Reactive magnetron sputtering model at making Ti-TiO$_x$ coatings

A G Luchkin and N F Kashapov
Kazan (Volga Region) Federal University, 18 Kremljovskaja str., Kazan 420008, Russian Federation
E-mail: AGLuchkin@kpfu.ru

Abstract. Mathematical model of reactive magnetron sputtering for plant VU 700-D is described. Approximating curves for experimental current-voltage characteristic for two gas input schemas are shown. Choice of gas input schema influences on model parameters (mainly on pumping speed). Reactive magnetron sputtering model allows develop technology of Ti – TiO$_x$ coatings deposition without changing atmosphere and pressure in vacuum chamber.

1. Introduction
Low-temperature plasma is widely used for surface modification and making functional coatings [1-4]. Magnetron sputtering of metal target at work and reactive gases mixture atmosphere has its difficulties such as unstable current-voltage characteristic [5]. There are several models of reactive sputtering process [6-9]. But they are not universal and for concrete experimental plant are needed in specific approximating equations system.

The aim of the paper is to create mathematical model of reactive magnetron sputtering for experimental plant VU-700D.

2. Experimental plant and model
Functional schema of experimental plant, discharge parameters are discussed in [10,11]. Metal Titanium target 100x500 mm$^2$ was used. Experimental plant provides gas input in region of magnetron target (schema “A”) and in region of substrate (schema “B”). Volt-ampere characteristics measured within input of work and reactive gases in vacuum chamber at different ratio. Voltage fixed at different values of discharge current.

Reactive magnetron sputtering model has several assumption: reactive gas (oxygen) is ideal diatomic gas; at the same time oxygen is pumped out, adsorbs on vacuum chamber walls and magnetron target and desorbs from magnetron target; there is oxide film on magnetron target surface and ratio of magnetron target surface covered by oxide film to total magnetron target surface is $\theta$ ($0 < \theta < 1$); $\theta = \theta(r)$, where $r$ – magnetron target radius. At stationary state for target we can write [9]:

$$\sigma kp (1 - \theta(r)) = \frac{\eta_0 j(r)\theta(r)}{e} + \frac{N \theta(r)}{\tau(T)},$$

(1)

where $\sigma = 1$ – oxygen adsorption coefficient, $k = 3.81 \times 10^{18}$ sm$^2$sec$^{-1}$Pa$^{-1}$ – quantity of oxygen atoms hits on the surface at 300 K, $\eta_0$ – sputtering coefficient, $e$ – electron charge, $j(r) = j_0 f(r)$ – current density. $N \theta(r)/\tau(T)$ – oxygen thermal desorption, $N$ – oxygen desorption centers density, $\tau(T)$ – oxygen presence time on target surface with temperature $T$. We assume that:
Material sputtering speed:
\[ R = \eta_m \frac{L}{e} = \eta_m \int_{r_1}^{r_a} j(r) \left(1 - \theta(r)\right) 2\pi r \, dr, \]
where \( \eta_m \) is material sputtering coefficient. Sputtered material homogeneously deposits on getter surface \( F \), where oxidation degree is \( \theta \) (\( 0 < \theta < 1 \)). Oxygen partial pressure in chamber depends on gas input volume \( D_0 \), pumping speed \( S_p \) and sputtering speed \( R \):
\[ p = \frac{D_0}{S_p - \gamma \theta R}, \]
where \( \gamma \) is about \( k_o T \). For \( \theta \) can be written [12]
\[ \theta = \frac{1}{2} \frac{k_p (1 - \theta)}{R/F}, \]
where adsorption coefficient \( \sigma = 1 \) and there is no desorption.
From (5) follows:
\[ \theta = \frac{1}{2} \frac{k_p R/F}{1 + \frac{k_p R/F}{F}}. \]

The insertion of (6) into (4) gives
\[ S_p p = \frac{D_0 - \gamma R \frac{k_p R/F}{1 + \frac{k_p R/F}{F}}}{2}. \]

From equation (1) define \( k \) and \( p \) and insert it into (7). After conversion we will have
\[ \frac{S_p}{k} \left[2R + \frac{\theta(r)}{1 - \theta(r)} \frac{\eta_0}{e} j(r) F\right] + \gamma FR = D_0 \frac{1}{\theta(r)} \frac{e}{j(r) \eta_0} \left[2R + \frac{\theta(r)}{1 - \theta(r)} \frac{e}{j(r) \eta_0} \theta_0 F\right]. \]

From equations (3) and (8) discharge current \( I \) could be defined as function of \( \theta_0 = \theta_0(r) \)
\( (0 < \theta_0 < 1) \)
\[ I(\theta_0) = \frac{B_2 D_0}{S_p} \left(\frac{1}{1 - \theta_0} + B_1 \frac{2A \eta_m (1 - \theta_0)}{\eta_0 F \theta_0} \frac{1}{\theta_0 F}\right), \]
where integrals
\[ B_1(\theta_0) = \frac{1}{A} \int_{r_1}^{r_a} \frac{f^2(r) 2\pi r \, dr}{\theta_0 + (1 - \theta_0) f(r)} \]
and
\[ B_2 = \frac{1}{A} \int_{r_1}^{r_a} f(r) 2\pi r \, dr \]
could be found from current density distribution function \( f(r) \) and effective target surface \( A \). \( D_0 \) – total gas input (argon and oxygen) [mW] or [Pa l/sec], \( F \) – getter surface square, \( \text{sm}^2 \), \( S_p = 6 \text{ l/sec} \) – pumping speed, \( \eta_m \) and \( \eta_0 \) – metal and oxide sputtering coefficients.

Target oxidation degree influence on current-voltage characteristic could be written as
\[ I = AC \left(\frac{U}{U''}\right)^b + cB_3 \theta, \]
where integral
\[ B_3 = \frac{1}{A} \int_{r_1}^{r_a} \frac{2\pi r \, dr}{\theta_0 + (1 - \theta_0) f(r)} \]
could be found from view of \( f(r) \). From equation (12) voltage expresses as
\[ U(\theta_0, I) = U'' \left(\frac{I}{eA}\right)^b + cB_3 \theta_0. \]

Parametric representation of current-voltage characteristic is given by equations (9) and (14). For results illustration we assume \( f(r) = B_1 = B_2 = B_3 = 1 \). Simplified calculations qualitatively match with current-voltage characteristic curves main behavior. Other distribution functions \( f(r) \) don’t change results seriously.
3. Results and discussions
Experimental current-voltage characteristics for different schemas of reactive gas input and their approximation are shown at pic. 1 and 2. Solid line – approximating curve, circles and squares – experimental data, increasing and decreasing current density respectively. Lower increasing part of approximating curve corresponds to “oxide” regime, when oxide deposits on substrate. Higher increasing part corresponds to “metal” regime, when substrate surface is coated by metal film. Middle part corresponds to forbidden states.

When discharge is burning the transparent coating is making. Increasing of discharge power at defined moment oxide film at target surface sputters totally and metallic coating is making. Discharge power decreasing results to opposite effect but at lower value. Using these transitions we can deposit on substrate surface Ti – TiOₓ coatings without changing atmosphere and pressure in vacuum chamber.

Pic. 1. Current-voltage characteristic approximation, schema “A”, 4•10⁻² Pa, oxygen – argon ratio is 2 to 1: — - U(I); ○ – increasing current density; □ - decreasing current density.

Approximations for schemas “A” and “B” differs only by \( S_p \) and \( c \). Pumping speed \( S_p \) for schema “A” grater pumping speed for schema “B” 4,5 times, coefficient \( c \) – 2 times. That difference could be explained if we remember that in schema “A” oxygen inputs directly into magnetron target region and that for oxide deposition on substrate surface responds target surface oxidation. Deviations of approximating curves from experimental current-voltage characteristics could be caused by model assumptions. For example, partial oxidation of titanium, other getter surfaces, etc.

4. Conclusions
Mathematical model of reactive magnetron sputtering for plant VU 700-D is described. Approximating curves for experimental current-voltage characteristic for two gas input schemas are shown. Choice of gas input schema influences on model parameters – pumping speed and coefficient \( c \). Reactive magnetron sputtering model allows develop technology of Ti – TiOₓ coatings deposition without changing atmosphere and pressure in vacuum chamber.
Pic. 2. Current-voltage characteristic approximation, schema “B”, $4 \cdot 10^{-2}$ Pa, oxygen – argon ratio is 2 to 1: — - $U(I)$; ○ – increasing current density; □ - decreasing current density.

Acknowledgements
The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

References
[1] Galyautdinov R.T., Kashapov N.F., Luchkin G. S. // Welding International. - 2003.- V. 17,- № 8.- P. 655 – 658.
[2] Galyautdinov R.T., Kashapov N.F., Luchkin G. S. // Applied physics. . - 2005.- № 6.- P. 88-93.
[3] Galyautdinov A.R., Galyautdinov R.T., Kashapov N.F., // Bulletin of KGTU. Tupolev. 2010.- № 4. - P. 122-128.
[4] Galyautdinov R.T., Kashapov N.F., Luchkin G. S. // Engineering-physical journal. -2002. - V.75.- № 5. - P 170-173.
[5] Kashapov N.F., Luchkin A.G. // Russian Physics Journal 57 (2014) № 3/3, P. 162-166.
[6] S. Berg, T. Nyberg // Thin Solid Films 476 (2005) 215 -230
[7] Anatoly A. Barybin and Victor I. Shapovalov Journal of Applied Physics 101, 054905 (2007); doi: 10.1063/1.2435795.
[8] E. V. Berlin, S.A. Dvinin, L.A. Seidman Vacuum technology and technic for thin film deposition and etching M: Technosphera, 2007. — 176 pp, ISBN: 978-5-94836-134-5.
[9] Steenbeck, K., Steinbeiss, E. & Ufert, K.-D. // Thin Solid Films. 1982. V. 92. P. 371—380
[10] N.F. Kashapov, A.G. Luchkin & G.S. Luchkin. J. Phys.: Conf. Series 479 (2013) 012019.
[11] Galyautdinov R.T., Kashapov N.F. & Luchkin A.G. // Bulletin of KGTU. Tupolev. 2013.- № 3. - P. 106-110.
[12] Ratter, E., Monatsch Chem, 95 (1964) 795.