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Simulation of reactive high-power impulse magnetron sputtering process of a metal (vanadium) target

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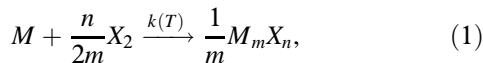
This paper presents a physicochemical model describing the process of high-power impulse reactive magnetron sputtering of a metal target. An increase in the pulse power density of the power source contributes to the heating of the target, which leads to an increase in the efficiency of spraying and the appearance of a flow of vaporized matter. The combination of these effects leads to an increase in the deposition rate of films of complex compounds. The presented paper presents the results of simulation of the sputtering process of a vanadium target in an Ar + O₂ medium, which demonstrated an increase in the sputtering rate by 8.5 times with an increase in power density from 0.5 kW/cm² to 1.5 kW/cm².

Keywords: reactive magnetron sputtering, HiPIMS, nonisothermal model, vanadium dioxide.

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Currently, high power impulse magnetron sputtering (HiPIMS) is a common vapor deposition technique for producing films of complex compounds [1,2]. The use of this technology allows to improve adhesion to the substrate, density and tribological properties of the obtained coatings, but the low deposition rate significantly complicates its practical application [3]. One of the simplest ways to eliminate this disadvantage is to increase the pulsed power density, but this leads to a change in the thermal regime of the atomized target and an increase in its temperature, which can adversely affect the performance of the atomization system. In connection with the above, it is of undoubted interest to develop a physical and mathematical model to evaluate the effect of power density on target temperature and coating deposition rate using the HiPIMS method.

The developed model is based on the basic postulate of chemical kinetics, represented in the non-isothermal model [4]. General view of the chemical reaction occurring during reactive atomization of a metallic target on its surface, substrate and vacuum chamber walls:



where M — target atom; n, m — stoichiometric coefficients; X_2 — reactive gas molecule, $k(T)$ — chemical reaction rate constant. Surface processes are described by changes in the degree of coverage of the chemical compound layer θ_i ($i = s, t, w$, subscript corresponds to a particular surface: substrate, target, and chamber walls, respectively) and mass flux densities.

The high-power pulsed operation of the magnetron favors heating the target to high temperatures. In this case, the temperature of the erosion zone may exceed the melting point. The variation of target surface temperature in HiPIMS mode was studied in detail in [5] using computer

simulations. The authors highlighted an expression describing the time dependence of the temperature of the metallic target:

$$T_t(t) = T_\infty - (T_\infty - T_0) \exp(-t/\tau), \quad (2)$$

where T_∞ — steady-state temperature, T_0 — coolant temperature, τ — process time constant. The rate of change in the degree of coverage of the θ_i target depends on the rate of formation of the layer of chemical reaction products (1) and its removal by sputtering during ion bombardment. However, heating the target can lead to additional effects. Firstly, due to thermoelectron emission there is an increase in the concentration of electrons in the gas discharge plasma. In turn, this leads to an increase in the degree of its ionization and, consequently, to enhanced atomization of the target surface. Secondly, when approaching the melting temperature of the target, an additional flux of vaporized matter occurs, which leads to a decrease in the degree of coverage of the target by the surface compound layer. Thus, the final rate of change of the degree of the target surface covered with chemical reaction products is defined as

$$\frac{d\theta_t}{dt} = \left(\frac{d\theta_t}{dt}\right)_{ch} - \left[\left(\frac{d\theta_t}{dt}\right)_{sp} + \left(\frac{d\theta_t}{dt}\right)_{ev} \right]. \quad (3)$$

The first summand in the right-hand side of formula (3) corresponds to the formation of the chemical compound layer, the second — its removal by atomization, and the third — its removal by evaporation. To determine the efficiency of the surface chemical reaction, the reactive gas balance equation inside the vacuum chamber is used

$$Q_0 = Q_p + Q_t + Q_w + Q_s, \quad (4)$$

where Q_0 — the amount of reactive gas introduced into the vacuum chamber; Q_p — the amount of reactive gas pumped

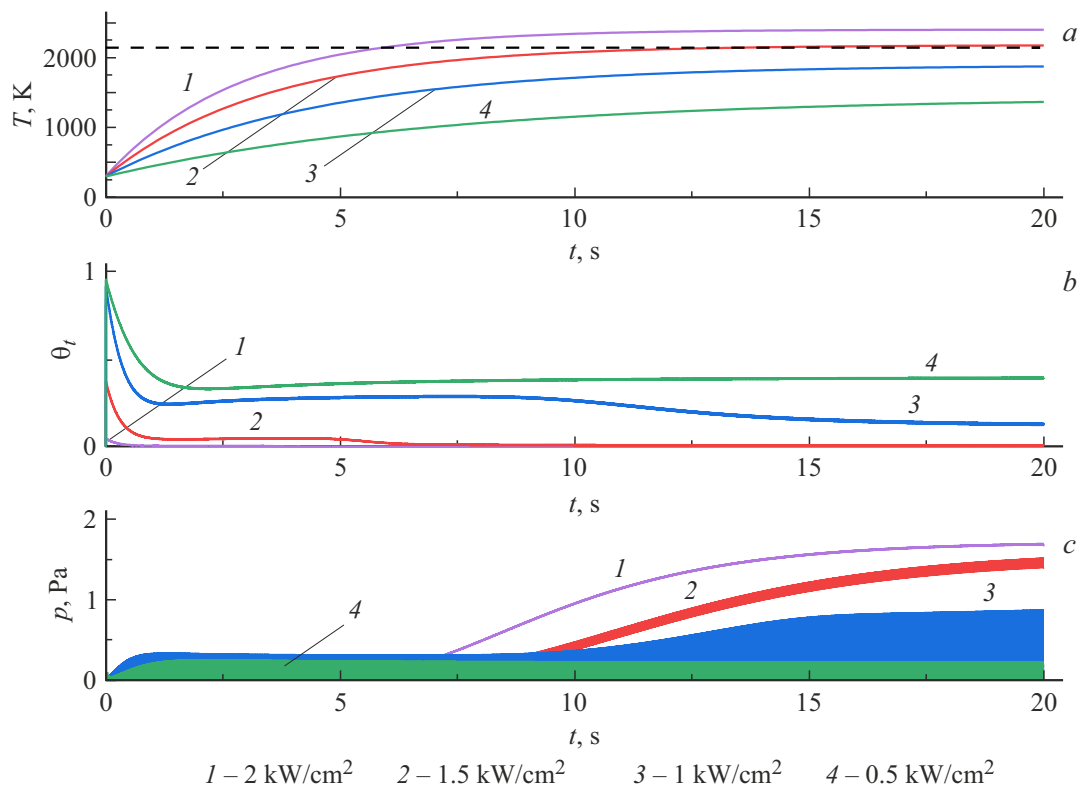
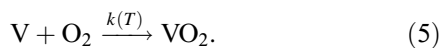


Figure 1. Time dependences of the target surface temperature (a), the degree of coverage of the target by the chemical compound layer (b), and the pressure in the vacuum chamber (c) at different values of the peak power density of the source. The dashed line marks the melting point of vanadium.

out by the vacuum pump; Q_s , Q_t , Q_w — the flow rate of reactive gas fueling the chemical reaction on the surfaces of the substrate, target and chamber walls, respectively. The system of equations for the steady-state case of direct current atomization of a metallic target is described in detail in [6].

To assess the influence of the considered effects on the process parameters of the sputtering process, the process of deposition of vanadium dioxide films by the HiPIMS method was modelled by numerical solution of the system of differential equations. In this case, the following surface chemical reaction occurs:



Parameters used in modelling the sputtering of a vanadium target in $\text{Ar} + \text{O}_2$ (subscript M corresponds to vanadium and C — vanadium dioxide): $Q_a = 10\,000$ cal/mol, $\tau_0 = 10^{-13}$ s, $\alpha_0 = 1$ [6], $A_M = 13.32$, $B_M = 26\,620$ [7], $A_C = 11.2$, $B_C = 27\,740$ [8], $\varphi_M = 4.3$ eV [9], $\varphi_C = 5.15$ eV [10], $S_C = 0.05$, $S_M = 0.53$ [11], $S_p = 0.07$ m³ · s⁻¹, $N_{ch} = 14.7 \cdot 10^{18}$ m⁻², $k_0 = 10^{30}$ m⁻² · s⁻¹, $E_a = 7.5 \cdot 10^{-20}$ J, $T_0 = 300$ K, $T_s = 600$ K, $T_w = 300$ K, $\gamma_M = 0.053$, $\gamma_C = 0.049$, $A_t = 0.0031$ m², $A_s = 0.0003$ m², $A_w = 1$ m². The influence of peak power density on the atomization process was investigated at constant values of pulse duration and frequency: 100 μs and 100 Hz, respectively.

In calculations, the flow rate of reactive gas, providing the films of a given stoichiometry, with increasing power applied to the target was changed in accordance with the obtained experimental data. The modeling results are shown in Fig. 1. The time-temperature dependences (Fig. 1, a) are obtained by solving the thermal conductivity equation according to the work [5]. It can be seen that increasing the power density to 1.5 kW/cm² allows to reach a temperature close to the vanadium melting point (2183 K), which corresponds to the operating mode under the so-called „hot“ target [6] conditions. The time dependences of the target coverage have two characteristic drops (Fig. 1, b). The first corresponds to an increase in the efficiency of the sputtering process due to an increase in the degree of plasma ionization, which is characteristic of the HiPIMS mode. The second is observed when temperatures close to the melting point of vanadium and its oxides are reached. The total pressure in the system (Fig. 1, c) increases with increasing peak power density, which is explained by decreasing consumption of reactive gas and formation of vapor flow of substances vaporized from the target surface. At the moment of switch-on after the first pulse, the target surface is covered by a layer of compound up to a maximum value of θ_t , determined primarily by the peak power density and reactive gas flow rate (Fig. 2, a). In the stationary regime (when the maximum temperature of the target

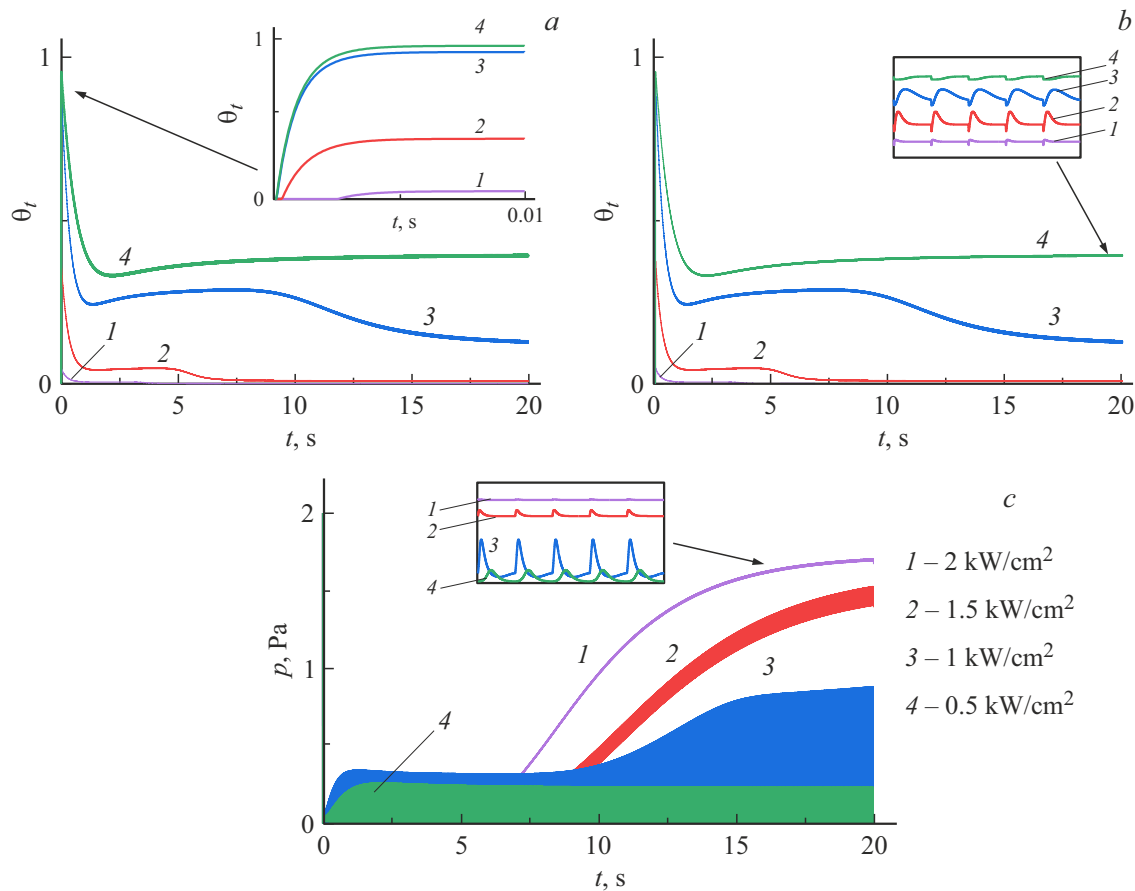


Figure 2. Time dependences of the degree of coverage of the target by the chemical compound layer (*a*, *b*) and the total pressure in the system (*c*) with the pulse behavior indicated on the inserts (inset on part *a* — after the first pulse, insets on parts *b* and *c* — in the steady-state regime).

erosion zone is reached), the obtained dependences have characteristic pulsations due to pulse feeding (Fig. 2, *b*, *c*). The aggregate of the obtained dependences allows us to assert that in the mode „of hot“ target the formation of a chemical compound layer on its surface is difficult. It is known that, as a rule, a metal has a higher atomization coefficient than its compounds, therefore the atomization rate „of a hot“ target increases. To calculate the atomization rate, the flux densities of substances resulting from evaporation and atomization from the target surface must be used:

$$R = [J_M(1 - \theta_t) + J_C\theta_t]A_t, \quad (6)$$

where J_M and J_C — total flux densities of atomized metal atoms and compound molecules, as well as substances arising during evaporation. The simulation results allowed us to determine that the atomization rate increases by a factor of 3 when the power density is increased from 0.5 to 1 kW/cm², and — by a factor of 8.5 when it is increased to 1.5 kW/cm². Further increases in power density can lead to overheating of the atomized target, its destruction and failure of the magnetron atomization system.

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Conflict of interest

The authors declare that they have no conflict of interest.

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