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Reactive Magnetron Sputtering Control Based on an Analytical Condition of Stoichiometry

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Abstract: The conditions for stoichiometric thin film deposition by reactive magnetron sputtering include the existence of a given ratio between the flux of the sputtered metallic atoms and the flux of the reactive gas molecules on the surface of the substrate. To meet this condition, a relationship based on the Berg model is formulated between the partial pressure of the reactive gas, the target coverage, and the sputtering current density. Given that the target coverage can be estimated online from the sputtering voltage, it is possible to create a control structure where the reactive gas partial pressure is controlled to obtain stoichiometric thin film deposition. Simulation results are presented based on the dynamic model of the sputtering process.

Keywords: Reactive magnetron sputtering, Berg model, state estimation, stoichiometry control.

1. Introduction

Reactive Magnetron Sputtering is the process in which a special thin coating layer is formed on a substrate to enhance its mechanical, chemical, and optical properties. During the process, noble gas ions bombard the surface of a target material that together with the applied reactive gas forms the coating compound. This is achieved by applying a negative potential to the target and by placing strong magnets behind it, in order to facilitate higher rate of noble gas ionization.

Amongst many beneficial thin film layers is the photocatalyst titania (TiO_2, rutile and anatase) which is obtained by sputtering Titanium in an Argon and Oxygen mixture in high vacuum conditions, typically at a pressure of fractions of Pascals [1]. TiO_2 is a highly preferred coating material due to its special optical characteristics and biocompatibility [2]. With its relatively high refractive index of 2.6 [3] and its good transparency to visible light it is suitable for dielectric interference filters [8].

In a multilayer configuration with SiO_2, it forms an effective antireflective coating. This multilayer combination has recently been used to coat Starlink satellites from SpaceX in order to minimize their reflection of sunlight, which had an unwelcome effect in astronomical observations [4].

These special characteristics can only be obtained if the deposited film is stoichiometric, meaning that there is an exact ratio of gas-to-metal during oxide formation. One way to obtain this is by sputtering in the poisoned mode, where the target surface is completely covered with a layer of compound, which is sputtered and delivered to the substrate surface. If higher sputtering rates are required, sputtering in the metallic mode is needed, where the metallic target particles are sputtered and they either react with the reactive gas on their way to, or once they arrive to the substrate surface. Sputtering in the transition mode is also possible but given the highly unstable nature of the process in this mode, feedback control has to be employed i.e. in the form of partial pressure control, or Plasma Emission Monitoring (PEM) [5].

As observed in [6] attention has to be paid to the distance between the target and the substrate in order to facilitate both the sputtering of metal from the target, as well as the formation of oxides on the substrate. This has been shown to be a criterion for stoichiometric deposition of the oxides of titanium.

Determination of the substrate composition is possible with the help of different ex-situ techniques that can be applied only after film formation. These Techniques include Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffraction (XRD), and X-Ray Photoelectron Spectroscopy (XPS) [8].

This paper focuses on a mathematical approach to determining the target coverage during sputtering in an online manner, to facilitate substrate coverage and stoichiometry control.

The following notation has been applied in the paper:

e- the electron charge ($1.6 \cdot 10^{-19}$ $[C]$);

R – ideal gas constant (8314 $\left[\frac{J}{kmolK}\right]$);

N_A – Avogadro's number ($6.023 \cdot 10^{26}$ $\left[\frac{1}{kmol}\right]$);

m_G- mass of the reactive gas molecule $[kg]$ (for O_2, $m_G = 32$ $[\mathrm{a.u.}] =$
$= 32 * 1.66 \cdot 10^{-27} [kg]$);

$k_B = 1.38 \cdot 10^{-23}$ $\left[\frac{J}{K}\right]$ - the Boltzmann constant;

T – the absolute temperature ($T = 300$ $[°K]$);

n_{GG} – the number of reactive gas atoms in a gas molecule ($n_{GG} = 2$ in case of the Oxygen);

n_{GM} – the number of reactive gas atoms in a compound molecule ($n_{GM} = 2$ in case of the TiO_2);

K_{sto} - the ratio of reactive gas molecules to metallic atoms needed to form the compound ($K_{sto} = 1$ in case of TiO_2);
V – the volume of the sputtering chamber $[m^3]$. ($V = 0.08\ [m^3]$);
p_G- the partial pressure of the reactive gas (O_2) in the sputtering chamber;
F_G- flux density of the reactive gas molecules (O_2) on the surfaces inside the sputtering chamber;
F_{IT}- flux density of the sputtering ions on the surface of the target (mainly Ar^+);
F_{MS}- flux density of sputtered metal atoms on the surface of the substrate;
θ_T- target coverage i.e. the fraction of the target surface covered by compound molecules;
θ_S- substrate coverage i.e. the fraction of the substrate area covered by compound molecules;
θ_C- the fraction of the condensation area corresponding to the wall of the sputtering chamber covered by compound molecules;
q_{in}- mass flow of the input reactive gas $\left[\frac{kg}{s}\right]$;
q_p- pumping mass flow of the vacuum pump $\left[\frac{kg}{s}\right]$;
A_T- the target area ($A_T = 3600 \cdot 10^{-6}\ [m^2]$);
A_C- the condensation area ($A_C = 16800 \cdot 10^{-6}\ [m^2]$);
A_S- the substrate area ($A_S = 600 \cdot 10^{-6}\ [m^2]$);
η_M- sputtering yield (efficiency) of the metal (number of Ti atoms sputtered by an incident Ar^+ion) ($\eta_M = 0.5$) [7];
η_{MG}- sputtering yield of the metal-gas compound (TiO_2) i.e. the number of compound molecules sputtered by one Ar^+ ion ($\eta_{MG} = 0.017$) [7];
α_{GT}, α_{GS}- sticking coefficients of the O_2 molecule to the metallic fraction of the target and to the metallic fraction of the substrate, respectively (the probability that the atoms of a reactive gas molecule reaching the metallic surface, are trapped in a metal-gas compound molecule) ($\alpha_{GT} = \alpha_{GS} = 1$) [7];
α_{GC} gettering efficiency of the sputtering chamber's surface (of the area covered by sputtered Ti atoms) ($\alpha_{GC} = 0.8$);
N_G- the surface density of the reactive gas atoms trapped within the compound molecules; (in our particular case the simulations have been carried out with a value of $N_G = 19.4 \cdot 10^{18}\ \left[\frac{atoms}{m^2}\right]$, based on the surface density of the compound molecules of $N_{TiO_2} = 9.7 \cdot 10^{18}\ \left[\frac{molecules}{m^2}\right]$ [8];)
I_d –the intensity of the discharge current;
J- the discharge current density on the surface of the target;
$Y_{SEE,M}$ – ion induced secondary electron emission yield of the metal (Ti) ($Y_{SEE,M} =$
$= 0.114$) [9];
$Y_{SEE,MG}$ – ion induced secondary electron emission yield of the surface covered with metal-gas compound (TiO_2) ($Y_{SEE,MG} = 0.08$ [10], [11]);

2. Analytical study of the conditions needed for stoichiometric sputtering

As mentioned in [6] the production of stoichiometric films on the substrate supposes a controlled ratio of incoming metallic and reactive gas particle fluxes. Assuming a Maxwellian velocity distribution, the flux density of the reactive gas molecules on any surface inside the sputtering chamber depends on the partial pressure p of the reactive gas according to the well-known relation [12].

$$F_G = \frac{p_G}{\sqrt{2\pi m_G k_B T}} \tag{1}$$

In a simplified approach, we assume that the flux F_{MS} of the metal atoms on the substrate surface is proportional to the flux of the metal atoms outsputtered from the target surface and to the ratio of the condensation and target surface areas. Here, the condensation surface A_C is introduced as a surface at the distance of the substrate from the target, delimited by the solid angle defined by the jet of outsputtered metallic atoms.

The desired ratio of these flux densities can be formulated as

$$\alpha_{GS}(n_{GG}F_G) = F_{MS}K_{sto} \tag{2}$$

The condition of stoichiometry in case of TiO_2 is $K_{sto} = 1$.

This yields the following condition

$$n_{GG}\alpha_{GS}\frac{p_G}{\sqrt{2\pi m_G k_B T}}A_C = F_{IT}\eta_M(1-\theta_T)A_T K_{Sto}. \tag{3}$$

This can further be rearranged to

$$p_G = \frac{1}{n_{GG}\alpha_{GS}}F_{IT}\eta_M(1-\theta_T)\frac{A_T}{A_C}K_{Sto}\sqrt{2\pi m_G k_B T}. \tag{4}$$

The target coverage θ_T is a state variable of the reactive magnetron sputtering process, the dynamic model of which can be formulated as:

$$\begin{cases} \frac{dp_G}{dt} = \frac{R\cdot T}{N_A\cdot m_G\cdot V}(q_{in} - q_p - \\ -m_G(\alpha_{GT}F_G(1-\theta_T)A_T + \alpha_{GC}F_G(1-\theta_C)(A_C - A_S) + \alpha_{GS}F_G(1-\theta_S)A_S)) \\ \frac{d\theta_T}{dt} = \frac{1}{N_G}(n_{GG}\alpha_{GT}F_G(1-\theta_T) - F_{IT}\eta_{MG}\theta_T) \\ \frac{d\theta_S}{dt} = \frac{1}{N_G}\left\{F_{IT}\left(\frac{A_T}{A_C}\right)[\eta_{MG}\theta_T(1-\theta_S) - \eta_M\theta_S(1-\theta_T)] + n_{GG}\alpha_{GS}F_G(1-\theta_S)\right\} \\ \frac{d\theta_C}{dt} = \frac{1}{N_G}\left\{F_{IT}\left(\frac{A_T}{A_C}\right)[\eta_{MG}\theta_T(1-\theta_C) - \eta_M\theta_C(1-\theta_T)] + n_{GG}\alpha_{GC}F_G(1-\theta_C)\right\} \end{cases} \tag{5}$$

This system is similar to [13], [14], but the substrate and condensation surface coverages are handled as separate state variables from the consideration that the conditions of bond formation on the substrate are different from the conditions on the wall of the chamber.

Thus, the state vector is defined as:

$$\boldsymbol{x} = [p_G, \theta_T, \theta_S, \theta_C]' \tag{6}$$

In order to determine the partial pressure of the reactive gas that satisfies the condition (4) of stoichiometry, the target coverage estimation can rely on the above dynamic model, or as a simplified approach, can be based on the discharge voltage measurement, as presented in Chapter 4.

In steady state the desired operating point can be determined using the Berg model [12].

$$\begin{cases} q_{in} - q_p - -m_G(\alpha_{GT} F_G (1-\theta_T) A_T + \\ +\alpha_{GC} F_G (1-\theta_C)(A_C - A_S) + \alpha_{GS} F_G (1-\theta_S) A_S) = 0 \\ n_{GG} \alpha_{GT} F_G (1-\theta_T) - F_{IT} \eta_{MG} \theta_T = 0 \\ F_{IT} \left(\frac{A_T}{A_C}\right) [\eta_{MG} \theta_T (1-\theta_S) - \eta_M \theta_S (1-\theta_T)] + \\ +n_{GG} \alpha_{GS} F_G (1-\theta_S) = 0 \\ F_{IT} \left(\frac{A_T}{A_C}\right) [\eta_{MG} \theta_T (1-\theta_C) - \eta_M \theta_C (1-\theta_T)] + \\ +n_{GG} \alpha_{GC} F_G (1-\theta_C) = 0 \end{cases} \tag{7}$$

Compared to [12], (7) is modified as mentioned for the dynamic model, but this has no influence on the relation between the target coverage and the partial pressure.

Thus, from the second equation of (7) it results:

$$\theta_T = \frac{n_{GG} \alpha_{GT} F_G}{n_{GG} \alpha_{GT} F_G + F_{IT} \eta_{MG}}. \tag{8}$$

The reactive gas flux density F_G is given in (1) versus the partial pressure, while for determining the sputtering ion flux density we'll consider two approaches.

In a simplified version,

$$F_{IT} \cong \frac{J}{e} = \frac{I_d}{A_T e}, \tag{9}$$

where the discharge current is an easily measurable quantity.

In a more accurate approach, the current due to the ion induced secondary electron emission, and thus the effect of the target coverage, is taken into account.

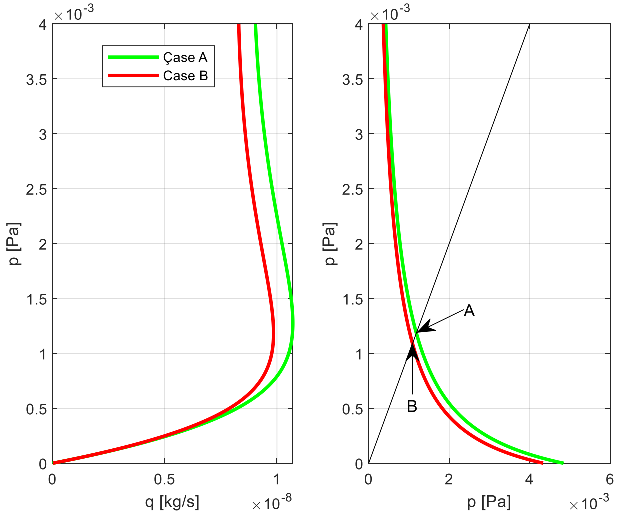
According to [15],

$$F_{IT} = \frac{J}{e} \frac{1}{1 + Y_{SEE,M}(1-\theta_T) + Y_{SEE,MG} \theta_T} \tag{10}$$

Hence, by substituting (10) into the second equation of (7), it results

$$\left(Y_{SEE,M} - Y_{SEE,MG}\right)\theta_T^2 + \left(Y_{SEE,MG} - 2Y_{SEE,M} - 1 - \frac{J}{e}\frac{\eta_{MG}}{n_{GG}\alpha_{GT}F_G}\right)\theta_T + \left(1 + Y_{SEE,M}\right) = 0 \qquad (11)$$

Fig. 1 shows a numerical example for the compound TiO_2 ($I_d = 0.7\ [A]$, $J = \frac{I_d}{A_t} = 194.4\ \left[\frac{A}{m^2}\right]$, $\eta_M = 0.5$, $\eta_{MG} = 0.017$). Right- and left-hand sides of (4) are plotted taking into account both versions (9) and (10). Thus, the partial pressure at which the ratio of sputtered metallic and reactive gas particles corresponds to stoichiometry can be determined by the intersection of these curves. It can be noticed that this pressure corresponds to a location on the p-q curve that is very close to the tipping point, where the target tips over to the poisoned state in case of increasing reactive gas flow.



a.) b.)

Figure 1: a.) The p-q characteristics of the system modelled in case *A* using (9) and in case *B* using (10)
b.) The graphical solution of (4) in the cases corresponding to (9) and (10)

Since the outsputtered metallic flux from the target, and the reactive gas flux reaching the substrate can be influenced by p and J, it can be assumed that the conditions needed for stoichiometry on the substrate surface can be reached by controlling the target conditions. For this to work, a way of determining and controlling the target coverage is needed. These tasks are covered in Chapter 3 and 4.

3. Target coverage control by manipulating the reactive gas partial pressure

For a given sputtering ion flux density F_{IT}, the relationship between the partial pressure of the reactive gas and target coverage can be found by inserting (1) into (9).

$$\theta_T = \frac{n_{GG}\alpha_{GT}\frac{p_G}{\sqrt{2\pi m_G k_B T}}}{n_{GG}\alpha_{GT}\frac{p_G}{\sqrt{2\pi m_G k_B T}} + F_{IT}\eta_{MG}}, \tag{12}$$

where we assume that F_{IT} is controlled by means of the discharge current in a fast control loop.

It can be seen in *Fig. 2* that the relationship (12) is a monotonic one. This means that the partial pressure can be used to directly influence the target coverage.

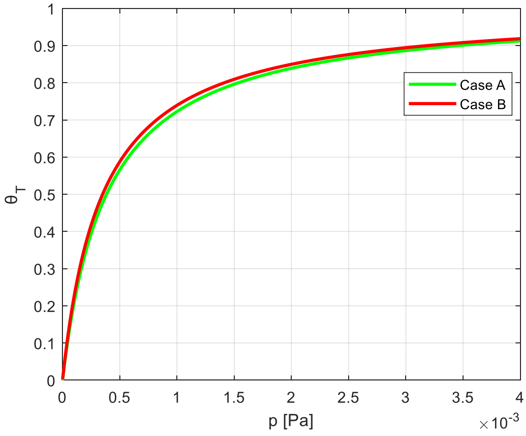


Figure 2: Target coverage as a function of reactive gas partial pressure

Any desired target coverage can be reached by keeping the reactive gas partial pressure at a corresponding value. This of course is only possible with the help of some feedback type control, since not all pressure values can be observed in an open loop manner, due to the hysteresis of the p-q characteristic curve.

4. Target coverage estimation based on the discharge voltage

A method is needed to determine the target coverage in an online manner, so that it can be used for control purposes. Since the target is used as an active electrode, its voltage, i.e. the discharge voltage between the target and the sputtering chamber, can be measured. The target voltage depends on the target conditions, being influenced by the secondary electron emission of the different materials that form the target and are exposed. In [15] a linear dependency of the Y_{SEE} (secondary electron emission yield) on the poisoned $Y_{SEE,MG}$ and metallic $Y_{SEE,M}$ target fractions, has been assumed. This is formulated in (13).

$$Y_{SEE} = Y_{SEE,M}(1 - \theta_T) + Y_{SEE,MG}\theta_T \tag{13}$$

In [10] and [11] the measured discharge voltage of different target materials both in metallic and poisoned mode has been reported. It has been observed, that target electrodes made of Al, Mg, Ce, and Y have lower discharge voltages when they are poisoned, but the opposite is true for the target electrodes made of Ag, Au, Cr, Cu, Nb, Pt, Re, Ta, Ti.

Due to the fact that $U_d \sim \frac{1}{Y_{SEE}}$ [16], Strijckmans [15] rewrites (14) in the following form

$$\frac{1}{U_d} = \frac{1}{U_M}(1 - \theta_T) + \frac{1}{U_{MG}}\theta_T, \tag{14}$$

where U_M and U_{MG} are the discharge voltages at a given discharge current and Ar pressure for a metallic target and a completely poisoned target, respectively. The exact method for determining these voltages is presented in detail in [10] and [11]. This allows for the target coverage to be calculated in an online manner during sputtering by monitoring the target discharge voltage U_d

$$\theta_T = \frac{\frac{1}{U_d(I_d, p_{Ar})} - \frac{1}{U_M(I_d, p_{Ar})}}{\frac{1}{U_{MG}(I_d, p_{Ar})} - \frac{1}{U_M(I_d, p_{Ar})}}. \tag{15}$$

This is further examined by Depla in [16] by testing different targets to see whether the target composition can be figured out from the target voltage. The results show a near exact match between the calculated and measured data. This supports (13), since a pure target partially covered by a compound behaves in the same way as any given surface of a target made of different constituents, given that the alloy is homogeneous.

5. Control structure for stoichiometric thin film deposition

A summary of the goals for a productivity-oriented control structure that can be used to produce films of a given stoichiometry is given below:

1. The controller can keep the system stable, preventing unwanted target poisoning.

2. The controller can manipulate inputs in such way as to reach a prescribed coating speed.
3. The controller can maintain stoichiometric coating of the substrate throughout the entire process.

In US patent 6,106,676 [17] a method for quick poisoning suppression is presented. It employs a cascade-type controller, which manipulates the reactive gas flow and the discharge current. The inner loop controls the partial pressure of the reactive gas by means of the discharge current, since the current controller is much faster than the mass flow controller. The outer, slower loop controls the deposition rate (function of the discharge current) by means of the reactive gas flow. The change of the partial pressure resulting from the manipulation of the gas flow is compensated by the variation of the discharge current.

A slight modification to [17] has been presented in [18], where instead of an optical emission sensor and feedback loop, the partial pressure is the quantity being controlled.

The ideas introduced in Chapters 2, 3, and 4, present a way to influence the condition of stoichiometric deposition by manipulating the partial pressure of the reactive gas. This requires in the control structure a block, which calculates the prescribed p_{Gref} based on the actual target coverage. The proposed control structure can be seen in *Fig. 3*.

The offline parameter identification block is needed to determine the sticking coefficients of the system [8].

In (4) the value of θ_T is needed, which can either be estimated according to the methods presented in (5) and (15).

The controller has been simulated with a current reference input that has a ramp, step transitions, and a constant portion. The results can be seen in *Fig. 4*.

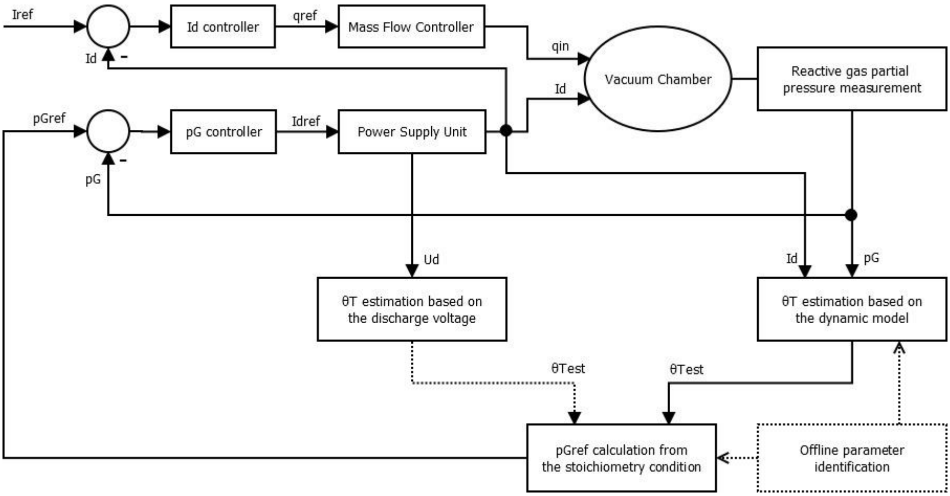


Figure 3: The proposed control structure for stoichiometric sputtering

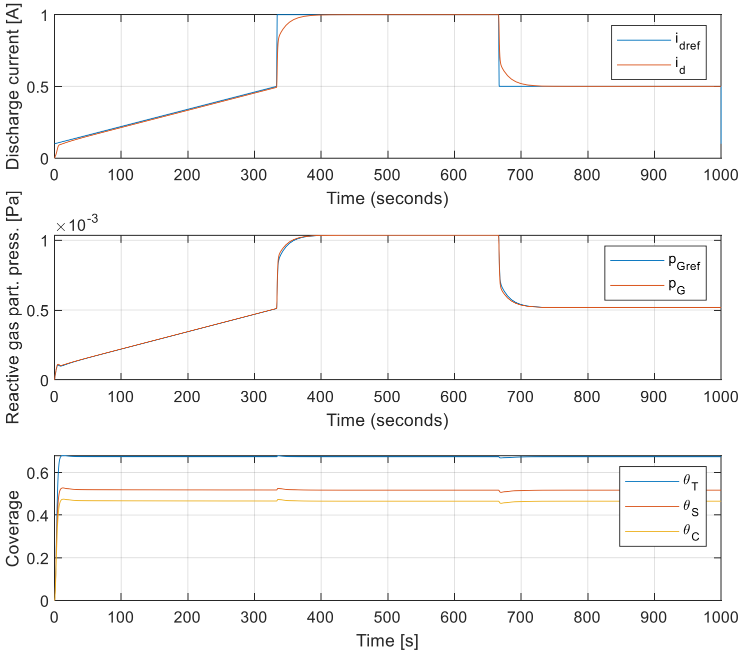


Figure 4: Simulation results obtained using the proposed control structure

6. Conclusions

An analytical study of the conditions needed for stoichiometric layer growth on the substrate surface is presented. It is shown that there is a monotonic relationship between the target coverage and the partial pressure of the reactive gas. Results are gathered from the literature that show that the target voltage, along with state estimation, can be used to calculate the target coverage. Combining these findings, a method is presented that facilitates stoichiometric film growth on the substrate surface.

A control structure employing two control loops is proposed, that can keep the system stable, while controlling the sputtering power, and which leads to stoichiometric film growth on the substrate surface.

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