

# Modeling of reactive sputtering and evaporation in a hot-target magnetron discharge

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**Abstract.** We theoretically consider the joint influence of hot-target effects and the pulsed nature of the discharge on the state of the target surface. We enhance the previously modified time-dependent Berg model by taking into account the evaporation of target material as well as the influence of target temperature on the rate of chemical reactions on its surface. The system of equations describes the state of the target in terms of poisoned area fractions  $\theta_1$  and  $\theta_2$ , where index 1 corresponds to the monoatomic surface layer, and index 2 – to the layer beneath the surface (subsurface layer). The processes of chemisorption on target surface, sputtering of reactive gas atoms from target, implantation of reactive gas ions to the sub-surface layer, material evaporation, and transfer between the layers are considered. A separate equation connects the atomic fluxes of reactive gas associated with target and substrate surfaces with the volumetric characteristics, such as gas injection rate and pumping speed. The system of equations is solved numerically, and test results are presented.

**Keywords:** reactive magnetron sputtering, evaporation, target poisoning, hot-target magnetron.

## 1. Introduction

The processes of obtaining oxide and nitride coatings in magnetron sputtering systems are associated with known effects of complex nonlinear and often unstable behavior of the deposition rate and film stoichiometry depending on the reactive gas flow. Controllability and productivity of such processes can be largely improved through modification of existing technologies and the development of new approaches. In particular, one can find evidences of a positive effect that a high temperature of a magnetron target has on the stability of the characteristics of the reactive sputtering process [1]. On the other hand, a number of scientific groups have been actively studying reactive deposition of oxides and nitrides in the high-power pulsed magnetron discharges (see, e.g., [2] and references therein), and have found favorable effects of high-power pulses on the controllability of the process.

Theoretical description of reactive magnetron sputtering process was given in a number of seminal papers [2–4], and reliable calculations can be made using these models. However, none of the existing models takes into account both time-dependent nature of pulsed discharge parameters and the target surface poisoning and heating effects. We therefore aim at developing such an extended model that could eventually be applied to predict the properties of hot-target reactive HiPIMS discharge modes.

## 2. Model construction

To build the model, we adapt the same main assumptions and the general approach that we previously used to describe the reactive MPPMS discharge [5]. In its turn, they were largely based on the original steady-state Berg model [3]. The concept is to write the equations for poisoned area fractions  $\theta_i$  of target and substrate surfaces ( $i = 1$  for monoatomic target surface layer,  $i = 2$  for the layer beneath the surface (subsurface layer), and  $i = 3$  for substrate surface) and the balance equation for reactive gas species flow in vacuum chamber. Here, we consider the change of poisoned area fractions due to processes of chemisorption on target and substrate surfaces (index “chem”), sputtering of reactive gas atoms from target (index “sput”), implantation of reactive gas ions into the sub-surface layer (index “impl”), target material evaporation (index “evap-m”), evaporation of compound species from target (index “evap-c”), knock-in events with reactive gas atoms (index “k”) and their backward transfer between the target layers (index “tr”). In these terms, the system of equations is

$$\dot{\theta}_1 = \dot{\theta}_1^{\text{chem}} - \dot{\theta}_1^{\text{sput}} - \dot{\theta}_1^{\text{k}} - \dot{\theta}_1^{\text{evap-c}} + \dot{\theta}_1^{\text{evap-m}} + \dot{\theta}_1^{\text{tr}}, \quad (1)$$

$$\dot{\theta}_2 = \dot{\theta}_2^{\text{impl}} + \dot{\theta}_1^{\text{k}} - \dot{\theta}_1^{\text{tr}}, \quad (2)$$

$$p_{\text{atm}} q = \left( \dot{\theta}_1^{\text{chem}} A_t + \dot{\theta}_3^{\text{chem}} A_s - \dot{\theta}_1^{\text{sput}} A_t - \dot{\theta}_1^{\text{tr}} A_t + \dot{\theta}_2^{\text{impl}} A_t \right) \frac{\xi}{A_{\text{cell}}} + pS, \quad (3)$$

where  $p_{\text{atm}}$  – atmospheric pressure,  $\xi = V_M p_{\text{atm}} / N_A$  – conversion factor to express flow rate in  $\text{Pa} \times \text{m}^3/\text{s}$  ( $V_M$  – volume of one mole of gas,  $N_A$  – Avogadro constant),  $A_t$  – target surface area,  $A_s$  – substrate surface area,  $A_{\text{cell}} = K \times (M/\rho N_A)^{2/3}$  is the effective area occupied by a single metal atom of target surface ( $K$  – fit parameter that depends on the surface state,  $M$  – molar mass,  $\rho$  – density),  $p$  – reactive gas pressure  $S$  – pumping speed.

Eq. (1) describes the poisoning state of the target surface. Eq. (2) describes the situation in the subsurface layer. The balance of reactive gas atoms supplied to the chamber is determined by Eq. (3).

The terms in the right parts of Eqs. (1–3) describing the processes that take into account the temperature effects are written in the following forms:

- $\dot{\theta}_1^{\text{chem}} = k[T_t] v[T_t]^{2m} (1 - \theta_1) A_{\text{cell}}$  — describes chemical reaction on the target surface;
- $\dot{\theta}_3^{\text{chem}} = k[T_s] v[T_s]^{2m} (1 - \theta_3) A_{\text{cell}}$  — describes chemical reaction on the substrate surface;
- $\dot{\theta}_1^{\text{sput}} = \frac{j}{e} \gamma_c \theta_1 A_{\text{cell}}$  — describes reactive gas species sputtering from the target surface;
- $\dot{\theta}_1^{\text{k}} = \frac{1}{Z} \frac{j}{e} \gamma_k d \theta_1$  — describes knock-in of reactive gas atoms from surface to subsurface layer;
- $\dot{\theta}_1^{\text{evap-c}} = \frac{10^{A_c - B_c/T_t}}{\sqrt{2\pi m_c k_B T_t}} (1 - \theta_1)(1 - \theta_2) A_{\text{cell}}$  — describes evaporation of compound species from target;

target;

- $\dot{\theta}_1^{\text{evap-m}} = \frac{10^{A_m - B_m/T_t}}{\sqrt{2\pi m_m k_B T_t}} (1 - \theta_1) \theta_2 A_{\text{cell}}$  — describes evaporation of target material species;
- $\dot{\theta}_1^{\text{tr}} = \frac{1}{Z} \frac{j}{e} \theta_2 (\gamma_{\text{mm}} (1 - \theta_1) + \gamma_{\text{mc}} \theta_1) A_{\text{cell}}$  — describes transfer of reactive gas atoms between layers.

layers.

In the equations above  $T_t$  – target temperature,  $T_s$  – substrate temperature,  $k[T_t]$  is the rate coefficient of chemical reaction on the target surface,  $v[T_t]$  is the target surface fraction covered by physically adsorbed reactive gas,  $k[T_s]$  is the rate coefficient of chemical reaction on the substrate surface,  $v[T_s]$  is the substrate surface fraction covered by physically adsorbed reactive gas,  $j$  – ion current density,  $p$  – reactive gas pressure,  $\gamma_c$  – partial sputter yield of gas atoms from compound,  $\gamma_{\text{mc}}$  – partial sputter yield of metal atoms from compound,  $\gamma_{\text{mm}}$  – sputter yield of metal atoms from metal surface,  $\gamma_k$  – knock-in yield,  $e$  – elementary charge,  $k_B$  – Boltzmann constant,  $m_c$  – mass of compound molecule,  $m_m$  – mass of target material atom,  $A_c$ ,  $B_c$ ,  $A_m$ ,  $B_m$  – constants. In (1–3) we also introduced stoichiometry factor  $Z$  that indicates the number of reactive gas atoms to form an oxide molecule.

This modified time-dependent model was used to calculate the reactive sputtering parameters under the conditions relevant to our experiments.

To simulate the onset of a pulsed discharge, we used comparatively slow introduction of reactive gas, and nearly instantaneous switching on the ion current. The adopted discharge current and reactive gas flow shapes in time are presented in Fig.1.

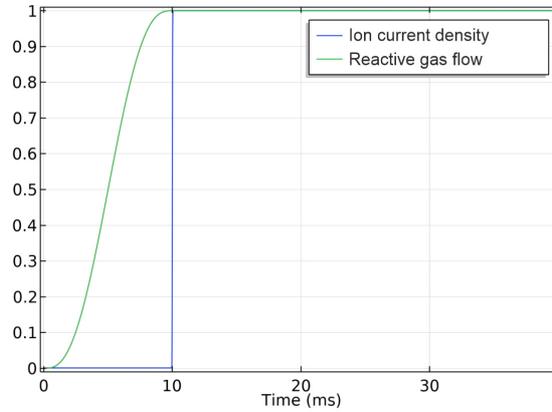


Fig.1. Normalized discharge current and reactive gas flow shapes used in calculations.

### 3. Numerical calculation results

All simulations were made in COMSOL Multiphysics software. When solving the numerical model, a limitation was imposed on the maximum value of the time differentiation step in the form:  $dt \ll e/(jA_{\text{cell}})$ . Such a limitation does not allow the situation when one cell is simultaneously bombarded by two ions (otherwise, for example, the event of double sputtering of a single atom would be possible). It appeared that a very prominent effect on the results is made by initial state of target surface subsurface layer ( $\theta_2$ ) as it serves as an additional reactive gas supply. The results for initially clean target subsurface ( $\theta_2 = 0$ ) are shown in Fig.2. Fig.2a shows the time evolution of surface poisoning fractions and reactive gas pressure in Pa. In Fig.2b, the main processes associated with reactive atom production and removal from the vacuum chamber are compared.

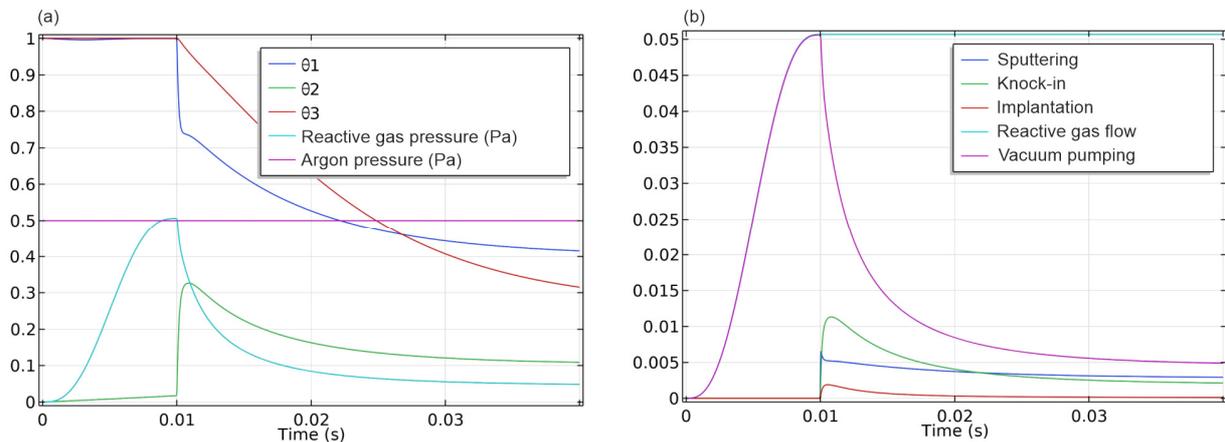


Fig.2. (a) Time dependences of poisoned fractions and reactive gas pressure. For comparison, the constant argon pressure level is shown. (b) Time dependences of relative fluxes of reactive species produced by different processes. Initial condition  $\theta_2 = 0$ .

The pulse shape correlates with the sharp changes in poisoned fraction curves. At  $\theta_2 = 0$ , gas absorption due to the implantation of highly ionized gas is observed.

The results for initially poisoned target subsurface ( $\theta_2 = 1$ ) are shown in Fig.3. Here, on the contrary, a sharp overshoot in the flow of the reactive gas from the target (and in the pressure of the reactive gas in the chamber) is observed.

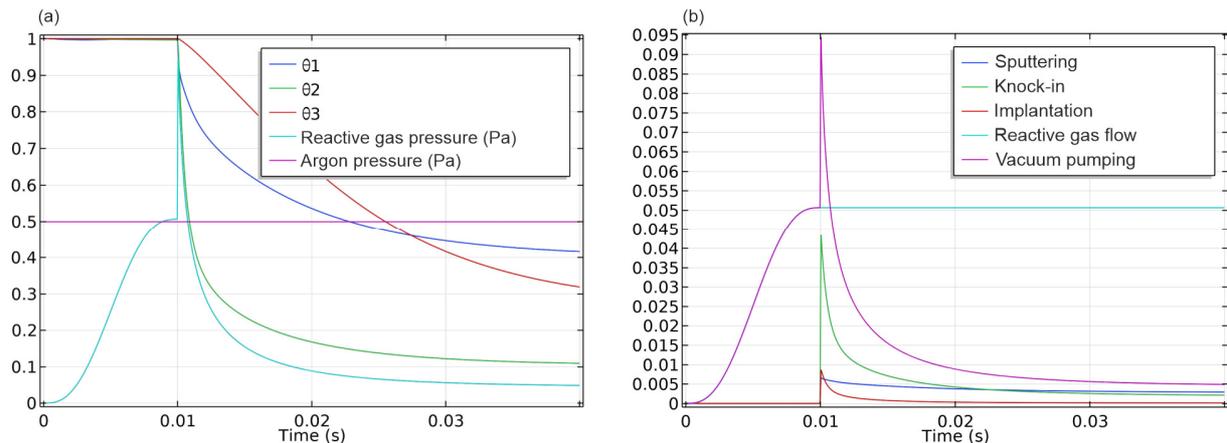


Fig.3. (a) Time dependences of poisoned fractions and reactive gas pressure. For comparison, the constant argon pressure level is shown. (b) Time dependencies of relative fluxes of reactive species produced by different processes. Initial condition  $\theta_2 = 1$ .

The initial chemical state of the subsurface layer has a great influence on the chemical reaction rate, especially at durations up to several milliseconds, which covers the entire range of HiPIMS discharges. Thus, when considering the features of short high-current pulses, it is especially important to choose the correct initial conditions. They can be determined by simulating a train of repetitive pulses. In this case, experimental verification and refinement of the coefficients used in the model are required.

#### 4. Conclusion

Known approaches to model the reactive sputtering process were enhanced by taking into account the temporal evolution of discharge current and thermal insulation of the target. Resulting system of equations can be solved numerically, e.g. using COMSOL Multiphysics software. The model predicts strong influence of initial poisoning conditions on the behavior of sputtering process. A solid set of experiments is needed to evaluate the coefficients used in the equations.

There are, however, phenomena relevant to hot-target magnetrons that were not included in the model. Specifically, partial melting of the target can be observed with the remaining of the solid top layer. We also plan to consider the direction of ejection of the reactive gas atoms from the subsurface layer, which could accelerate the surface poisoning. The model can be improved by considering the spatial distribution of the ion current density on the target surface, as well.

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#### 5. References

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