and \( m_0 \) are the saturated vapor pressure and the mass of a particle of a material of a homogeneous surface. The concept of "homogeneity" is important. We assume that the target surface in the most general case can have three regions (see fig. 1). One of them, occupying the relative part of the \( \theta_{t1} \) surface, is coated by an oxide, the second, coated by a nitride, has a relative area \( \theta_{t2} \). The remaining part \( 1 - \theta_{t1} - \theta_{t2} \) is an uncoated metal. Each of these areas is called homogeneous. Developing the model, we further introduce refinement indices in \( \text{(2)} \), where it’s required;

2) two stationary modes are possible for a target: metallic or reactive. In the first case, its surface is an uncoated metal and produces only titanium atoms, which create a corresponding film on the surfaces of the substrate and the wall. In the reactive mode, the target generates fluxes of TiO\(_2\) and TiN molecules, which are deposited on the surfaces of the substrate and the chamber walls and create layers of oxynitride;

3) the discharge current \( j \) is the sum of the currents that have arisen on parts of the target surface with different physical properties. If the entire surface of the target is homogeneous, then the current density is

\[
j = (1 + \gamma) j_+ + j^-,
\]

where \( \gamma \) and \( j^- \) are the coefficient of ion-electron emission and the current density of thermionic emission, respectively, for the target coating material. The value \( j^- \) is given by the Richardson-Dushman law:

\[
j^-(T_t) = AT_t^2 \exp\left(-\frac{\varphi_t}{kT_t}\right),
\]

where \( A \approx 120 \text{ A cm}^{-2} \text{ K}^{-2} \); \( k = 1.38 \times 10^{-23} \text{ J K}^{-1} \) is the Boltzmann constant; \( \varphi_t \) is the work function of electrons from the target surface. In order to take into account all possible target coatings (metal, oxide and nitride) in the given task, it is necessary to assign the indices \( m, c_1, u, c_2 \) in the expressions \( \text{(3)} \) and \( \text{(4)} \) to the values \( \gamma, j^- \) and \( \varphi_t \). Taking into account all components, the expression for the current density of the discharge is now written in the form
\[ j = (1 - \theta_{t1} - \theta_{t2})[(1 + \gamma_m)j_+ + j_{m1} + \theta_{t1}[(1 + \gamma_c)j_+ + j_{c1}]] + \theta_{t2}[(1 + \gamma_c)j_+ + j_{c2}]; \quad (5) \]

4) in order to support the reactions (1), all surfaces consume reactive gases. We denote the oxygen fluxes by \( Q_{o1}, Q_{o2}, Q_{w1}, \) and the nitrogen fluxes to these surfaces by \( Q_{n2}, Q_{w2} \).

Using assumptions 1–6, the basic postulate of chemical kinetics and the Langmuir isotherm, as it was done in [5], we obtain a system of sixteen algebraic equations. The first six describe the equilibrium on the surface:

- target (see fig. 1)
  \[ J_{chj}(T_1(j_+)) + J_{c}(j_+) = 0, \quad j = 1, 2, \quad (6) \]

where \( J_{chj}(T_1(j_+)) \) is the density of the j-chemical flux, which is created by reactions (1) due to the fluxes of oxygen \( J_1 \) and nitrogen \( J_2 \). The surface of the target, as shown in fig. 1, has three regions. Therefore, it is the source of three fluxes with the density:

\[ J_{mt}(j_+) = J_{msp}(j_+) + J_{mev}(T_1(j_+)) \]

(7)

for metal and

\[ J_{c1}(j_+) = J_{csp}(j_+) + J_{cev}(T_1(j_+)), \quad j = 1, 2 \]

(8)

for oxide \((j = 1)\) and nitride \((j = 2)\). The first terms on the right-hand sides of (7) and (8) reflect sputtering, the second - evaporation;

- substrate and walls
  \[ J_{chj}(T_i) + J_{m1}(j_+) = J_{c}(j_+), \quad j = 1, 2; \quad i = s, w. \quad (9) \]

The second group of six equations sets the fluxes of oxygen

\[ Q_{i1} = J_{ch1}(T_i)A_i, \quad i = t, s, w \]

(10)

and nitrogen on each of the three internal surfaces of the vacuum chamber:

\[ Q_{i2} = 0.5J_{ch2}(T_i)A_i, \quad i = t, s, w \]

(11)

The last group consists of equations, two of which describe the operation of a vacuum pump

\[ Q_{pj} = c^0p_jS_p, \quad j = 1, 2 \]

(12)

and two - the balance of gas fluxes:

\[ Q_{p} = Q_{t1} + Q_{s1} + Q_{w1} + Q_{p}, \quad j = 1, 2 \]

(13)

In expression (12) we use the notation \( c^0 = 2.5 \times 10^{25} \text{ Pa}^{-1} \text{m}^{-3} \) – the size coefficient that transfers the flux of \( Q_{pj} \) from \( pV \) units to the measurement unit, which is more convenient for calculation: the number of particles per time unit; \( S_p \) – evacuation speed of the vacuum chamber; \( p_j \) - the partial pressure of the \( j \)-reactive gas.

The system of algebraic equations (6), (9)–(13) contains three independent variables: the fluxes \( Q_{pj} \), \((j = 1, 2)\) and the discharge current density \( j \) (5). The dependent variables are the partial gas pressures \( p_j \)(j = 1, 2), the gas fluxes \( Q_{t1}, Q_{s1}, Q_{w1}, Q_{w1} \) and \( Q_{pj} \) and the fractions of the three surfaces \( \theta_{t1} \) and \( \theta_{t2} \) \((i = t, s, w)\), coated by a solid solution of \( \text{TiO}_2 + \text{TiN} \). The system (6), (9)–(13) was solved numerically. The approximating expression connecting the target temperature in kelvins with the ion current density in amperes per square meter is

\[ T_1(j_+) \approx 293 + 1520(1 - \exp[-0.00438 j_+]), \quad (14) \]

Equations (6), (9)–(13) taking into account (14) were solved in the range of current densities from 200 to 400 A/m² and nitrogen flow rates \( Q_{n2} \) from 0 to 0.3 cm³/min. Figure 2 shows the S-shaped dependences \( p = f(Q_{n1}) \) outlining that the process is characterized by a hysteresis effect. Figure 2 also
shows that the increase in nitrogen consumption leads to the shift of the transition points in the target operating modes, and the derivative $dp/dQ_{01}$ has discontinuities. In addition, an increase in nitrogen consumption leads to a decrease in the width of the hysteresis loop.

As the current density increases, the transition points are shifted to the region of higher oxygen flow rates (figure 3) and the hysteresis width increases. In addition, the calculations showed that when the hot and cold targets are sputtered, the dependences $p = f(Q_{01})$ are different (figure 4).

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