
Pulsed Mode Reactive Magnetron Sputtering

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Declaration of Authorship

I, **Róbert Rossi MADARÁSZ**, declare that this thesis titled, '*Pulsed Mode Reactive Magnetron Sputtering*' and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
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Abstract

My Doctoral Thesis begins with providing insight into the world of reactive magnetron sputtering, a field that has been extensively studied in the past few decades. The process essentially consists of the removal of material from a target surface and its deposition onto a substrate, forming a special thin coating layer to enhance its mechanical, chemical, and optical characteristics. Material removal is accomplished via high energy noble gas ions which bombard the surface of the target due to a DC electric field. 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. The presence of the reactive gases introduced in the sputtering chamber to influence the composition of the film deposited on the substrate greatly influences the processes on the surface of the target as well.

First, insight into the current state of computational modeling regarding reactive magnetron sputtering systems is provided. A detailed compilation of developed models is gathered and grouped into categories based on the phenomena being modeled. After gaining the necessary insight into the current state of research, the goals are formulated: the need for parameter identification, deeper studies involving formation of stoichiometric films in closed loop controlled systems, practical experiments with power electronics converters

for the pulsed mode discharge process, and behavioral models to facilitate the dimensioning of these. Afterwards, the goals are addressed one by one in the following Chapters.

Offline parameter identification of the Berg model is undertaken and a graphical parameter estimation method is developed using simplified equations that contain only the most significant terms in both metallic and poisoned modes of operation, using approximations that are based on numerical examples. Special experiment conditions are also formulated that better facilitate the identification of the most important model parameters.

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, a control structure has been proposed where the reactive gas partial pressure is controlled to obtain stoichiometric thin film deposition.

A second control structure is proposed for a two-gas reactive magnetron sputtering process, using a model that is suitable for modeling the coverage of the substrate with ternary compounds. Assuming its observability, the ternary compound coverage is controlled by means of the gas flow of oxygen supplied in a continuous fashion, with the oxygen partial pressure limitation dependent on the nitrogen partial pressure. The control characteristics have been derived and the dynamic behavior of the proposed stoichiometry control structure has been simulated based on the parameters of a laboratory sputtering chamber.

Experiments have been carried out to identify the current-voltage characteristics of the vacuum chamber with the supply of different gases, and gas mixtures in the usable pressure domain in order to identify the requirements for the design of a pulsed DC converter that is suitable for the ignition and sustaining of the plasma inside the sputtering chamber. Based on these requirements, a power electronic converter has been built and control routine has been implemented, which together are suitable for plasma ignition and for the control of the discharge current.

A new behavioral model of the magnetron discharge has been proposed that can be used to study the interaction between the pulsed discharge and the driving power electronic converter. The underlying physical phenomena have been investigated based on the literature, and practical measurement results have been qualitatively reproduced by pSpice simulation using the proposed model in case of a pulsed power supply based on inductive energy storage.

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Chapter 1

State of the art

1.1 Introduction

The goal of the survey is to offer a brief insight into the current state and results of different mathematical and computer modeling techniques and approaches used to investigate reactive magnetron sputtering.

Sputtering is a subclass of PVD - Physical Vapor Deposition, which is an essential process in manufacturing integrated circuits, photovoltaic modules, specialized optical and mechanical equipment. It is a process used for the creation of extremely thin (even down to atomic) coating layers on different surfaces in order to achieve better physical, chemical, optical or electrical characteristics than those of the coated material itself. Among others, the use of this technique allows the formation of transparent but also conducting layers, which are essential in optics. The process essentially consists of the removal of material from one or more target surfaces and their deposition onto a surface that is required to have improved characteristics, also known as the substrate. This removal process is accomplished with the help of high energy noble gas ions which bombard the surface of the target due to the presence of an electric field. With the addition of a magnet behind the target one can achieve magnetron sputtering, greatly increasing the ionization efficiency and the sputtering yield.

With the introduction of one or more reactive gases into the vacuum chamber, reactive magnetron sputtering is achieved, which allows the formation of different compounds like oxides and nitrides. Reactive magnetron sputtering has been extensively studied and modeled in the past few decades.

There are several approaches and technologies used for magnetron sputter-

ing, such as DC (direct current) sputtering, pulsed DC sputtering, AC (alternating current) sputtering, HiPIMS (high power impulse magnetron sputtering) and RF (radio frequency) sputtering. All of the different coating techniques mentioned require highly specialized operating environments in order to function correctly. The creation of a high vacuum environment (pressure in the range of a few Pascals) is mandatory. At such low pressures, different metals begin to evaporate, hindering the insertion of any nonspecialized equipment into the sputtering chamber. Simple questions as measuring the total or partial pressure inside the chamber become ever more difficult, requiring special processes to be put in place and the indirect calculation of the desired quantity from the gathered data. In situations like these, the use of a state identification algorithm becomes favored. From the control perspective, the system quickly becomes complex when one simply attempts to count the number of inputs, outputs and their non-linear cross coupled effect on each other. Each of the magnetron sputtering processes sets particular challenges from the point of view of modeling. This Chapter concentrates on gathering and presenting only computer modeling approaches used for DC reactive magnetron sputtering.

Due to the specifics of the environment, the overwhelming amount of process values to which attention has to be paid, the lack of quick and reliable access to measurable data, control of the process becomes complex enough that many laboratory experiments are conducted in an open-loop fashion. Therefore, reliable reproduction of experiments is still nearly impossible.

These constraints have compelled researchers to develop, test and validate complex models of the process. Most of the time, financial reasons are the main driving force behind the need for modeling, especially in industrial applications. The simplest desire that can be placed is the optimization of the process to achieve maximum yield. Another desire, which is far more complex is the achievement of required stoichiometric ratios between the deposited materials on the surface.

This Chapter [68] is structured as follows: Section 1.1 gives a brief introduction to the field of study, Section 1.2 gives an overview of several prominent research results in the field of modeling, Section 1.3 presents the different modeling tasks and challenges, and finally, Section 1.4 outlines directions that are likely to be further pursued.

1.2 Literature survey of modeling approaches

Reactive magnetron sputtering is a complex process with several interacting subprocesses, representing difficult modeling tasks on their own. One of the possible approaches is the development of multi-physics models by coupling the models which describe the plasma, the magnetic field, the transportation phenomena in the chamber, the interaction of particles with the target, the thin film deposition on the substrate, etc. Such a model based on the perfect understanding of the physical phenomena would represent a perfect tool for the industry. However, the feasibility of a "virtual sputter tool" [58] resulting from this bottom-up approach is low, mainly because the level of understanding of different phenomena is not the same, and there will always be a weak element in the chain which might vitiate the overall results. A top-bottom model development, leading to a "holistic model" [58], seems to be more feasible. According to this approach, the development starts from a simplest possible model which describes "well enough" the phenomena of interest, and further on this model suffers extensions according to the necessities to cover other phenomena as well. Contrary to these "white box" approaches, the input-output modeling of the system, which has little to do with the understanding of the details of its physics, can be very useful for control purposes [61].

According to the bottom-up approach, one may study the phenomena that are taking place inside the plasma discharge between charged particles. Such a model must also consider the magnetic field present in the chamber and its effects on the movement of charged particles.

A very intriguing phenomenon that can be modeled is the interaction between particles at the surface level of the target, where collisions either lead to implantation or material removal.

Particle-surface interactions are also studied at the substrate, where the formation of crystallographic structures is analyzed.

The top-bottom approach is represented in this Chapter by the extensions of the Berg model, the simplest one, which can efficiently describe the hysteresis phenomena in case of a single target, single reactive gas magnetron sputtering. These are macroscopic models based on equilibrium equations, and are not more complicated than necessary to reproduce the essential behavior of the system, trying to remain simple enough to facilitate control.

1.2.1 Modeling of magnetron discharges

An electric discharge taking place in vacuum can be divided into the following categories: dark, glow and arc discharge, each with a higher discharge current than the former.

According to Bogaerts et al. [9] there are three types of model categories for plasma discharges:

1. Fluid models, which are modeling species in the discharge as ones being in hydrodynamic equilibrium. The equations that govern are the continuity equations (fluxes and densities of the species) and the Poisson equation for the electric field. The fluid model is considered to be the simplest but also the most inaccurate one.
2. Kinetic models, which describe the plasma species as beams of particles. The movement of particles is described by the Boltzmann transport equations, combined with the Poisson equation.
3. Monte Carlo simulations, that describe the different plasma particles separately on a statistical basis. This is considered to be the most accurate method, but it requires considerable computational effort.

Depla and Mahieu compiled a comprehensive study on modeling the electric discharge in reactive magnetron sputtering [26]. They have grouped models into two main categories i.e. analytical and numerical. They further split numerical into fluid and kinetic ones. In this approach, kinetic types are either based on numerical solutions of the Boltzmann equation or on Monte Carlo simulations, which are also called particle simulations.

Wendt and Lieberman [59, 60] developed a two dimensional analytical model of the discharge process, taking into account both magnetic and electric fields.

Fluid models [14, 22, 23] have also been presented. These models calculate the electric field distribution by coupling the Poisson equation to the continuity and conservation of energy and momentum equations.

The solution of the Boltzmann equation has been widely used for modeling plasma discharges. The addition of the Lorentz force term complicates the solver, as presented by Porokhova et al. in [49, 50, 51].

In Monte Carlo simulations the path of a small number of particles is analyzed, their movement and their collisions being modeled using probabilities and random numbers [53, 29].

Hybrid models have been conceived with the assumption that heavy ions are practically not affected by the magnetic field, as opposed to the relatively

lightweight electrons. Therefore, ions can be modeled by a fluid model and electrons can be modeled as particles. This assumption combines high precision of particle simulation codes with lower computational efforts of fluid codes [52, 35]. Bogaerts et al. have presented several papers modeling the magnetron discharge process using Monte-Carlo and hybrid Monte-Carlo simulations [11, 9, 10, 12].

Particle in Cell-Monte Carlo Collision (PIC-MCC) simulations are considered to be the most powerful available numerical tools. PIC-MCC simulations combine MC methods with the simulation of the electric field being produced by an external power supply and with the spatial distribution of the charged particles in the plasma [8].

1.2.2 Modeling particle-target interaction

When studying particle-target interactions at the surface of the target, one may find in the literature that depending on the kinetic energy and the incident angle of impact, some ions reach the surface and through chemisorption get chemically attached to the outermost layer. Others may effectively transfer their kinetic energy and lead to material removal from the target, and some may be so energetic that they get implanted into the subsurface and stay there until enough material is removed for them to resurface. Depla, Strijckmans and separately Kubart extended existing models by also considering chemisorption, knock-on yield, ion implantation, redeposition and reaction rate, leading to far more accurate but also far more complex models [25, 27, 56, 57, 36, 6].

According to [48] Monte Carlo type simulation codes, which have been proven to be the most effective, have the following major components:

1. the cross-section data for all processes being considered,
2. the algorithms used for the particle transport,
3. the methods used for geometry representation and to handle particle passage through volumes,
4. the methods to determine quantities of interest and analysis of the information obtained during the simulation.

Such an example is TRIM, which is a Monte Carlo computer program that calculates the interactions of energetic ions with amorphous targets (see Fig. 1.1). SRIM is a collection of software packages that calculate many features

of the transport of ions in matter (see Fig. 1.2). Both programs were developed and are maintained by [James F. Ziegler](http://www.srim.org/) and can be downloaded from <http://www.srim.org/>.

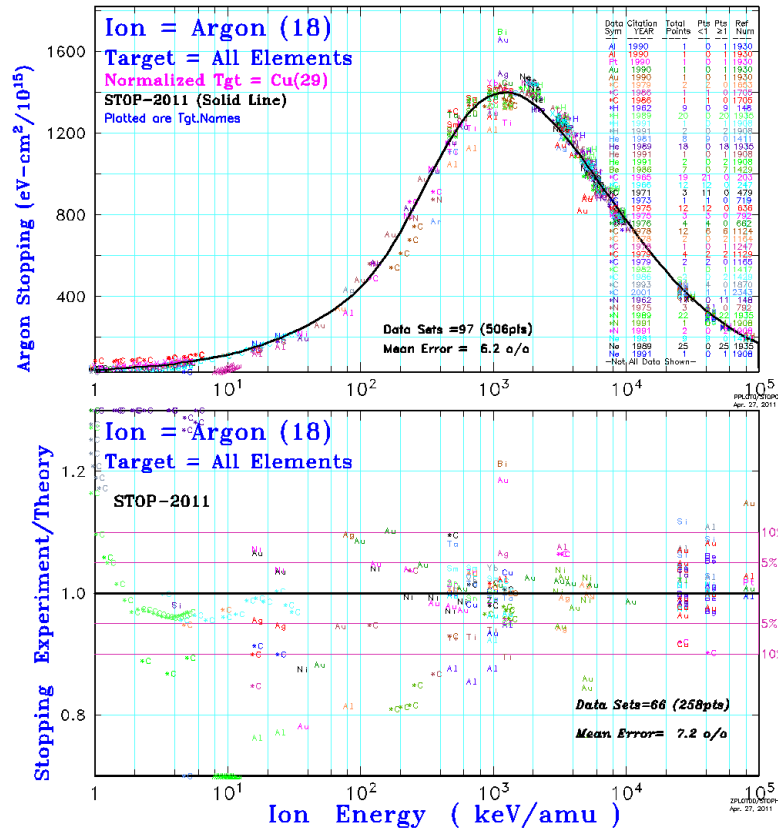


Figure 1.1: Application example of the TRIM program. Stopping range as a function of accelerated Argon ion energies using different targets; comparison of historically measured and simulated data (from <http://www.srim.org/>).

Other MC based simulation packages are TRIDYN [44, 45], KALYPSO [32] and ACAT [67]. A comprehensive compilation and review of many other simulation codes for surface-ion interactions can be found in Chapter 1.2 of [26].

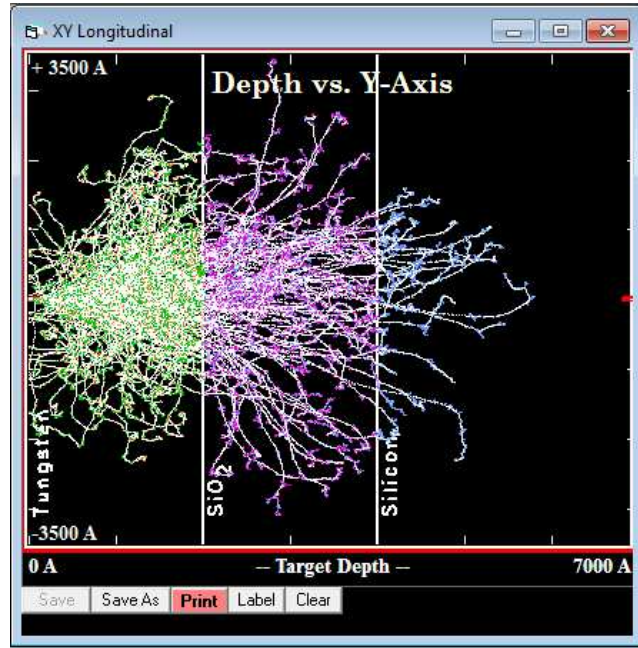


Figure 1.2: Application example of the SRIM program. Simulation of implantation depth of Boron ions into a multilayered W/SiO₂/Silicon target using SRIM-2013.00 software (from <http://www.srim.org/>).

1.2.3 Modeling crystal formation on the substrate surface

Modeling the growth of the deposited layer on the substrate is one of the most complex aspects of modeling the sputtering process. The set of particles arriving at the substrate include not only outspattered particles from the target, but also electrons, gas ions and neutrals [26]. The incoming particles either settle at the surface by forming chemical bonds depending on the sticking coefficient of the atomic pair in discussion, or they migrate on the surface until they reach a large enough crystal lump where they can take part in crystal formation on the grain boundary [30]. Because of this, the formation of a large area, even layer is not too common, rather ragged microstructures are formed [47]. The modeling of such microstructures is essential for example in the fabrication of microelectronics, where one may want to fill a narrow trench or via. In [7] the formation of some crystal structures is predicted based on operating conditions.

An example software is SiMTra, which is a binary collision Monte Carlo pro-

gram (see Fig. 1.3) that allows the user to simulate the transport of sputtered particles through the gas phase flux during sputtering.

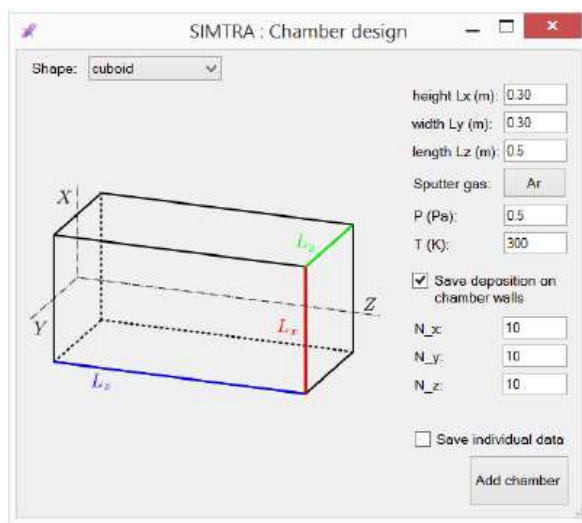


Figure 1.3: An input dialog screen of the SIMTRA software package used to configure the simulation setup (from <http://www.draft.ugent.be/>).

1.2.4 Macroscopic modeling of the reactive sputtering process

Similarly to those described in the previous sections, it is obvious that one must find a balance between complex accurate modeling and simple straightforward usability when developing a model. Berg et al. developed a model that found a balance between simplifications whilst still being accurate enough to predict outcomes of experiments [3, 5, 4]. This model is commonly referred to in the literature as "Berg's Model". The model was constructed by focusing on the equilibrium equations, studying independent contributions to different quantities used to describe the process (see Figure 1.4). The main area where this model proved to be more successful than others is in the modeling of the hysteresis behavior. There have been a number of models [31, 1, 54] developed before Berg's Model that had problems reproducing the hysteresis behavior.

Berg employed variables θ_i to denote the coverage of the surfaces of interest (target and substrate) with compound molecules (the normalized amount of reacted surface area). The coverage takes values in the interval of $[0, 1]$, where a value of 1 denotes a fully covered surface. This model is a monolayer surface

model which only considers a chemisorption mechanism on the target (and substrate) surfaces. No redeposition can be considered.

The equation that defines the balance between supply and consumption of the reactive gas is given in Eq. (1.1), with the definitions of gas consumption on the surface of the target Q_t in Eq. (1.2), gas consumption on the surface of the substrate Q_c in Eq. (1.3) and of pumping flow Q_p in Eq. (1.4). The supply and usage of reactive gas is also presented in Fig. 1.4. The sticking coefficients are denoted with α , the flux of reactive gas atoms with F and the corresponding areas of the studied surfaces with A . S represents the pumping speed while P represents the partial pressure.

$$Q_{\text{tot}} = Q_t + Q_c + Q_p \quad (1.1)$$

$$Q_t = \alpha F(1 - \theta_t)A_t \quad (1.2)$$

$$Q_c = \alpha F(1 - \theta_c)A_c \quad (1.3)$$

$$Q_p = SP \quad (1.4)$$

The balance equations describing the interactions on the target and substrate surface are given in Eq. (1.5) and (1.6), respectively. The outspattered compound F_c and metallic F_m flux is given in Eq. (1.7) and (1.8), respectively. Y denotes the sputtering yield, q is the electron charge and J denotes the ion current density of the background gas. Equations (1.1-1.8) have been presented in this form in [26].

$$\frac{J}{q}Y_c\theta_t = \alpha 2F(1 - \theta_t) \quad (1.5)$$

$$F_c(1 - \theta_c) + 2Q_c = F_m\theta_c \quad (1.6)$$

$$F_c = \frac{J}{q}Y_c\theta_tA_t \quad (1.7)$$

$$F_m = \frac{J}{q}Y_m(1 - \theta_t)A_t \quad (1.8)$$

Due to the reactive gas poisoning of the target, a process that tends to reduce the sputtering yield, a hysteresis can be observed due to the positive

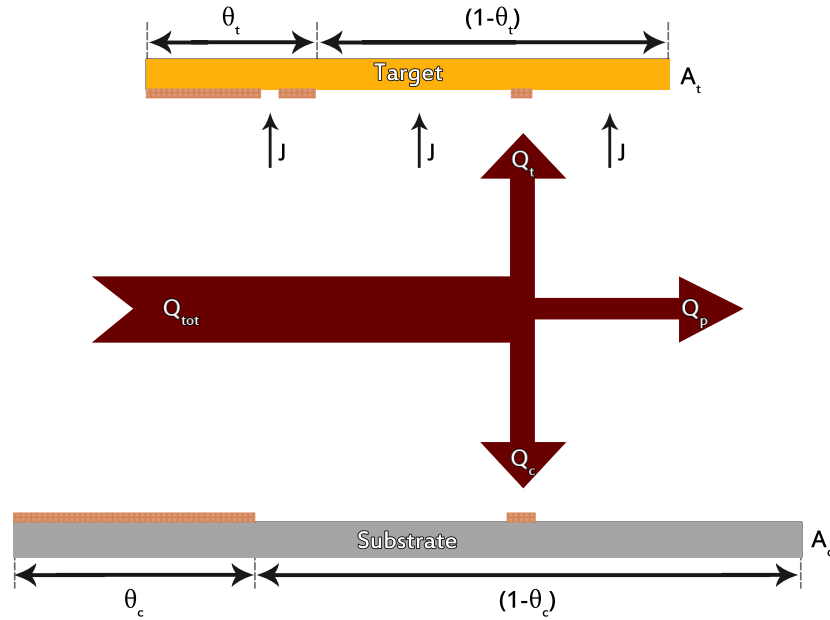


Figure 1.4: The supply and consumption of reactive gas during sputtering [5].

feedback between the partial pressure of the reactive gas and the target surface coverage (see Fig. 1.5). Since the publication of the Berg model, several extensions based on equilibrium equations have been developed in order to include modeling of multiple targets, multiple reactive gases, ion implantation, particle redeposition, multiple deposited layers, deposition of multiple compounds, spatial resolution and dynamics of phenomena, etc.

Given that many times the formation of complex films is required, which in turn require more than one reactive gas, Carlsson et al. further developed the model to work with two reactive gases as inputs, though only considering binary compounds as result of the interaction processes [15].

The research group named **DRAFT**, led by Diederik Depla, made their work of more than a decade available free of charge as a downloadable package from their university website <http://www.draft.ugent.be/>. The package contains their model named RSD2013 and it also comes with a detailed PDF guide to help the researcher quickly get started. The package also includes a piece of software called SIMTRA, which aids the simulation of deposition profiles. This model is an extension of the Berg model, having the most important extra fea-

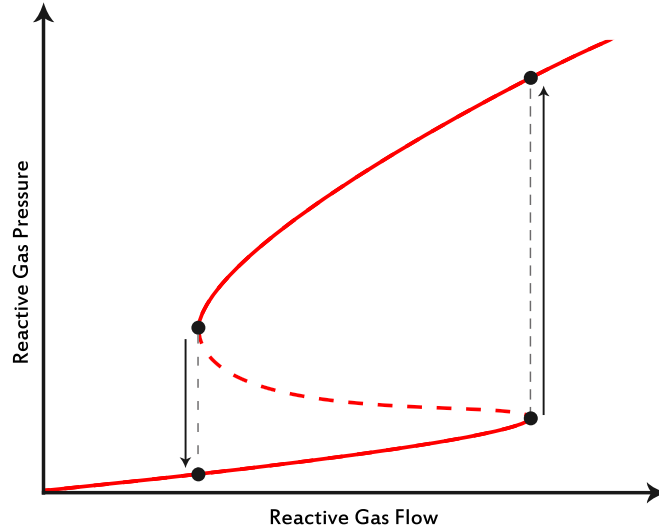


Figure 1.5: The observed hysteresis behavior of the system on a p-q plot [5].

ture of subsurface implantation of reactive gas ions/atoms and the compound forming 2nd order reaction mechanism in the subsurface. A chemisorption mechanism governs the reaction on the surface and redeposition of sputtered material back on the target is taken into account [58].

1.3 Modeling tasks and challenges

Throughout the following subsections a comparative study analysis is given under each modeling task.

1.3.1 Parameter identification approaches

One of the biggest, if not the biggest challenge in modeling reactive magnetron sputtering is the lack of readily available parameters or tools to obtain those parameters.

The lack of identified sticking coefficients led Bogaerts et al. [13] to attempt to identify them by trying to select the ones that would have had resulted in correct estimation of the process, after the experiment was undertaken. The chosen experimental setup was one, in which the sticking coefficient played

a significant role. The ion density at a certain distance from the substrate was measured and simulated. They performed the simulation for every possible value of the sticking coefficient and later checked which ones were in accordance with the measured data. What they found is that two given circumstances resulted in different parameters, meaning that the model wasn't detailed enough and some other effect also had to be considered. Their result, however, narrowed the plausible range for the sought parameter.

Leroy et al. attempted the parameter identification by analyzing samples of deposited films and estimating the actual content of a given material in them [37, 38]. Having this estimate, it was possible to calculate what the missing parameter should have had been. An extensive guide has been given on how this should be undertaken. The process requires several specialized equipment and techniques (XPS - X-ray Photoelectron Spectroscopy, EPMA - Electron-probe microanalysis) and complex calculations to be able to reach a result.

Strijckmans et al. also undertook this challenge of parameter identification in [56]. They used their most detailed RSD2013 model, missing only 3 parameters (see Fig. 1.6), and wrote a parallel C++ program to run the model on a supercomputer, to see which parameter sets would be usable.

The parameter fitting algorithm has two main components: a parameter set selection component and a parameter set evaluation component. A 2-D representation of the parameter set selection component can be seen in Fig. 1.7. Increasing the dimensionality of the parameter space is feasible, though with increased computational load. Three ordered lists have been employed to differentiate between unfinished (U), finished (F) and rejected (R) parameter sets. A parameter set is considered rejected (R) when the result of the model simulation does not agree with the measured data.

The evaluation component has an acceptance criterion which is determined by the PQ - pressure-flow relation of the simulation result. The critical flow values (the limits of the unstable region) are observed at three different current values and the maximum of the six squared errors is considered.

Before this study there was complete disagreement among researchers, many of them having measured completely different values for the same parameter. The results of this attempt further narrowed down the possible range of parameter sets.

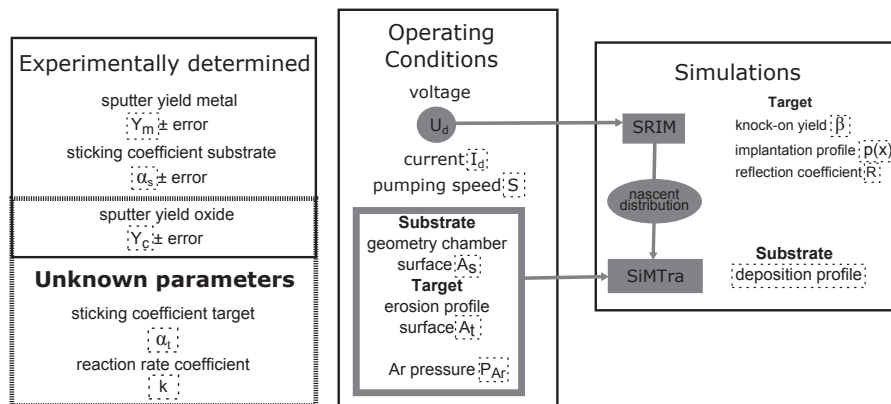


Figure 1.6: A scheme visualizing the input parameters of the RSD2013 model [58]

1.3.2 Modeling the produced compounds

Berg et al. laid down the foundation for macroscopic modeling of magnetron sputtering with one reactive gas [3, 4, 5]. When the need arose to model binary or ternary compounds this model has been expanded.

Carlsson et al. published an article where two reactive gases were used and binary compounds were modeled [15]. This model neglected ternary compounds for the sake of simplicity. When the growth of a ternary compound such as of TiO_xN_y is the requirement, one must find a different model.

Kelemen et al. published a macroscopic model that studies the formation of ternary compounds on the substrate [33]. The model follows the same approach as the two mentioned above, allocating 8 regions on the substrate covered with different active, passive, binary and ternary compounds.

1.3.3 Modeling different magnetron types

Dual magnetron co-sputtering allows the deposition of alloy material without having to manufacture alloy targets [55, 43, 34]. Multicomponent models have also been developed and analyzed in [17, 18, 46]. This setup requires two separate magnetrons to be installed, each of them becoming the anode of the other during sputtering. Such a setup requires a power supply that

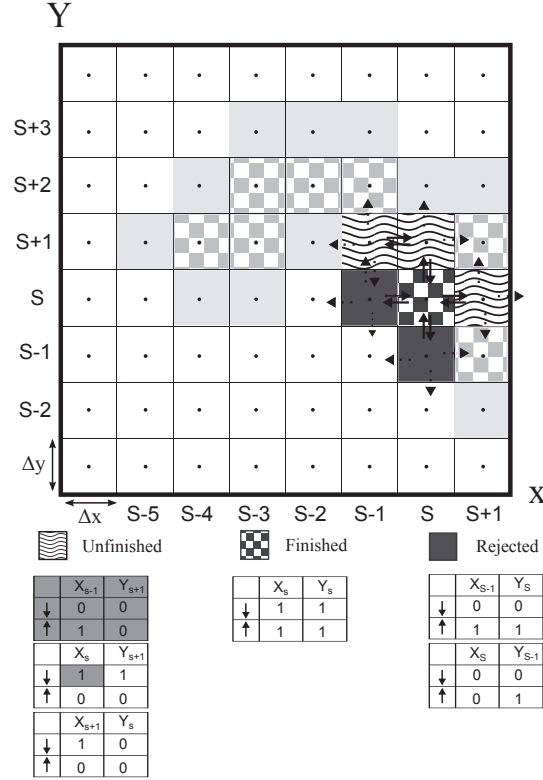


Figure 1.7: A 2-D illustration of the parameter selecting component of the searching algorithm [58].

can generate pulsed bipolar signals. Given the fact, that each magnetron is switched between anode and cathode roles, the typical charge build-up on poisoned areas is neutralized due to sequential target bombing with ions as well as electrons. The absence of local charge build-up also leads to an arc free operation, which is mandatory for consistent large area, even layer deposition.

Cylindrical rotating magnetron sputtering was introduced to reduce the operational costs of large scale industrial coaters, due to the inherent disadvantages of sputtering of stationary planar magnetrons. One of these disadvantages is the well-known formation of a so-called "race track", a high erosion zone on the surface of the target, that is caused by the inhomogeneous magnetic field that "shapes" the plasma above the target. By rotating the target

with respect to the magnetic field no high erosion zone is formed. This leads to a very efficient process due to the uniform wear the target experiences. The uniform wear maximizes target usability by avoiding the formation of a localized deep race track. The effects of rotation have been modeled and the influences of rotation speed have been studied in [27, 24, 42, 39]. It was observed that the rotation speed highly influences the shape and location of the hysteresis curve.

1.3.4 Modeling for control structure synthesis

The study of the system dynamics and the control structure synthesis require the development of time dependent, dynamic models. Based on macroscopic models, several authors have developed time dependent models, usually in state-space formulation [33, 57, 19, 20, 21, 2]. When derived from the original Berg model, the dynamic model represents a control-affine system of third order with linear and bilinear terms [61]. Woelfel et al. also presented the Berg model in a state-space form along with a detailed explanation of its construction (Eq. (1.9) and (1.10)). Coefficients $a_{i,j}$ and $b_{i,j}$ include parameters like sticking coefficients, sputtering efficiencies, sputtering current density, gas constant, temperature, etc. The state variables are the partial pressure of the reactive gas and the coverages of the target and of the substrate, while the input of the system is the input flow rate of the reactive gas.

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} P \\ \theta_t \\ \theta_s \end{pmatrix} \quad (1.9)$$

$$\begin{aligned} \dot{x}_1(t) &= x_1(t)(-a_{1,1} + a_{1,2}x_2(t) + a_{1,3}x_3(t)) + bu(t) \\ \dot{x}_2(t) &= a_{2,12}x_1(t)(1 - x_2(t)) - a_{2,2}x_2(t) \\ \dot{x}_3(t) &= a_{3,13}x_1(t)(1 - x_3(t)) + a_{3,23}x_2(t)(1 - x_3(t)) - a_{3,32}x_3(t)(1 - x_2(t)) \end{aligned} \quad (1.10)$$

The magnetron sputtering system is essentially nonlinear, but several studies attempt to use linearization around the equilibrium points to study the stability and controllability of the system. Due to the difficulties to apply the results of control theory, there have been studies and even patents on how to control a system of such dynamics through heuristic synthesis of complex control structures. In [81] a control structure was presented in which the chosen manipulated quantities influence the controlled variable indirectly, through a chain of effects in the system.

Woelfel had a different approach by studying the essential input-output interactions in different operating conditions in order to develop a simplified model that was conceived with the aim of being practical for control purposes [61, 62, 63, 66]. Woelfel et al. presented a control design method that is based on artificial neural networks and ordinary differential equations [65, 64]. The goal of using neural networks was to decouple the plasma, electrical and gas subsystems from each other. Two multilayer perceptron type networks have been used, both employing a hidden layer of 10 neurons with sigmoid activation functions.

My work also concentrates on control structure synthesis [40]. It started with the assumption that an on-line state identification algorithm can be developed, and with its use, the stoichiometry of the process can be controlled. The input-output characteristics have been plotted to observe the location of the peak of the substrate coverage with the desired compound (see Fig. 1.8). By selecting a preferred subsurface by formulating first order equations to delimit a monotone region (see Fig. 1.9) it was possible to conceive a state-dependent state limiting algorithm that can operate the system with two independent continuously pumped reactive gas inputs. This came as a proposed alternative for RGPP - Reactive Gas Pulsed Process [16, 41] which for the sake of stability had to compromise on stoichiometry. These results shall be presented in detail in Chapter 4.

One would be mistaken by thinking that better control of the process can only be achieved by ever more complicated control structures. Some researchers focused on model reduction, in order to facilitate the implementation of less complex control algorithms. The work done by Woelfel et al. concentrates on developing models that suffice the control goal [66]. It was mentioned that most results in the field were provided from either a vacuum science or a thin solid film approach, therefore most models developed were not usable for control purposes. It was emphasized that not enough work has been done to identify the input-output behavior of the reactive sputtering process.

They recognized [61] that for control purposes the Berg model can be reduced to the Abel differential equation (see Eq. (1.11)). In Eq. (1.11) the system input $u(t)$ is the gas flow and the system output $y(t)$ is the sputtering voltage.

$$\dot{y}(t) = Ay^3(t) + By^2(t) + Cy(t) + D + Eu(t) \quad (1.11)$$

Using this model it was later demonstrated that a venerable PID (proportional–integral–derivative) type controller can be used to control and stabilize

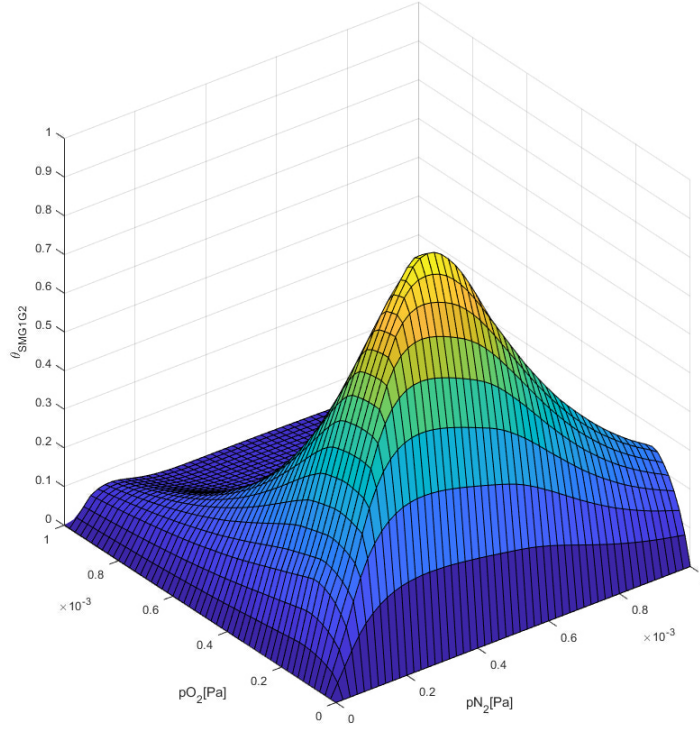


Figure 1.8: Substrate coverage with $\theta_{MG_1G_2}$ at $I = 0.1[A]$ for different reactive partial pressure combinations [40].

the complex system. Detailed description has been given for the necessary preconditions that are needed to apply the given tuning rules [63].

In [61], the parameter identification of the reduced model in Eq. (1.11) has been presented. The identification process begins with the construction of a matrix using the inputs and outputs of the system (see Eq. (1.12)). According to this approach, the parameters are identified from measured samples of the system input, system output and of the derivative of the system output.

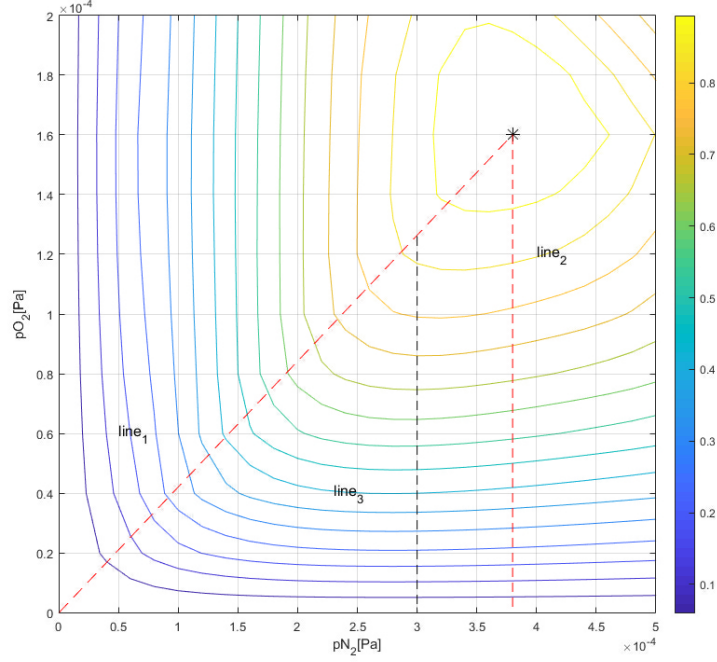


Figure 1.9: The contour plot of the substrate coverage and the lines used to delimit the preferred area [40].

$$\underbrace{\begin{pmatrix} y_{m1}^3 & y_{m1}^2 & y_{m1} & 1 & u_{m1} \\ y_{m2}^3 & y_{m2}^2 & y_{m2} & 1 & u_{m2} \\ y_{m3}^3 & y_{m3}^2 & y_{m3} & 1 & u_{m3} \\ y_{m4}^3 & y_{m4}^2 & y_{m4} & 1 & u_{m4} \\ y_{m5}^3 & y_{m5}^2 & y_{m5} & 1 & u_{m5} \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}}_M \underbrace{\begin{pmatrix} A \\ B \\ C \\ D \\ E \end{pmatrix}}_n = \underbrace{\begin{pmatrix} \dot{y}_{m1} \\ \dot{y}_{m2} \\ \dot{y}_{m3} \\ \dot{y}_{m4} \\ \dot{y}_{m5} \\ \vdots \end{pmatrix}}_r \quad (1.12)$$

Calculating the Moore-Penrose type left pseudoinverse matrix gives the parameter vector $\mathbf{n}$ of the system under examination (see Eq. (1.13)). The parameter vector obtained by Eq. (1.13) can be used to calculate the parameters of the original state-space system ($a_{i,j}$). Equations (1.11-1.13) have been presented in this form in [66].

$$\mathbf{n} = \mathbf{M}^+ \mathbf{r} \tag{1.13}$$

1.4 Conclusion and challenges

In 2019, Depla et al. published an article on the current opportunities and challenges in modeling reactive magnetron sputtering [28]. They mentioned four areas that still need considerable attention:

1. redeposition of sputtered atoms,
2. studying I-V characteristics,
3. sample rotation,
4. pulsing discharge currents.

In my opinion, in future research on this topic emphasis should and probably will be placed on the following key points:

1. delimitation of ranges for some parameters in macroscopic models with the aid of the results obtained from detailed kinematic modeling,
2. precise identification of parameters with the help of the macroscopic dynamic models using measureable data such as partial pressures, gas flows, substrate temperatures, spectrum intensities, voltages and current values,
3. the use of online parameter identification algorithms to identify real-time substrate coverage and composition, mainly for control purposes,
4. development of macroscopic models that, from the perspective of process control, adequately integrate the models used to describe phenomena on the surfaces of both target and substrate as well as models used to describe the state of the plasma discharge.

Chapter 2

Parameter identification

2.1 Introduction

This Chapter deals with the parameter identification of a reactive magnetron sputtering and thin film deposition model in order to accomplish the model-based control of the corresponding technological process. The process consists of the bombardment of a target with Ar^+ ions, which leads to the sputtering of this material and its subsequent deposition on a substrate, forming compounds with the reactive gases also present in the low-pressure sputtering chamber.

Due to the reactive gases, several mechanisms make the process itself highly nonlinear, and one of the first mathematical models which succeeded to reflect its particularities was elaborated by Berg et al. [3]. This macroscopic model is presented in (2.1). It assumes the presence of a single reactive gas and a single sputtering target. It is based on equilibrium equations of the reactive gas on the target and substrate surfaces and it assumes the formation of a monolayer of compound on the surface of the target.

The model plausibly reflects the hysteresis of different variables upon the variation of the reactive gas inlet. However, there are still several aspects of the sputtering and deposition process that can't be captured by this model, including the description of the compound thickness formed on the target and the influence of the inert gas pressure on the hysteresis. One of the latest modifications meant to overcome these limitations led to the development of the RSD model [58], which includes the mechanism of reactive gas implantation in the target. Unlike the target and substrate coverage, the partial pressure of the reactive gas can be relatively easily measured and its hysteresis upon the inlet reactive gas quantity variation can be revealed.

My goal is to investigate the possibility of reproducing this practical behavior as closely as possible, using the steady-state analytical solution of the system of equations constituting the Berg model.

In order to find the parameters α_c , α_t , η_M and η_G , I consider the derivative of the function $q_{in}(p)$, derive its extrema and identify negligible terms in different pressure ranges so that the simplifications result in straightforward parameter identification methods. The parameters identified in this offline manner are going to be used in the dynamical model for state estimation and state feedback control [40].

Other modeling and parameter identification methods can be found in [13], [37], [38], [56] and a survey of the different approaches can be found in [68].

Throughout this Chapter [75] I focus on oxygen as the reactive gas and titanium as the target material, and the model assumes the formation of a TiO_2 thin film on the substrate.

2.2 Derivation of the steady state $p - q$ characteristics

The equations of the Berg model are:

$$\begin{cases} \alpha_t F(1 - \theta_t) - \eta_G J \theta_t = 0 \\ \alpha_c F(1 - \theta_c) + \eta_G J \frac{A_t}{A_c} \theta_t (1 - \theta_c) - \eta_M J \frac{A_t}{A_c} (1 - \theta_t) \theta_c = 0 \\ q_{in} - q_p - M_{O_2} [\alpha_t F(1 - \theta_t) A_t + \alpha_c F(1 - \theta_c) A_c] = 0 \\ q_p = S p \\ F = K p \\ K = \frac{1}{\sqrt{2\pi k_B T M_{O_2}}} \end{cases} \quad (2.1)$$

The notation is:

- A_t effective target surface area,
- A_c condensation surface area,
- θ_t target coverage: the ratio between the area covered with TiO_2 compound and A_t ,
- θ_c the coverage of the condensation surface,
- α_t reactive gas molecule sticking probability on the target surface,

- α_c reactive gas molecule sticking probability on the condensation surface,
- η_M number of Ti atoms sputtered by one Ar^+ ion,
- η_G number of TiO_2 molecules sputtered by one Ar^+ ion,
- q_{in} reactive gas input mass flow,
- q_p reactive gas pumping mass flow,
- S pumping speed of the turbomolecular pump,
- J bombarding Ar^+ ion flux density on the target surface,
- F flux density of the reactive gas molecules,
- M_{O_2} the mass of one oxygen molecule,
- T the absolute temperature.

For a significant range of the model parameters the $q_{\text{in}} = f(p)$ function is not injective and the stable operating points obtained upon the variation of the inlet reactive gas flow lie on the hysteresis curve shown in Fig. 2.1. The operating points on the A – B negative slope segment of the $p(q_{\text{in}})$ characteristic, are unstable.

From (2.1) it results:

$$q_{\text{in}} = \underbrace{Sp}_{q_p} + \underbrace{M_{\text{O}_2} K \alpha_t A_t f_1(p)}_{q_{G_1}} + \underbrace{M_{\text{O}_2} K \alpha_c A_c f_2(p)}_{q_{G_2}}, \quad (2.2)$$

where

$$\begin{cases} f_1(p) &= p(1 - \theta_t) \\ f_2(p) &= p(1 - \theta_c) . \end{cases} \quad (2.3)$$

The function $f_1(p)$ has no extrema, thus on its own it cannot account for the tipping points A and B. Therefore, the consideration of the effect of the condensation area is essential. Proof of this observation is given in (2.4).

$$\frac{df_1(p)}{dp} = \frac{d}{dp} \left(\frac{\eta_G J p}{\alpha_t K p + \eta_G J} \right) = \frac{\eta_G^2 J^2}{(\alpha_t K p + \eta_G J)^2} > 0 \quad (2.4)$$

Hence $f_1(p)$ is monotonous for any value of p .

The following notation is used

$$\begin{cases} x &= 1 - \theta_t \\ y &= 1 - \theta_c . \end{cases} \quad (2.5)$$

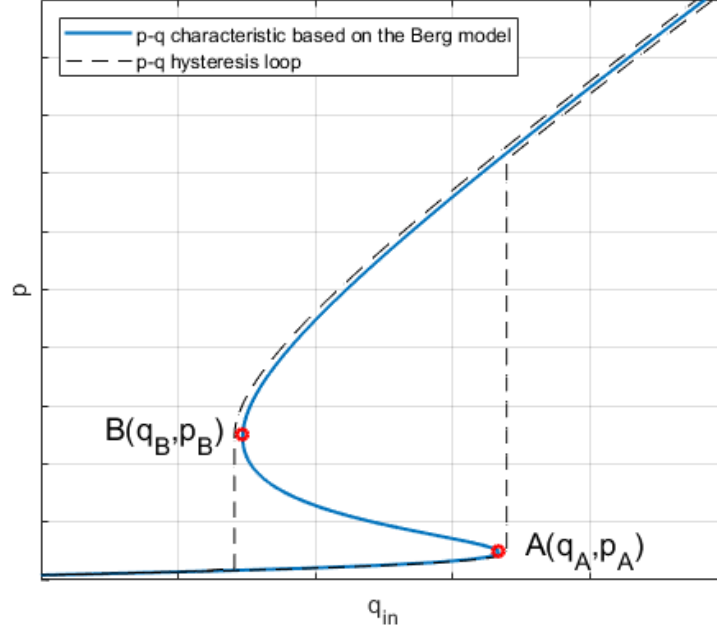


Figure 2.1: Matlab representation of the reactive gas flow- partial pressure characteristic based on the Berg model and the hysteresis behaviour in case of slow variation of the input reactive gas flow [75].

From the first two equations in (2.1) :

$$x = \frac{\eta_G J}{\alpha_t K p + \eta_G J} , \quad (2.6)$$

$$y = \frac{\eta_M J x}{\alpha_c K K_a p + \eta_G J + \Delta \eta J x} , \quad (2.7)$$

where

$$\begin{cases} \Delta \eta &= \eta_M - \eta_G \\ K_a &= \frac{\Lambda_c}{\Lambda_t} . \end{cases} \quad (2.8)$$

In order to identify simplification possibilities in $q_{in}(p)$, a numerical example is considered:

$$\begin{aligned}
\alpha_t &= \alpha_c = 1 , \\
\eta_M &= 3, \eta_G = 0.3, \Rightarrow \Delta\eta = 2.7 , \\
A_t &= 0.84 \times 10^{-2} \text{ m}^2, A_c = 0.22 \text{ m}^2 \Rightarrow K_a = 26.2 , \\
K &= 2.69 \times 10^{22}, p = 0.015 \text{ Pa}, I = 0.7 \text{ A} , \\
J &= \frac{I}{A_t e} = 5.2 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1} .
\end{aligned} \tag{2.9}$$

With these assumptions it results:

$$x = \frac{1.56 \times 10^{20}}{4.03 \times 10^{20} + 1.56 \times 10^{20}} = 0.279 . \tag{2.10}$$

As it can be seen in (2.10) the two terms in the denominator of x are comparable in magnitude, therefore neither can be neglected. In the same conditions:

$$y = \frac{4.35}{105.7 + 1.56 + 3.91} = 0.039 . \tag{2.11}$$

In (2.11) the second and third terms of the denominator are at least one order of magnitude smaller than the first one. Thus, an adequate approximation of y and $f_2(p)$ is:

$$y \cong \frac{\eta_M J x}{\alpha_c K K_a p} , \tag{2.12}$$

$$f_2(p) = p y \cong \frac{\eta_M J x}{\alpha_c K K_a} . \tag{2.13}$$

2.3 Determination of the extrema

The operating point $A(q_A, p_A)$ provides good deposition rate and stoichiometry. Therefore, the coordinates of the extrema are of interest from a process control point of view.

The derivative of q_{in} is :

$$\frac{dq_{in}}{dp} = \frac{d}{dp} \left[S p + M_{O_2} \alpha_t K A_t f_1(p) + M_{O_2} \alpha_c K A_c f_2(p) \right] . \tag{2.14}$$

Using (2.13), the derivative of $f_2(p)$ is approximated as

$$\frac{df_2}{dp} = \frac{\eta_M J}{\alpha_c K K_a} \frac{dx}{dp} = \frac{\eta_M J}{\alpha_c K K_a} \frac{-\eta_G J \alpha_t K}{(\alpha_t K p + \eta_G J)^2} \quad (2.15)$$

Substituting (2.4) and (2.15) into (2.14) it results:

$$\begin{aligned} \frac{dq_{in}}{dp} &\cong S + M_{O_2} \alpha_t K A_t \frac{\eta_G^2 J^2}{(\alpha_t K p + \eta_G J)^2} + \\ &+ M_{O_2} \alpha_c K A_c \frac{\eta_M J}{\alpha_c K K_a} \left(- \frac{\eta_G J \alpha_t K}{(\alpha_t K p + \eta_G J)^2} \right), \end{aligned} \quad (2.16)$$

$$\frac{dq_{in}}{dp} \cong S - \frac{M_{O_2} \alpha_t K A_t J^2 \eta_G \Delta \eta}{(\alpha_t K p + \eta_G J)^2}, \quad (2.17)$$

$$\frac{dq_{in}}{dp} = 0 \Rightarrow \alpha_t K p_B + \eta_G J = \pm \sqrt{\frac{M_{O_2} \alpha_t K A_t J^2 \eta_G \Delta \eta}{S}}, \quad (2.18)$$

$$p_B = \frac{J}{\alpha_t K} \left(\pm \sqrt{\frac{M_{O_2} \alpha_t K A_t \eta_G \Delta \eta}{S}} - \eta_G \right). \quad (2.19)$$

The negative root is due to the fact that the approximation (2.12) becomes void at low pressures, since the first term in the denominator of (2.7) decreases while the third, neglected term increases. However, (2.19) indicates correctly the fact that p_B is proportional to the discharge current (see the practical results in Fig. 2.2).

Calculation of $\frac{dq_{in}}{dp}$ without relying on approximations yields (2.26) as follows:

$$\frac{df_1}{dp} = \frac{\eta_G^2 J^2}{(\alpha_t K p + \eta_G J)^2}, \quad (2.20)$$

$$\frac{df_2}{dp} = \frac{d}{dp}(py) = \frac{d}{dp} \left(\frac{p \eta_M J x}{\alpha_c K K_a p + \eta_G J + \Delta \eta J x} \right). \quad (2.21)$$

Substituting x into (2.21) it results:

$$f_2(p) = py = \frac{d}{dp} \left(\frac{p \eta_M J \frac{\eta_G J}{\alpha_t K p + \eta_G J}}{\alpha_c K K_a p + \eta_G J + \Delta \eta J \frac{\eta_G J}{\alpha_t K p + \eta_G J}} \right), \quad (2.22)$$

$$f_2(p) = \frac{\eta_G \eta_M J^2 p}{\alpha_t \alpha_c K^2 K_a p^2 + \eta_G J K (\alpha_t + K_a \alpha_c) p + \eta_G \eta_M J^2}, \quad (2.23)$$

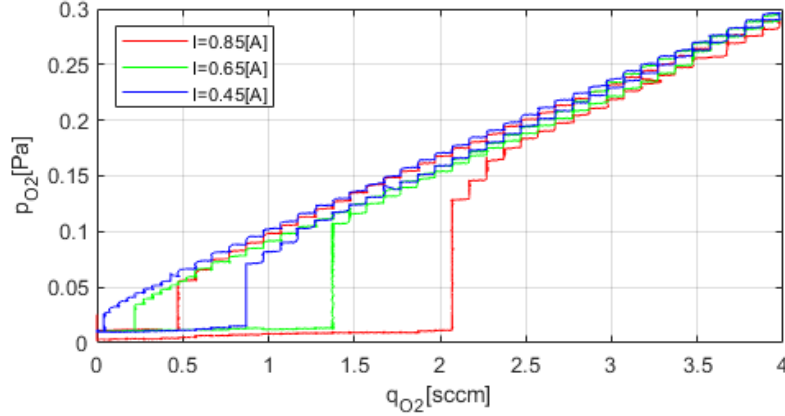


Figure 2.2: Measured data of the variation of the O_2 partial pressure upon a slow variation of its input flow q_{O_2} , for different discharge current intensities [75].

$$\frac{df_2}{dp} = \frac{-\eta_G \eta_M J^2 \alpha_t \alpha_c K^2 K_a p^2 + \eta_G^2 \eta_M^2 J^4}{(\alpha_t \alpha_c K^2 K_a p^2 + \eta_G J K (\alpha_t + K_a \alpha_c) p + \eta_G \eta_M J^2)^2}, \quad (2.24)$$

$$\frac{dq_{in}}{dp} = S + M_{O_2} \alpha_t K A_t \frac{df_1(p)}{dp} + M_{O_2} \alpha_c K A_c \frac{df_2(p)}{dp}. \quad (2.25)$$

Substituting $\frac{df_1}{dp}$ and $\frac{df_2}{dp}$ into (2.25) I get (2.26).

$$\begin{aligned} \frac{dq_{in}}{dp} = & S + M_{O_2} \alpha_t K A_t \frac{\eta_G^2 J^2}{(\alpha_t K p + \eta_G J)^2} + \\ & + \frac{M_{O_2} \alpha_c K A_c (-\eta_G \eta_M J^2 \alpha_t \alpha_c K^2 K_a p^2 + \eta_G^2 \eta_M^2 J^4)}{(\alpha_t \alpha_c K^2 K_a p^2 + \eta_G J K (\alpha_t + K_a \alpha_c) p + \eta_G \eta_M J^2)^2} \end{aligned} \quad (2.26)$$

It is possible that the third term of (2.26) becomes negative. However, if it is positive, the entire equation becomes positive, leading to a situation characterized by no hysteresis.

Thus, if (2.27) is true, no hysteresis will be observed

$$\eta_G \eta_M J^2 > \alpha_t \alpha_c K^2 K_a p^2. \quad (2.27)$$

This is proven by the practical observations that

- significantly large sputtering efficiencies,

- relatively large discharge currents,
- low sticking probabilities,
- small partial pressures

all contribute to avoid hysteresis.

It is also well known that sufficiently large pumping efficiencies (S) also lead to a hysteresis free operation, though such systems are uneconomic. This is also reflected in (2.26) since large values of (S) prevent its right side from crossing zero.

Since two roots of (2.26) can easily be measured (see Fig. 2.1), data acquisition at different discharge currents and pumping speeds can also aid parameter identification.

2.4 Graphical parameter identification

The weight of the terms of (2.2) in different pressure ranges is examined. We first start by examining the poisoned mode corresponding to high reactive gas pressures. Then we continue with the lower reactive gas pressure range, characteristic of the metallic mode.

2.4.1 Poisoned mode - high reactive gas pressures

The following notation is used:

$$f_1(p) = \frac{\eta_G J p}{\alpha_t K p + \eta_G J} = \frac{\text{Num}_{f_1}}{\text{Den}_{1f_1} + \text{Den}_{2f_1}}. \quad (2.28)$$

A numerical example for a relatively high pressure of $p = 0.05$ Pa yields:

$$\begin{aligned} \text{Den}_{1f_1} &= 0.13 \times 10^{22}, \\ \text{Den}_{2f_1} &= 0.0156 \times 10^{22} \ll \text{Den}_{1f_1}. \end{aligned} \quad (2.29)$$

Thus, if p is relatively large, Den_{2f_1} is by an order of magnitude smaller than Den_{1f_1} , and it can be omitted to obtain:

$$f_1(p) \cong \frac{\eta_G J p}{\alpha_t K p} = \frac{\eta_G J}{\alpha_t K} = \text{ct.} \quad (2.30)$$

The terms of $f_2(p)$ are denoted in the following manner:

$$\begin{aligned}
f_2(p) &= \frac{\eta_G \eta_M J^2 p}{\alpha_t \alpha_c K^2 K_a p^2 + \eta_G J K (\alpha_t + K_a \alpha_c) p + \eta_G \eta_M J^2} = \\
&= \frac{\text{Num}_{f_2}}{\text{Den}_{1f_2} + \text{Den}_{2f_2} + \text{Den}_{3f_2}} .
\end{aligned} \tag{2.31}$$

For a relatively large pressure of $p = 0.05$ Pa, the following results are obtained:

$$\begin{aligned}
\text{Den}_{1f_2} &= 0.47 \times 10^{44} , \\
\text{Den}_{2f_2} &= 0.057 \times 10^{44} \ll \text{Den}_{1f_2} , \\
\text{Den}_{3f_2} &= 0.0024 \times 10^{44} \ll \text{Den}_{2f_2} .
\end{aligned} \tag{2.32}$$

At this pressure, Den_{2f_2} and Den_{3f_2} are several orders of magnitude smaller than Den_{1f_2} and can be omitted to obtain:

$$f_2(p) \cong \frac{\eta_G \eta_M J^2 p}{\alpha_t \alpha_c K^2 K_a p^2} = \frac{\eta_G \eta_M J^2}{\alpha_t \alpha_c K^2 K_a p} . \tag{2.33}$$

Substituting (2.30) and (2.33) into (2.2) I get (2.34).

$$q_{\text{in}} \cong Sp + M_{O_2} \alpha_t K A_t \frac{\eta_G J}{\alpha_t K} + M_{O_2} \alpha_c K A_c \frac{\eta_G \eta_M J^2}{\alpha_t \alpha_c K^2 K_a p} \tag{2.34}$$

In (2.35) I denoted three terms of (2.34) with q_p as pumping flow, q_{G_1} and q_{G_2} as getter flows. A qualitative representation of the contribution of these terms to the total gas flow can be seen in Fig. 2.3.

$$q_{\text{in}}^* \cong \underbrace{Sp}_{q_p} + \underbrace{M_{O_2} A_t \eta_G J}_{q_{G_1}^*} + \underbrace{M_{O_2} A_c \frac{\eta_G \eta_M J^2}{\alpha_t K K_a p}}_{q_{G_2}^*} \tag{2.35}$$

The intersection of the asymptote of (2.34) with the q axis marks the value of q_{G_1} (see Fig. 2.4). This in turn can be used to calculate η_G . S can also be found by calculating the slope of the asymptote.

However, practical measurement data (see Fig. 2.2) show that this asymptote can either intersect the p axis, or it can cross the origin, as presented in [56].

Graphical identification of S and q_{G_1} can be done according to the following relations:

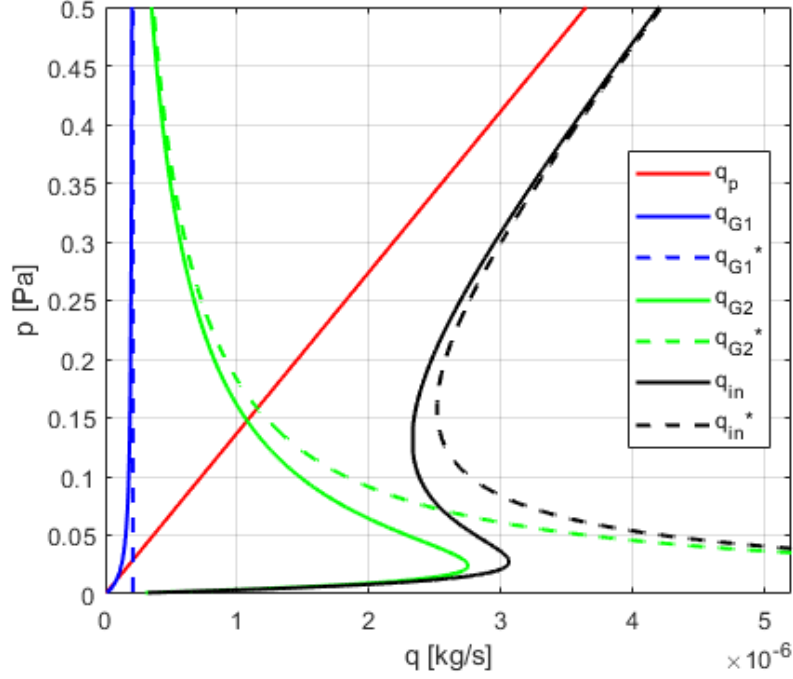


Figure 2.3: The terms of (2.2) and their approximations according to (2.35) [75].

$$\begin{aligned}\hat{S} &= \frac{\Delta q}{\Delta p} = 7.1 \times 10^{-6} \text{ kgPa}^{-1}\text{s}^{-1}, \\ q_{\hat{G}_1} &= 0.08 \times 10^{-6} \text{ kgs}^{-1}.\end{aligned}\tag{2.36}$$

The actual parameters used to generate Fig. 2.4 were:

$$\begin{aligned}S &= 7.04 \times 10^{-6} \text{ kgPa}^{-1}\text{s}^{-1}, \\ q_{G_1} &= M_{O_2} A_t \eta_G J = 0.07 \times 10^{-6} \text{ kgs}^{-1}.\end{aligned}\tag{2.37}$$

From these identified values it is easy to compute η_G as well (2.38). A more accurate identification of η_G can be obtained at higher discharge currents.

$$\hat{\eta}_G = \frac{q_{G_1}^*}{M_{O_2} A_t J}\tag{2.38}$$

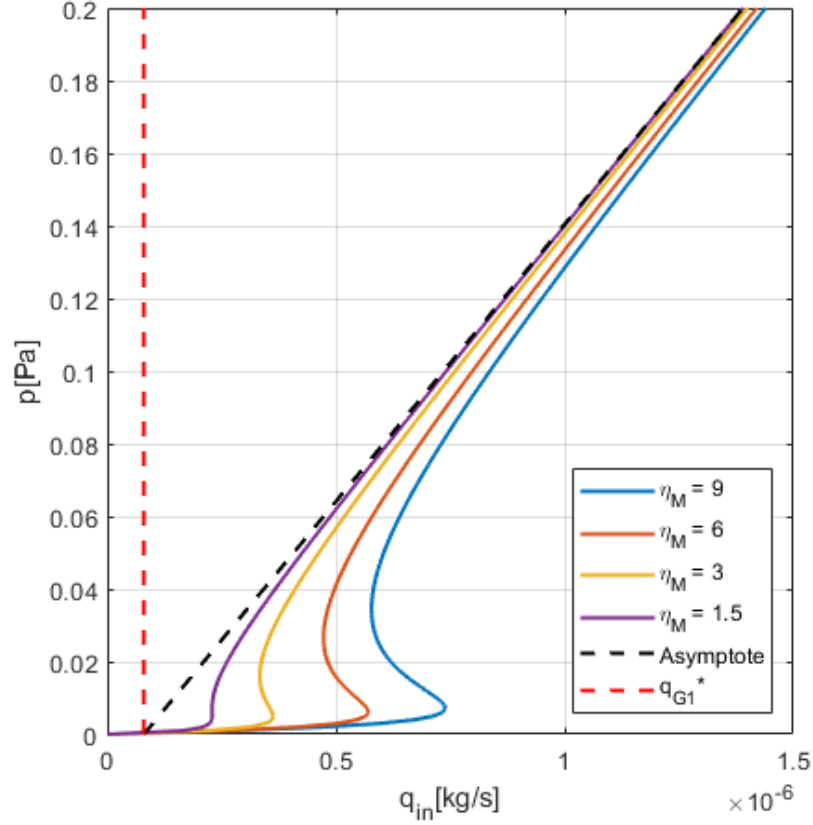


Figure 2.4: $p - q$ characteristics for graphical parameter identification [75].

It can be observed in Fig. 2.4 that although the parameter η_M has an effect on the shape of the characteristic, it does not affect the identified parameters. This is expected, given that η_M only plays a role in the metallic operation mode, in other words, in the lower pressure domain.

One may also conclude from (2.34) that with a given q_{in} and S a small increase of J leads to a large decrease of p , therefore it is a viable method for keeping the system from passing the tipping point. This technique has been used in several control algorithms [40].

2.4.2 Metallic mode - lower reactive gas pressures

In this section similar steps are followed as in section 2.4.1, but for significantly lower pressures. I start from (2.2) and use the notation of (2.28) to calculate the terms using the following example data:

$$\begin{aligned} I &= 3 \times 0.7 \text{ A} \Rightarrow J = 15.6 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}, \\ p &= 0.003 \text{ Pa}, \\ \text{Den}_{1f_1} &= 0.8 \times 10^{20}, \\ \text{Den}_{2f_1} &= 4.68 \times 10^{20} \gg \text{Den}_{1f_1}. \end{aligned} \quad (2.39)$$

Since Den_{1f_1} is almost an order of magnitude smaller than Den_{2f_1} it can be omitted, leading to (2.40).

$$f_1(p) \cong \frac{\eta_G J p}{\eta_G J} = p \quad (2.40)$$

The terms in the expression of $f_2(p)$ are:

$$\begin{aligned} \text{Den}_{1f_2} &= 17.06 \times 10^{40}, \\ \text{Den}_{2f_2} &= 102.7 \times 10^{40} \gg \text{Den}_{1f_2}, \\ \text{Den}_{3f_2} &= 219 \times 10^{40} \gg \text{Den}_{1f_2}. \end{aligned} \quad (2.41)$$

It can be noticed that $\text{Den}_{2f_2} \gg \text{Den}_{1f_2}$ and $\text{Den}_{3f_2} \gg \text{Den}_{1f_2}$, but Den_{2f_2} and Den_{3f_2} are comparable. Omitting Den_{1f_2} leads to (2.42):

$$\begin{aligned} f_2(p) &\cong \frac{\eta_G \eta_M J^2 p}{\eta_G J K(\alpha_t + K_a \alpha_c) p + \eta_G \eta_M J^2} = \\ &= \frac{\eta_M J p}{K(\alpha_t + K_a \alpha_c) p + \eta_M J}. \end{aligned} \quad (2.42)$$

Here one can also see that $f_2(p)$ is independent of η_G , which is expected, since the metallic part of the characteristic is being examined.

In order to obtain (2.43) I substitute (2.40) and (2.42) into (2.2).

$$\begin{aligned} q_{\text{in}} \cong q'_{\text{in}} &= \underbrace{Sp}_{q_p} + \underbrace{M_{O_2} \alpha_t K A_t p}_{q'_{G_1}} + \\ &\quad + \underbrace{M_{O_2} \alpha_c K A_c \frac{\eta_M J p}{K(\alpha_t + K_a \alpha_c) p + \eta_M J}}_{q'_{G_2}}. \end{aligned} \quad (2.43)$$

Calculating the terms of q_{in} for the following data:

$$\begin{aligned}
 I &= 3 \times 0.7 \text{ A} \Rightarrow J = 15.6 \times 10^{20} \text{ m}^2 \text{ s}^{-1}, \\
 p &= 0.003 \text{ Pa}, \\
 q_p &= 2.18 \times 10^{-8} \text{ kgs}^{-1}, \\
 q'_{G_1} &= 3.6 \times 10^{-8} \text{ kgs}^{-1}, \\
 q'_{G_2} &= 64 \times 10^{-8} \text{ kgs}^{-1}
 \end{aligned} \tag{2.44}$$

it can be noticed that $q'_{G_2} \gg q'_{G_1}, q'_{G_2} \gg q_p$, therefore

$$q_{\text{in}} \cong q''_{\text{in}} = q'_{G_2} = \frac{M_{\text{O}_2} \alpha_c K A_c \eta_M J p}{K(\alpha_t + K_a \alpha_c) p + \eta_M J}. \tag{2.45}$$

Further reducing the pressure (and increasing the discharge current), $K(\alpha_t + K_a \alpha_c) p$ declines to a point where it becomes negligible compared to $\eta_M J$. At this point, (2.46) becomes a good approximation of the reactive gas flow-partial pressure characteristic.

$$q_{\text{in}} \cong q'''_{\text{in}} = \frac{M_{\text{O}_2} \alpha_c K A_c \eta_M J p}{\eta_M J} = M_{\text{O}_2} \alpha_c K A_c p \tag{2.46}$$

Therefore, at pressures $p < p_c$ where the characteristic is approximately linear (see Fig. 2.5), the slope of the curve can be used to identify graphically the α_c parameter.

Fig. 2.6 represents the $q_{\text{in}} - p$ characteristic in metallic mode and its approximations according to (2.43), (2.45) and (2.46).

The result of the graphical identification is

$$M_{\text{O}_2} \alpha_c K A_c = \frac{q_D}{p_D} \Rightarrow \hat{\alpha}_c = \frac{q_D}{p_D} \frac{1}{M_{\text{O}_2} K A_c} = 0.74 \tag{2.47}$$

and the parameter that has been used to generate the curves was $\alpha_c = 1$.

It would be even better to identify the $\alpha_c A_c$ product instead of α_c , because A_c itself is also unknown, and they always appear as a product in the equations.

2.5 Determination of α_t and η_M

I have already found solutions for identifying η_G and $\alpha_c A_c$ parameters. One solution for identifying η_M es α_t might be to solve the following system of equations:

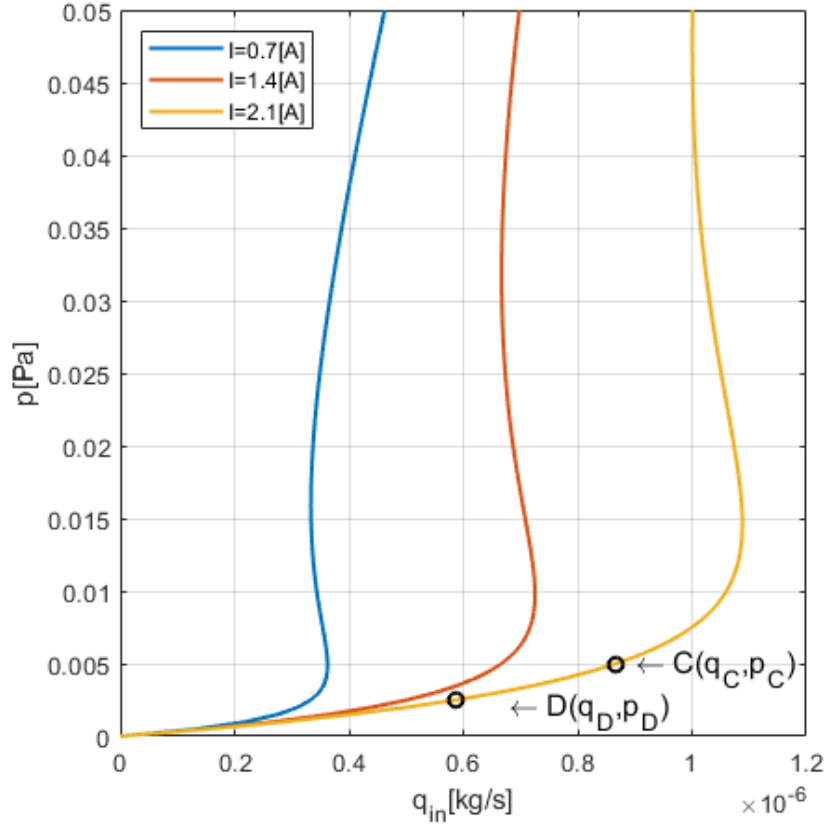


Figure 2.5: The linear segment of the characteristic used to identify α_c [75].

$$\begin{cases} q_{in_1} = f(p_1, \alpha_t, \eta_M) \\ q_{in_2} = f(p_2, \alpha_t, \eta_M) \end{cases} \quad (2.48)$$

which leads to nonlinear equations of the form (2.49).

$$A\alpha_t^2 + B\alpha_t + C\alpha_t\eta_M + D\eta_M + E = 0 \quad (2.49)$$

For two different pressure values two sets of coefficients are obtained:

$$\begin{cases} p_1 \Rightarrow A_1, B_1, C_1, D_1, E_1 \\ p_2 \Rightarrow A_2, B_2, C_2, D_2, E_2 . \end{cases} \quad (2.50)$$

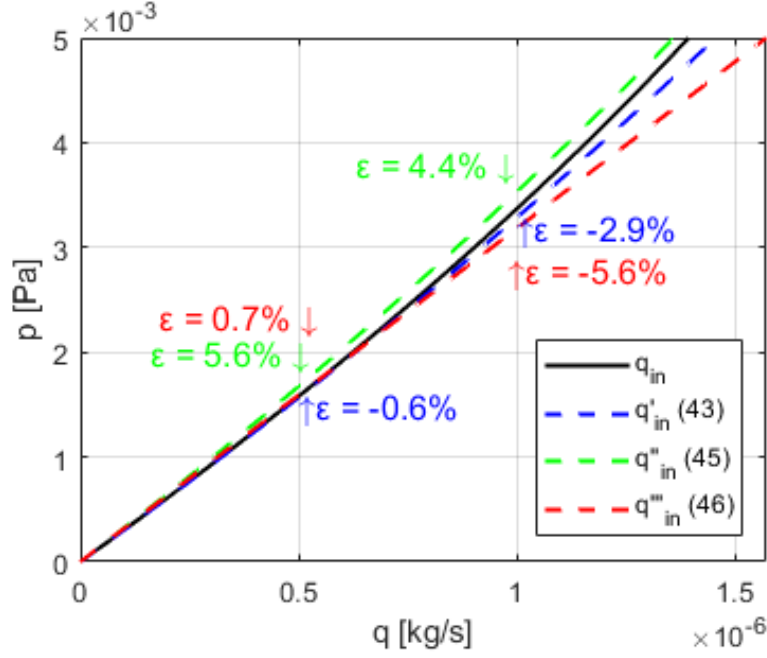


Figure 2.6: Approximations of the $q_{in} - p$ characteristic in metallic mode, according to (2.43), (2.45) and (2.46) [75].

Expressing η_M from both equations of the form (2.49) it results:

$$\frac{A_1 \alpha_t^2 + B_1 \alpha_t + E_1}{C_1 \alpha_t + D_1} = \frac{A_2 \alpha_t^2 + B_2 \alpha_t + E_2}{C_2 \alpha_t + D_2}, \quad (2.51)$$

$$X \alpha_t^3 + Y \alpha_t^2 + Z \alpha_t + W = 0, \quad (2.52)$$

$$\begin{cases} X &= A_1 C_2 - A_2 C_1 \\ Y &= B_1 C_2 - B_2 C_1 + A_1 D_2 - A_2 D_1 \\ Z &= E_1 C_2 - E_2 C_1 + B_1 D_2 - B_2 D_1 \\ W &= E_1 D_2 - E_2 D_1. \end{cases} \quad (2.53)$$

The solution of (2.53) leads to $\hat{\alpha}_t$ and $\hat{\eta}_M$.

2.6 Overview

The parameter identification of the classical macroscopic reactive magnetron sputtering model is feasible using both analytical and graphical methods. Simplification of the analytically determined gas flow-pressure relation is possible in both the metallic and the poisoned operation modes in order to provide a support for the graphical determination of the reactive gas sticking coefficient on the condensation surface and of the sputtering yield of compound molecules. Determination of the sputtering yield of the target metal and of the reactive gas sticking coefficient on the target surface is possible both analytically and by least squares curve fitting, which is the subject of further study. However, the structural uncertainty of the model is a concern because the practical measurement results do not support the model-based theoretical findings developed for the compound sputtering yield determination.

Thesis 1. A graphical identification method has been developed, which is suitable for determining the main parameters of the Berg Model so that they can be used for fine-tuning a control algorithm.

Chapter 3

Stoichiometry control

3.1 Introduction

Amongst many beneficial thin film layers is the photocatalyst titania (TiO₂-rutile and anatase) TiO₂ (rutile) which is obtained by sputtering Titanium in an Argon and Oxygen mixture in high vacuum conditions, typically at a pressure of fractions of Pascals [69]. TiO₂ is a highly preferred coating material due to its special optical characteristics and biocompatibility [70]. With its relatively high refractive index of 2.6 [71] and its good transparency to visible light it is suitable for dielectric interference filters [75]. In a multilayer configuration with SiO₂, 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 [72]. 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 target particles are sputtered and they either react 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 ie. in the form of partial pressure control, or Plasma Emission Monitoring (PEM) [73]. 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) [75]. This Chapter focuses on a mathematical approach to determining the target and in turn the substrate coverage during sputtering in an online manner, to facilitate substrate coverage and stoichiometry control.

The foundation of this Chapter [128], just like in Chapter 2, is based on the Berg Model [5], however a different set of symbols will be employed. The reason for this is that Equation 2.1 is the static model used in the literature, but the thought process in this Chapter is one that needs a static model that is derived from a dynamic model. This, in turn, brings new quantities and symbols. One major difference is that the model in this Chapter deals with reactive gas at the atomic level, compared to the literature, where it is dealt with at the molecular level.

The following notation has been applied:

- e – the electron charge ($1.6 \cdot 10^{-19}$ [C]);
- R – ideal gas constant (8314 [$\frac{\text{J}}{\text{kmol} \cdot \text{K}}$]);
- N_A – Avogadro’s number ($6.023 \cdot 10^{26}$ [$\frac{1}{\text{kmol}}$]);
- m_G – mass of the reactive gas molecule [kg]
(for O_2 , $m_G = 32$ [a.u.] = $32 \cdot 1.66 \cdot 10^{-27}$ [kg]);
- $k_B = 1.38 \cdot 10^{-23}$ [$\frac{\text{J}}{\text{K}}$] – 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]
($V = 0.08 [\text{m}^3]$);
 - 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 [kg/s];
 - q_P – pumping mass flow of the vacuum pump [kg/s];
 - A_T – the target area ($A_T = 3600 \cdot 10^{-6} [\text{m}^2]$);
 - A_C – the condensation area ($A_C = 16800 \cdot 10^{-6} [\text{m}^2]$);
 - A_S – the substrate area ($A_S = 600 \cdot 10^{-6} [\text{m}^2]$);
 - η_M – sputtering yield (efficiency) of the metal (number of Ti atoms sputtered by an incident Ar^+ ion)
($\eta_M = 0.5$), [20];
 - η_{MC} – sputtering yield of the metal-gas compound (TiO_2), i.e., the number of compound molecules sputtered by one Ar^+ ion ($\eta_{MC} = 0.017$), [20];
 - 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
($\alpha_{GT} = \alpha_{GS} = 1$) [20];

- α_{GC} – getting efficiency of the sputtering chamber’s surface ($\alpha_{GC} = 0.8$);
- N_G – the surface density of the reactive gas atoms trapped within the compound molecules [atoms/m²] ($N_G = 19.4 \cdot 10^{18}$), based on the surface density of the compound molecules of $N_{TiO_2} = 9.7 \cdot 10^{18} \left[\frac{\text{molecules}}{\text{m}^2} \right]$, [75];
- 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) ($Y_{SEE,M} = 0.114$), [76];
- $Y_{SEE,MG}$ – ion-induced secondary electron emission yield of the surface covered with metal-gas compound (TiO₂) ($Y_{SEE,MG} = 0.08$). [77, 78]

3.2 Analytical study of the conditions needed for stoichiometric sputtering

As mentioned in [74] 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 [5].

$$F_G = \frac{p_G}{\sqrt{2\pi m_G k_B T}} \quad (3.1)$$

In a simplified approach, it is assumed that the flux F_{MS} of the metal atoms on the substrate surface is proportional to the flux of the metal atoms outspattered 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 outspattered metallic atoms. The desired ratio of these flux densities can be formulated as

$$\alpha_{GS}(n_{GG}F_G) = F_{MS}K_{sto} . \quad (3.2)$$

The condition of stoichiometry in case of TiO_2 is $K_{\text{sto}} = 1$. This yields the following condition

$$n_{\text{GG}}\alpha_{\text{GS}}\frac{p_{\text{G}}}{\sqrt{2\pi m_{\text{G}}k_{\text{B}}T}}A_{\text{C}} = F_{\text{IT}}\eta_{\text{M}}(1 - \theta_{\text{T}})A_{\text{T}}K_{\text{sto}}. \quad (3.3)$$

This can further be rearranged to

$$p_{\text{G}} = \frac{1}{n_{\text{GG}}\alpha_{\text{GS}}}F_{\text{IT}}\eta_{\text{M}}(1 - \theta_{\text{T}})\frac{A_{\text{T}}}{A_{\text{C}}}K_{\text{sto}}\sqrt{2\pi m_{\text{G}}k_{\text{B}}T}. \quad (3.4)$$

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

$$\begin{cases} \frac{dp_{\text{G}}}{dt} = \frac{RT}{N_{\text{A}}m_{\text{G}}V} \left\{ q_{\text{in}} - q_{\text{p}} - m_{\text{G}}[\alpha_{\text{GT}}F_{\text{G}}(1 - \theta_{\text{T}})A_{\text{T}} + \right. \\ \quad \left. + \alpha_{\text{GC}}F_{\text{G}}(1 - \theta_{\text{C}})(A_{\text{C}} - A_{\text{S}}) + \alpha_{\text{GS}}F_{\text{G}}(1 - \theta_{\text{S}})A_{\text{S}} \right\}, \\ \frac{d\theta_{\text{T}}}{dt} = \frac{1}{N_{\text{G}}} [n_{\text{GG}}\alpha_{\text{GT}}F_{\text{G}}(1 - \theta_{\text{T}}) - F_{\text{IT}}\eta_{\text{MG}}\theta_{\text{T}}], \\ \frac{d\theta_{\text{S}}}{dt} = \frac{1}{N_{\text{G}}} \left\{ F_{\text{IT}}\left(\frac{A_{\text{T}}}{A_{\text{C}}}\right) [\eta_{\text{MG}}\theta_{\text{T}}(1 - \theta_{\text{S}}) - \right. \\ \quad \left. - \eta_{\text{M}}\theta_{\text{S}}(1 - \theta_{\text{T}})] + n_{\text{GG}}\alpha_{\text{GS}}F_{\text{G}}(1 - \theta_{\text{S}}) \right\}, \\ \frac{d\theta_{\text{C}}}{dt} = \frac{1}{N_{\text{G}}} \left\{ F_{\text{IT}}\left(\frac{A_{\text{T}}}{A_{\text{C}}}\right) [\eta_{\text{MG}}\theta_{\text{T}}(1 - \theta_{\text{C}}) - \right. \\ \quad \left. - \eta_{\text{M}}\theta_{\text{C}}(1 - \theta_{\text{T}})] + n_{\text{GG}}\alpha_{\text{GC}}F_{\text{G}}(1 - \theta_{\text{C}}) \right\}. \end{cases} \quad (3.5)$$

This system is similar to [79, 19], 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:

$$\mathbf{x} = [p_{\text{G}}, \theta_{\text{T}}, \theta_{\text{S}}, \theta_{\text{C}}]^{\text{T}}. \quad (3.6)$$

In order to determine the partial pressure of the reactive gas that satisfies the condition 3.4 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 Section 3.4. In steady state the desired operating point can be determined using the Berg model [5].

$$\begin{cases} q_{\text{in}} - q_p - m_G(\alpha_{GT}F_G(1 - \theta_T)A_T + \\ + \alpha_{GC}F_G(1 - \theta_C)(A_C - A_S) + \alpha_{GS}F_G(1 - \theta_S)A_S) = 0, \\ n_{GG}\alpha_{GT}F_G(1 - \theta_T) - F_{IT}\eta_{MG}\theta_T = 0, \\ F_{IT}\left(\frac{A_T}{A_C}\right)[\eta_{MG}\theta_T(1 - \theta_S) - \eta_M\theta_S(1 - \theta_T)] + n_{GG}\alpha_{GS}F_G(1 - \theta_S) = 0, \\ F_{IT}\left(\frac{A_T}{A_C}\right)[\eta_{MG}\theta_T(1 - \theta_C) - \eta_M\theta_C(1 - \theta_T)] + n_{GG}\alpha_{GC}F_G(1 - \theta_C) = 0. \end{cases} \quad (3.7)$$

Compared to [5], 3.7 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 3.7 it results:

$$\theta_T = \frac{n_{GG}\alpha_{GT}F_G}{n_{GG}\alpha_{GT}F_G + F_{IT}\eta_{MG}}. \quad (3.8)$$

The reactive gas flux density F_G is given in 3.1 versus the partial pressure, while for determining the sputtering ion flux density we'll consider two approaches. In a simplified version,

$$F_{IT} \simeq \frac{J}{e} = \frac{I_d}{A_T e} \quad (3.9)$$

where the discharge current is an easily measurable quantity. In a more accurate approach, the current due to the secondary electron emission, and thus the effect of the target coverage, is taken into account. According to [58],

$$F_{IT} = \frac{J}{e} \frac{1}{1 + Y_{\text{SEE},M}(1 - \theta_T) + Y_{\text{SEE},MG}\theta_T}. \quad (3.10)$$

Hence, by substituting 3.10 into the second equation of 3.7, it results

$$\begin{aligned} & (Y_{\text{SEE},M} - Y_{\text{SEE},MG})\theta_T^2 + \\ & + (Y_{\text{SEE},MG} - 2Y_{\text{SEE},M} - 1 - \frac{J}{e} \frac{\eta_{MG}}{n_{GG}\alpha_{GT}F_G})\theta_T + \\ & + (1 + Y_{\text{SEE},M}) = 0. \end{aligned} \quad (3.11)$$

Fig. 3.1 shows a numerical example for the compound TiO_2 ($I_d = 0.7 \text{ [A]}$, $J = \frac{I_d}{A_t} = 194.4 \left[\frac{\text{A}}{\text{m}^2}\right]$, $\eta_M = 0.5$, $\eta_{MG} = 0.017$). Right- and left-hand sides of 3.4 are plotted taking into account both versions 3.9 and 3.10. Thus, the partial

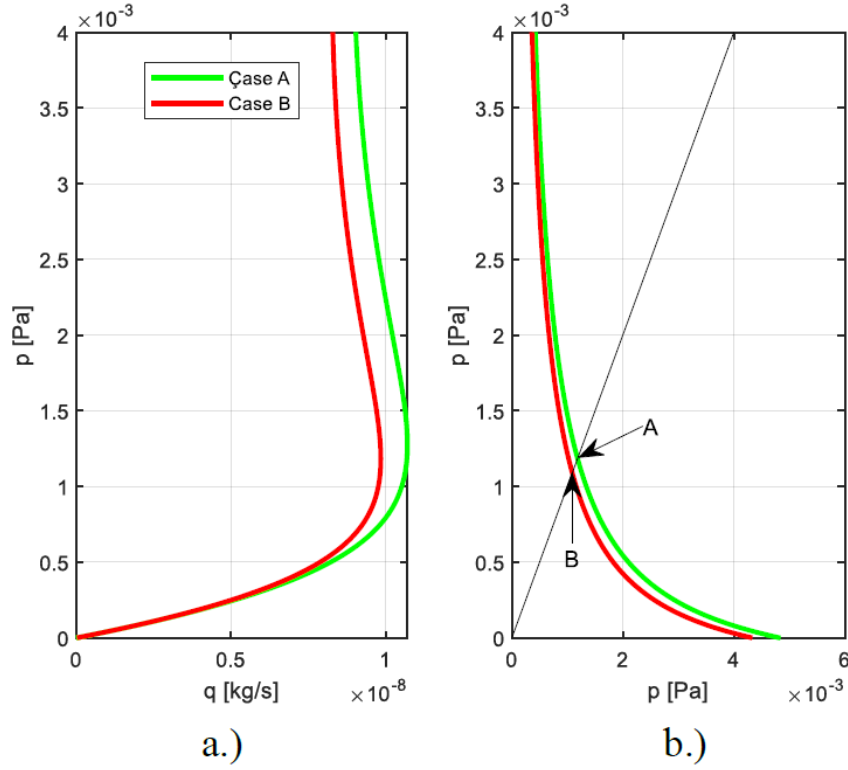


Figure 3.1: a.) The p - q characteristics of the system modelled in case A using 3.9 and in case B using 3.10 b.) The graphical solution of 3.4 in the cases corresponding to 3.9 and 3.10 [128].

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.

Since the outspattered 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 Section 3.3 and 3.4.

3.3 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 3.1 into 3.9.

$$\theta_T = \frac{n_{GG}\alpha_{GT}\frac{p_G}{\sqrt{2\pi m_G k_B T}}}{n_{GG}\alpha_{GT}\frac{p_G}{\sqrt{2\pi m_G k_B T}} + F_{IT}\eta_{MG}}, \quad (3.12)$$

where I assume that F_{IT} is controlled by means of the discharge current in a fast control loop. It can be seen in Fig. 3.2 that the relationship 3.12 is a monotonic one. This means that the partial pressure can be used to directly influence the target coverage.

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.

3.4 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 [58] 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 3.13.

$$Y_{SEE} = Y_{SEE,M}(1 - \theta_T) + Y_{SEE,MG}\theta_T \quad (3.13)$$

In [77] and [78] 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

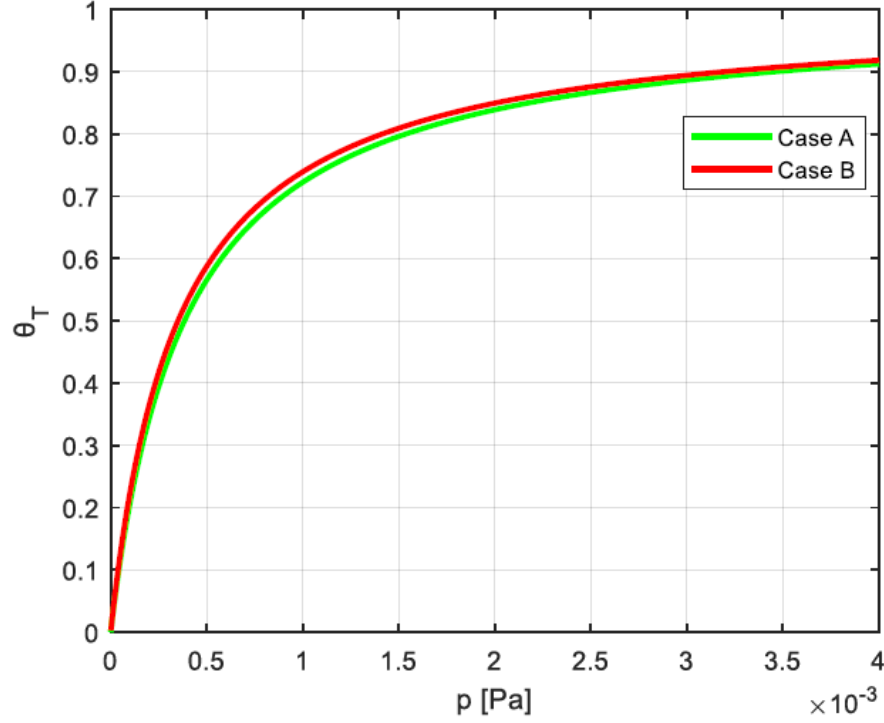


Figure 3.2: Target coverage as a function of reactive gas partial pressure [128].

of Ag, Au, Cr, Cu, Nb, Pt, Re, Ta, Ti. Due to the fact that $U_d \propto 1/Y_{SEE}$ [80], Strijckmans [58] rewrites 3.14 in the following form

$$\frac{1}{U_d} = \frac{1}{U_M}(1 - \theta_T) + \frac{1}{U_{MG}}\theta_T \quad (3.14)$$

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 [77] and [78]. This allows for the target coverage to be calculated in an online manner during sputtering by monitoring the target discharge voltage U_d

$$\theta_T = \frac{\frac{1}{U_d(I_d, p_{Ar})} - \frac{1}{U_M(I_d, p_{Ar})}}{\frac{1}{U_{MG}(I_d, p_{Ar})} - \frac{1}{U_M(I_d, p_{Ar})}}. \quad (3.15)$$

This is further examined by Depla in [80] 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 3.13, 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.

3.5 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 in a swift manner.
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 [81] 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 [81] has been presented in [40], where instead of an optical emission sensor and feedback loop, the partial pressure is the quantity being controlled. The ideas presented in Sections 3.2, 3.3, and 3.4, 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

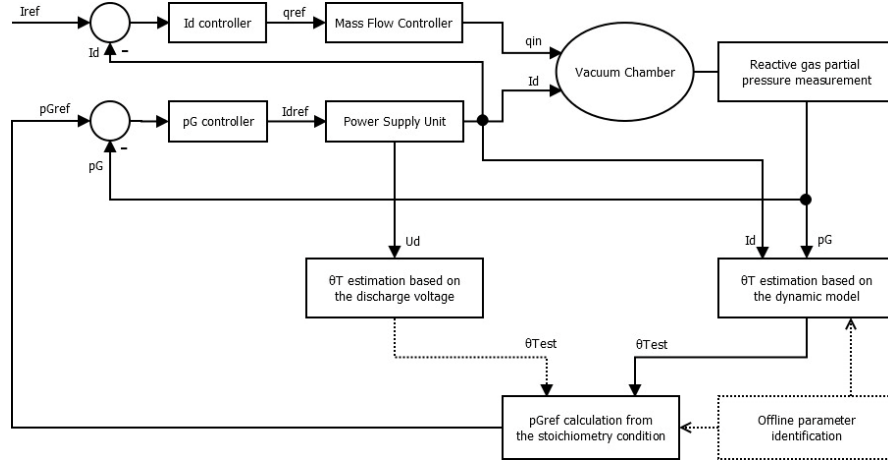


Figure 3.3: The proposed control structure for stoichiometric sputtering [128].

actual target coverage. The proposed control structure can be seen in 3.3. The offline parameter identification block is needed to determine the sticking coefficients of the system [75]. In 3.4 the value of θ_T is needed, which can either be estimated according to one of the methods presented in 3.5 and 3.15, or can take advantage of both estimations with the help of sensor fusion. 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 3.4.

3.6 Overview

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, that can control the sputtering power, and which leads to stoichiometric film growth on the substrate surface.

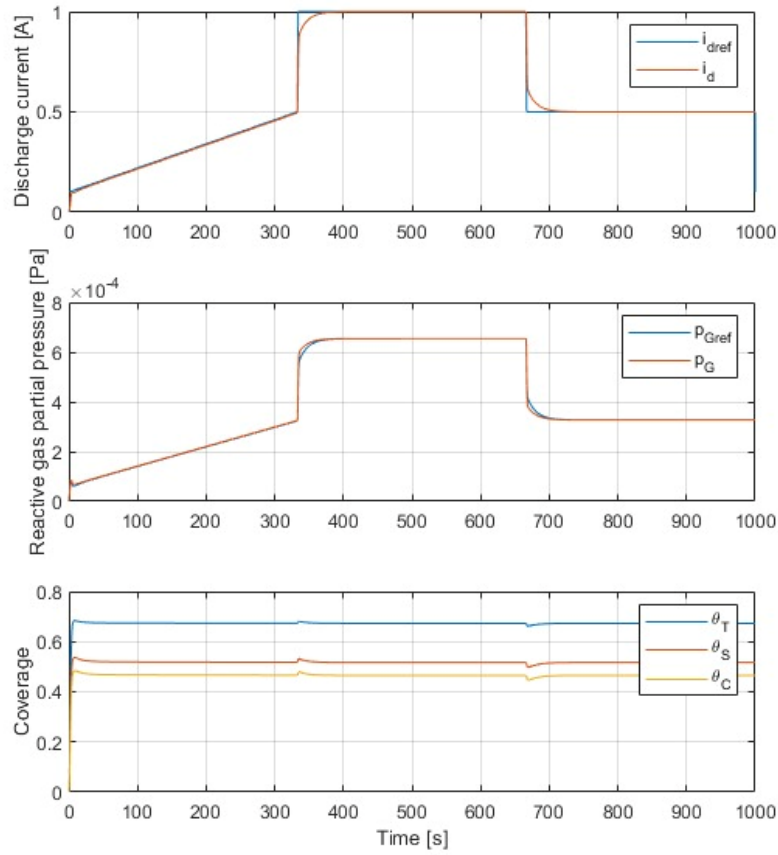


Figure 3.4: Simulation results of the proposed control structure [128].

Thesis 2. A control structure employing two control loops is proposed, that can keep the system stable, that can control the sputtering power, and which leads to stoichiometric film growth on the substrate surface.

Chapter 4

Stoichiometry of ternary compound

4.1 Introduction

Reactive magnetron sputtering has been extensively studied in the past few decades. The process essentially consists of the removal of material from a target surface and its deposition onto a substrate. Material removal is accomplished via high energy noble gas ions which bombard the surface of the target due to a DC electric field. The presence of the reactive gases introduced in the sputtering chamber to influence the composition of the film deposited on the substrate greatly influences the processes on the surface of the target as well.

A successful approach to modeling the one reactive gas sputtering process involves the use of Berg's model [4, 5]. This model has been extended by Carlsson et al. to model the complex behavior in the case of two reactive gases [15]. This approach considers the deposition of only binary compounds, ex. $MG_1 \equiv TiO_2$, $MG_2 \equiv TiN$. There has also been an approach in [33] to further extend this model to consider also ternary compounds, such as $MG_1G_2 \equiv TiO_xN_y$.

Among many studies dedicated to the examination of the physical phenomena, as described in [66], only a few concentrate on the control tasks of the reactive magnetron sputtering process. However, its open loop operation is either impossible or has poor results from the points of view of the deposition rate and film structure [82, 20, 62, 63].

A cascade control structure has been presented in US patent nr. 6,106,676

[81]. In it, the authors claim to have achieved improved control performance in the presence of a single reactive gas, controlling the emission and thus the operating point by means of the power supply, and the sputtering power by means of the oxygen flow.

Stable operation in the presence of two reactive gases has been achieved with a technique called RGPP - Reactive Gas Pulsing Process [41, 16]. Pulsed injection of the second reactive gas is used to avoid process instabilities. The way in which the second reactive gas is injected greatly influences the resulting film stoichiometry. Experiments have been made with different pulse shapes, durations and frequencies [83, 84, 85].

Control of partial pressures in the two reactive gas sputtering process has also been investigated in [86, 87, 88]. These studies either use a dedicated partial pressure controller or do not mention the control structure employed.

The goal set out in this Chapter is the design of a control structure that is suitable for controlling the amount of ternary compound deposited on the substrate.

In section 4.2 the behavior of the two gas reactive sputtering process is examined and control loops are developed in order to manipulate the desired quantities. In section 4.3 the proposed control structure is tested on the model described in [33].

All notations are similar to those used in [33]. G_1 , O_2 and Oxygen, G_2 , N_2 and Nitrogen as well as M, Ti and Titanium shall be used interchangeably throughout this Chapter [40].

4.2 Control considerations and controller design

4.2.1 Control of the sputtering power

Fig. 4.1 shows that in the glow discharge phase, which is of interest for the process, the discharge voltage is somewhat independent of current. However, the discharge characteristics vary with the state of the chamber, and the discharge voltage is somewhat variable during the sputtering process. Nevertheless, it is considered that the sputtering power is controlled by means of the discharge current.

In order to achieve superior control performance, similarly to those described in [81], Nitrogen flow is used as the manipulating quantity for the process current.

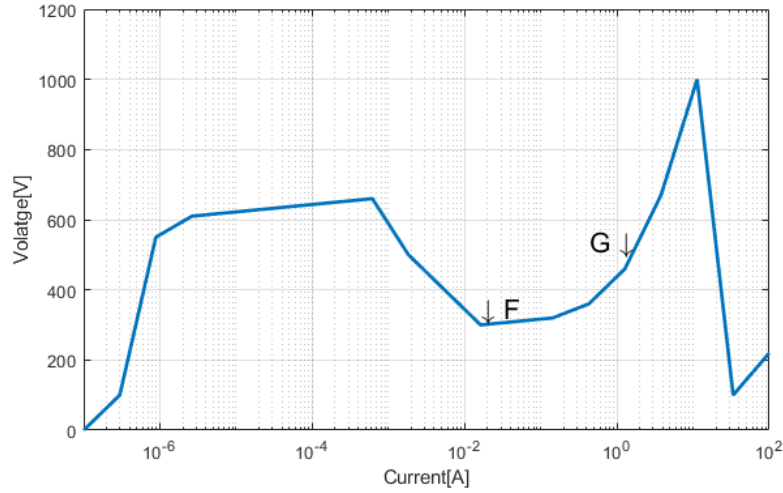


Figure 4.1: U-I plot of a gas discharge, with the F and G sections of interest for the sputtering process [40].

4.2.2 Control of the partial pressure

In Fig. 4.2 it can be observed that at the tipping point of the $p_{N_2} - q_{N_2}$ trajectory a slight current increase avoids the sudden increase of the partial pressure.

To combat such a sudden pressure increase, the sputtering process current, i.e.: the bombarding Ar ion flux, has to be increased in order to allow the process to "consume" more reactive gas. Increasing the current can be achieved relatively fast. Therefore, controlling the sputtering current is a good quenching method for combating sudden partial pressure increases, and thus is a good method for pressure control. A possible control structure is presented in Fig. 4.3, which is inspired from those presented in [81]. It is important to note that in [81] the controlled parameter is the optical emission of the plasma and not the partial pressure.

Effect chain

If the pressure has increased above the reference value, the current shall be increased. Greater current leads to decreasing pressure. If the current value has increased above the reference value, the Nitrogen flow is decreased. Decreasing nitrogen flow also leads to decreasing pressure.

If the pressure has fallen below the reference value, the current shall be

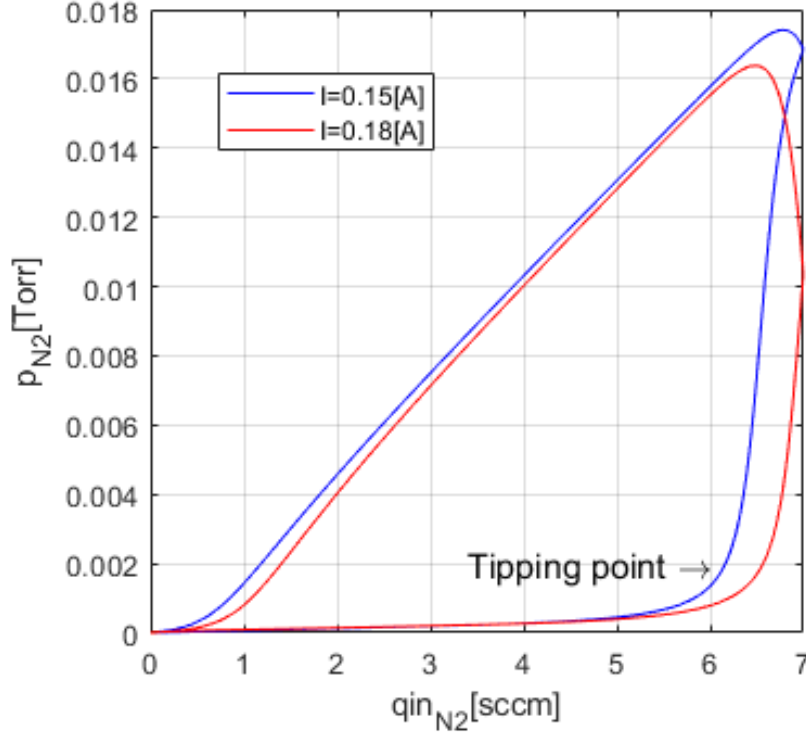


Figure 4.2: Increasing the discharge current lowers the partial pressure [40].

decreased. Lower current leads to increasing pressure. If the current value has fallen below the reference value, the Nitrogen flow is increased. Increasing nitrogen flow also leads to increasing pressure.

A suitable control structure and hardware setup for igniting the plasma and controlling the discharge current was presented in [117].

4.2.3 Control of the ternary compound coverage on the substrate

In order to study the ternary compound coverage on the substrate, the internal states of the model and their behavior shall be considered. Controlling this state is possible only with the help of an internal state identification algorithm, which is not covered in this Chapter. It is well known that excess Oxygen flow into the chamber can lead to a phenomenon called "target trapping" where

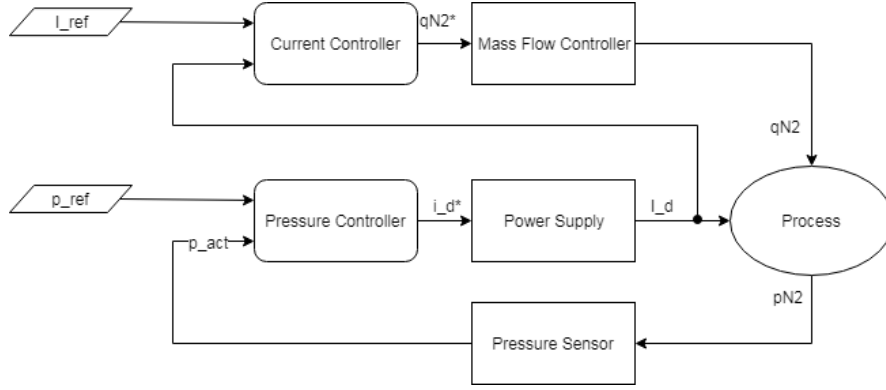


Figure 4.3: Control structure for power and partial pressure [40].

the target becomes completely poisoned, thus leading to a difficult restart of the process (Fig. 4.4).

In order to get a better understanding of the ternary compound deposition process, the following situation has been simulated: the Oxygen partial pressure is repeatedly ramped at periodically increasing constant partial pressures of Nitrogen (Fig. 4.5). This procedure scans the domain of interest of the $p_{N_2} - p_{O_2}$ plane. At every point on this plane, the actual $\theta_{MG_1G_2}$ is saved. The substrate coverage with ternary compound TiO_xN_y can thus be plotted as a two variable function of the partial pressures of the two reactive gases (Fig. 4.6).

Considering that the flow of Nitrogen is set by the sputtering power control block, controlling the $\theta_{MG_1G_2}$ is possible only by manipulating p_{O_2} . This means that for a given Nitrogen partial pressure, the effect of p_{O_2} on $\theta_{MG_1G_2}$ becomes a one variable function, as seen in Fig. 4.7. The two sections of the curve, delimited by the apex, could both be used for control, though only the left side is considered favorable for the process. For this section, an increase of p_{O_2} results in an increase of $\theta_{MG_1G_2}$.

The question thus raised, is to find the subarea of the whole surface, for which this condition is true. Delimiting the region, based on this condition, can best be done by examining the contour plot of the identified surface. Using two lines as shown in Fig. 4.8, it is possible to delimit a region where $\theta_{MG_1G_2} = f(p_{O_2})$ is monotonic, for a given pair of p_{N_2} and I values. The equations defining these lines are given in (4.1) and (4.2). In case of equation (4.2), p_{N_2} is chosen to be the value for which the apex of the surface is obtainable. Equation (4.3) is used to provide a safety margin for potential overshoots resulting from

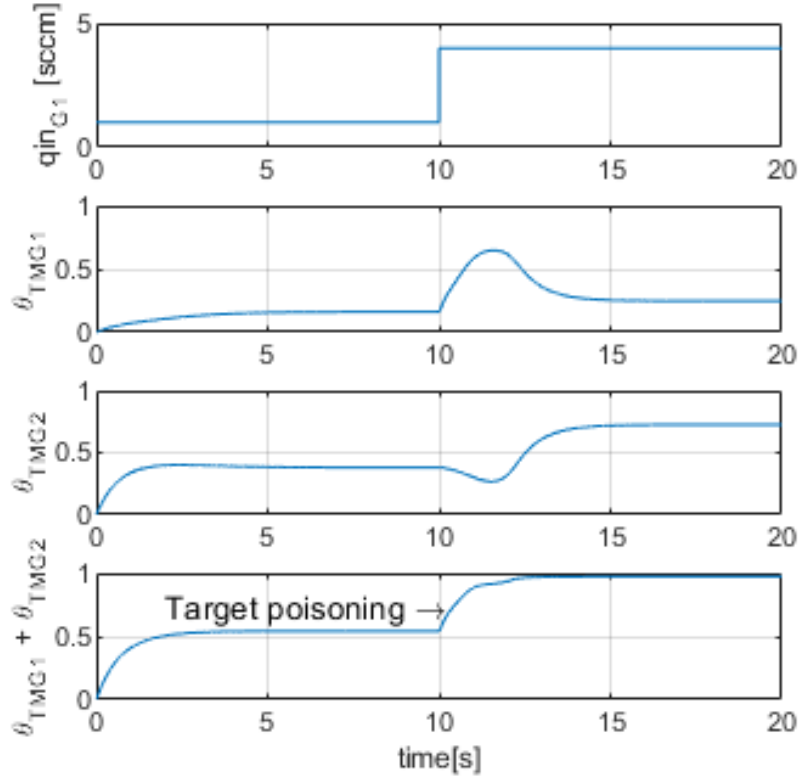


Figure 4.4: Too high input flow of Oxygen (G1) leads to the complete poisoning of the target [40].

the partial pressure control. In the case of the surface in discussion, $m_1 = 2.375$ and $m_2 = 0.8$.

$$\text{line}_1 : p_{O_2} = p_{N_2}/m_1 \quad (4.1)$$

$$\text{line}_2 : p_{N_2} = p_{\hat{N}_2} \quad (4.2)$$

$$\text{line}_3 : p_{N_2} = m_2 * p_{\hat{N}_2} \quad (4.3)$$

Since the plotted surface is current dependent, the effect of the sputtering current is investigated. The entire surface is replotted and the position of the

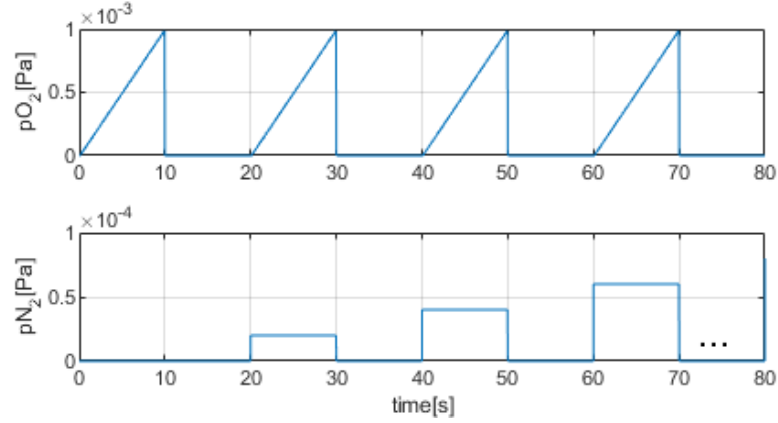


Figure 4.5: Excerpt of the inputs of the model that were used to identify substrate coverage and reactive gas partial pressure relationships [40].

apex is noted. The highest partial pressure of Nitrogen that results in the maximum substrate coverage at different current values is displayed in Fig. 4.9. A line can be used to approximate the highest allowable Nitrogen partial pressure for different discharge currents (equation 4.4). In the case of the surface identified, $m_3 = 90\mu\text{Pa}$ and $m_4 = 2.9 \frac{\text{mPa}}{\text{A}}$.

$$\text{line}_4 : \hat{p}_{\text{N}_2} = m_3 + I * m_4 \quad (4.4)$$

With the help of those described in section 4.2.1 and 4.2.2, using equations 4.1, 4.2, 4.3, 4.4 to hold the operating point on the preferred subsurface, a new control algorithm can be formulated:

1. I_{ref} is defined by the technological process
2. $\hat{p}_{\text{N}_2} = m_3 + I_{\text{ref}} * m_4$
3. $p_{\text{N}_{2\text{reflim}}} = m_2 * \hat{p}_{\text{N}_2}$
4. p_{N_2} is controlled with I_{disch}
5. I_{disch} is controlled with q_{N_2}
6. $\theta_{\text{MG}_1\text{G}_{2\text{ref}}}$ is defined by the technological process
7. $\theta_{\text{MG}_1\text{G}_2}$ is controlled with $p_{\text{O}_{2\text{ref}}}$

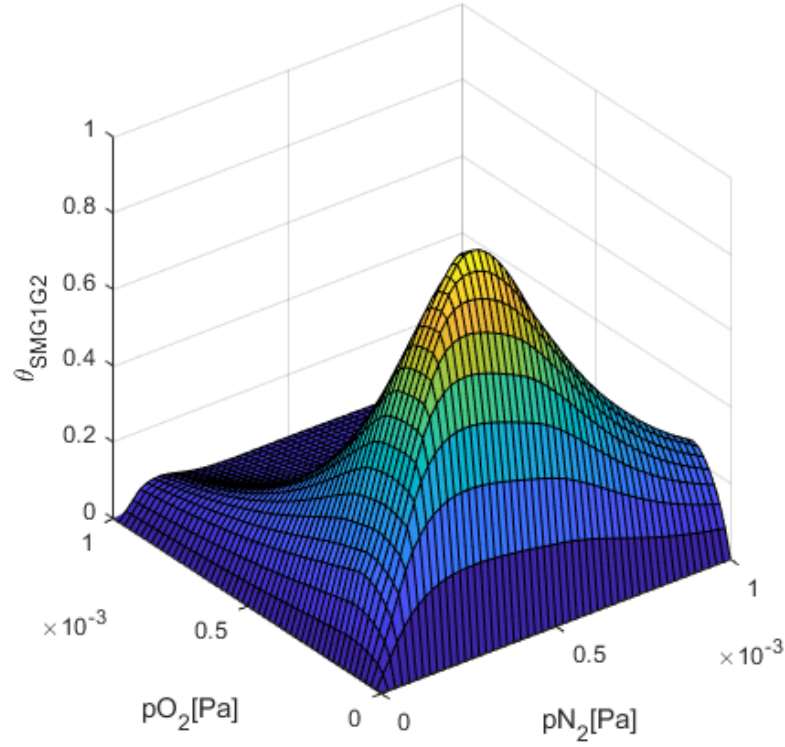


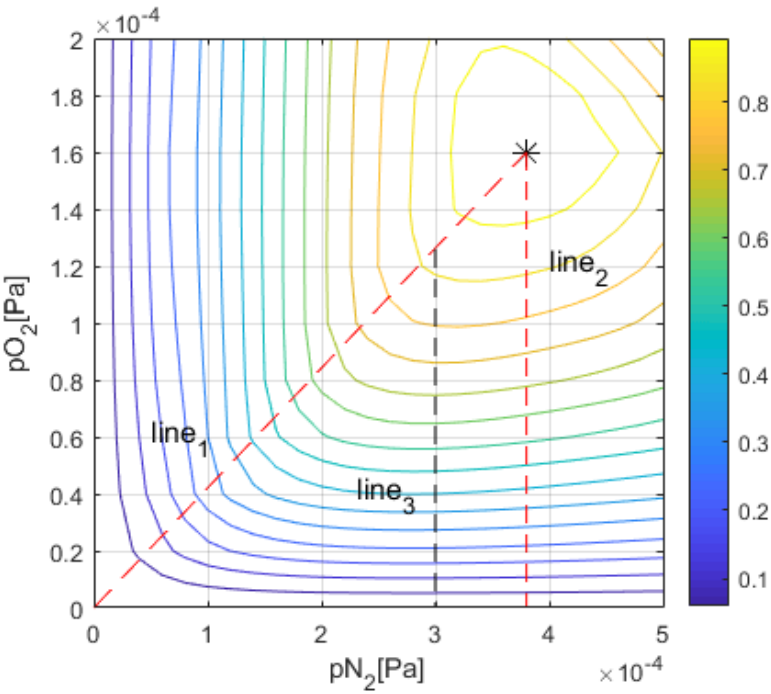
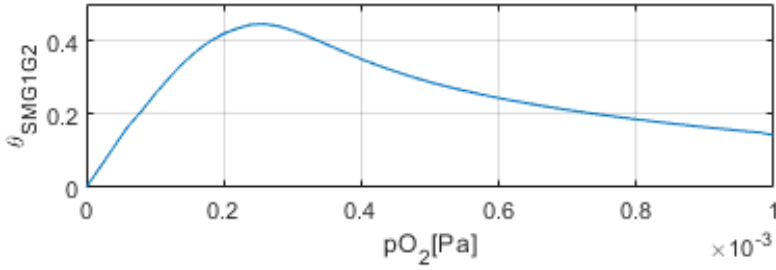
Figure 4.6: Substrate coverage with $\theta_{\text{MG}_1\text{G}_2}$ at $I = 0.1 [\text{A}]$ for different reactive partial pressure combinations [40].

8. $p_{\text{O}_2\text{reflim}} = p_{\text{N}_2}/m_1$
9. p_{O_2} is controlled with q_{O_2}

The corresponding control structure can be seen in Fig. 4.10.

4.3 Results

The sticking coefficients used in this Chapter are shown in equation 4.5.



$$\alpha_S = \begin{bmatrix} 0.1 & 0 & 0 & 0 & 0 & 0.2 & 0 & 0.1 \\ 0.1 & 0 & 0 & 0 & 0 & 0 & 0.2 & 0.4 \\ 0.5 & 0.5 & 1 & 1 & 0 & 0.5 & 0.5 & 1 \\ 0.5 & 1 & 0.5 & 0 & 0.5 & 0.5 & 0.5 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \quad (4.5)$$

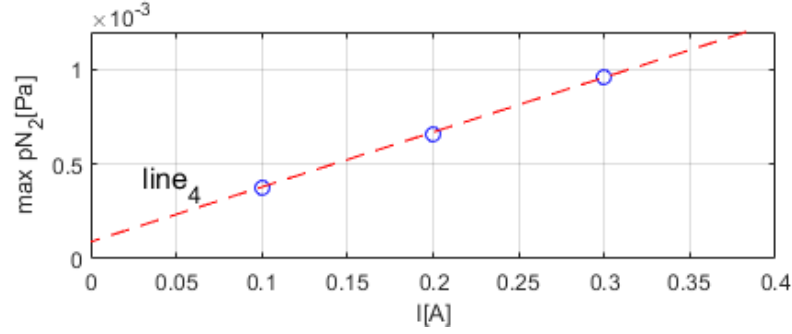


Figure 4.9: Maximum allowed p_{N_2} as a function of discharge current [40].

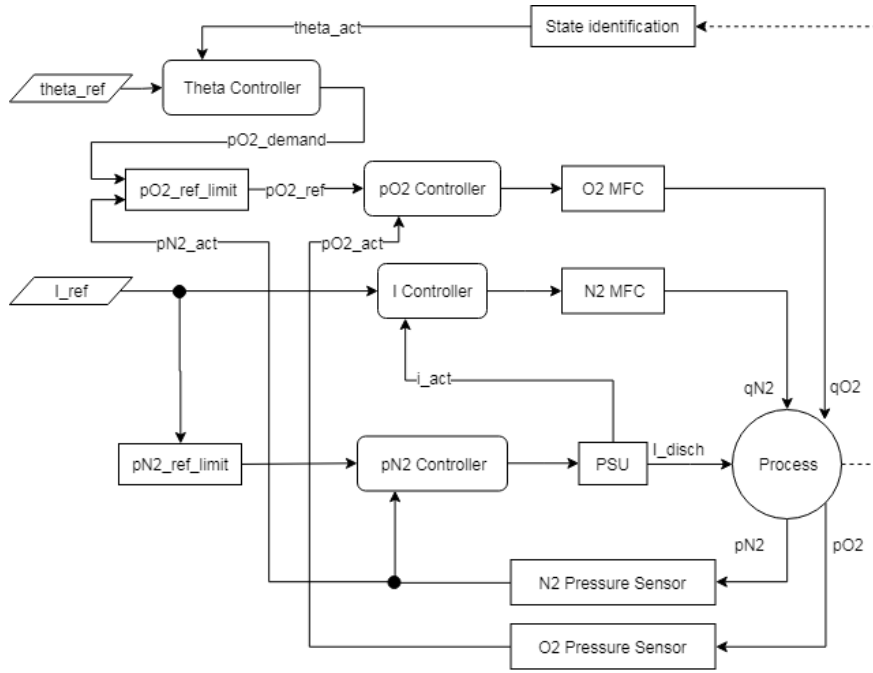


Figure 4.10: Control structure for power and substrate coverage with $\theta_{MG_1G_2}$ [40].

There is a wide variety of possible controllers to use for each of the four control blocks needed. Given that this Chapter focuses on the qualitative demonstration of the operation of a control structure, too much effort hasn't been placed on complex control blocks and their respective tuning, instead

a very basic set of four PI control blocks has been used. The result of the controlled system's response to several separate step inputs is shown in Fig. 4.11.

Control performance depends mostly on accurate parameter identification of the sputtering system in use, performance of the Mass Flow Controllers (MFC) and butterfly valves, the accuracy of the pressure sensing gauges employed and of course on the certainty of the state identification algorithm.

4.4 Overview

A new control algorithm and a corresponding control structure is proposed that provides stable operation of the process using two continuously supplied reactive gases. The novelty of the proposed algorithm consists in the extension of reactive magnetron sputtering control algorithms to the two-gas reactive magnetron sputtering process, and the definition of current-dependent monotony domains in the space of the partial pressures. The stoichiometry of the deposited film is influenced by controlling the amount of coverage of the ternary compound TiO_xN_y on the substrate.

By implementing the proposed limiting algorithms, thus maintaining the operating point on the desired subsurface, the trapped state of the target can be avoided.

The reference inputs of the control structure are practical for thin film growing procedures, offering possibility to define the requested substrate coverage and the sputtering process power, thus the speed of the process. Implementation in engineering practice is conditioned by the successful identification of the substrate surface coverage by the desired compound, and fast partial pressure measurement of the two reactive gases.

Thesis 3. A new control algorithm and a corresponding control structure is proposed that provides stable operation of the process using two continuously supplied reactive gases.

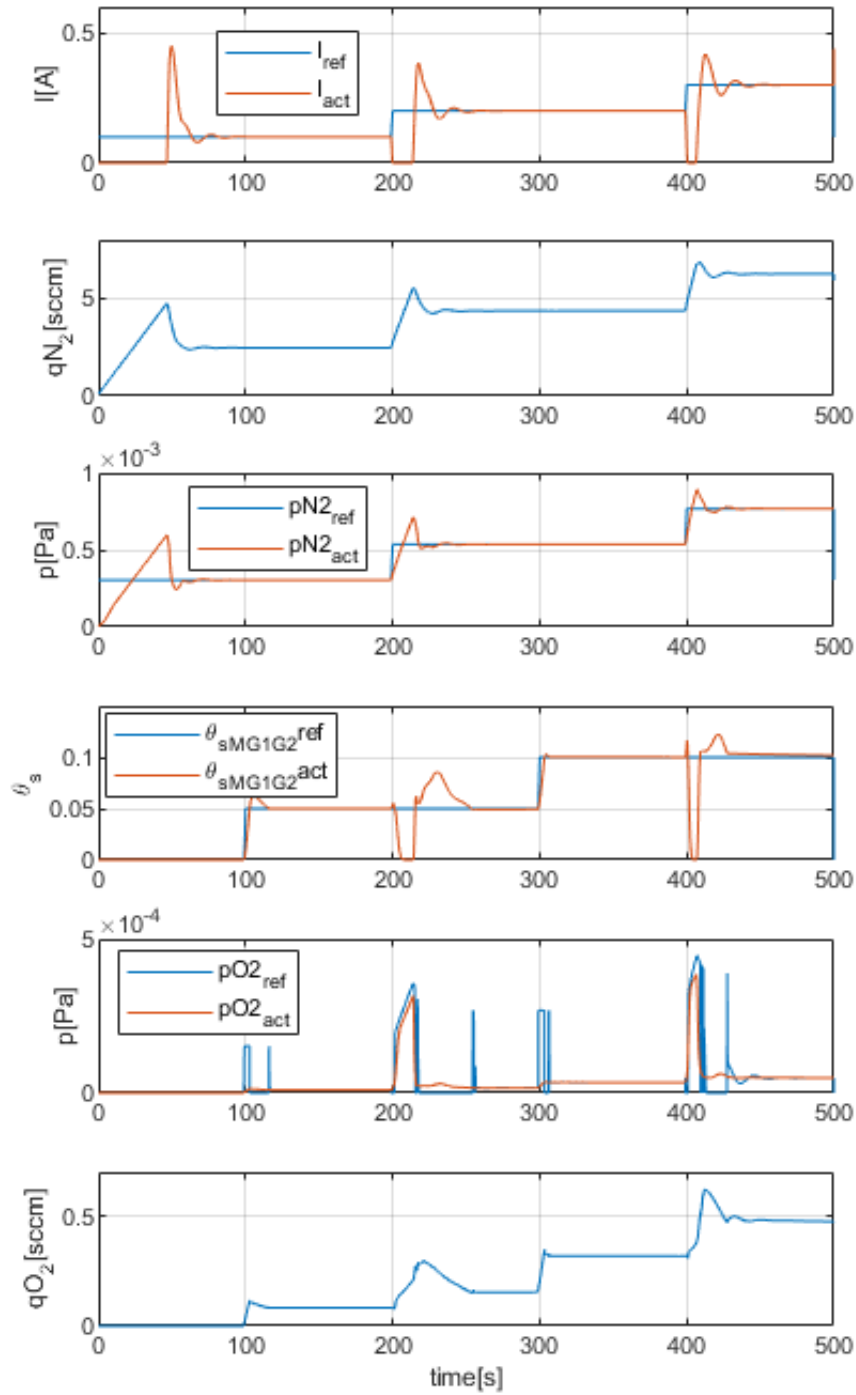


Figure 4.11: The simulation results of the new control structure for several separate step inputs [40].

Chapter 5

Pulsed mode magnetron sputtering

5.1 Introduction

Materials coated with thin films combine the ease of machining and the low cost of the coated material with the special characteristics and benefits of the coating material. The physical vapor deposition processes, widely used for thin film coating, require different types of special power supplies for the ignition and sustaining of the plasma inside the sputtering chamber.

Pulsed DC power can provide several benefits over continuous DC power, including the possibility of avoiding the charge build-up on the target, and modification of the energy distribution of the particles participating in the sputtering and deposition process [89]. Depending on the characteristics of the power supply, one can get different shapes of the discharge voltage and current pulses, associated to phenomena in the plasma that are more or less useful from the point of view of the process. Usually, one can obtain only approximately constant current or constant voltage pulses, but this might not even be a concern, as the target is to obtain the desired technological results.

For the design of the power supply, a good understanding of the interaction between the power electronic converter and the plasma developed in the sputtering chamber is necessary. The operation of the converter depends on the behavior of the load represented by the magnetron sputtering chamber with different states of the plasma, while the phenomena in the plasma are influenced by the output impedance of the power supply.

The objective of this Chapter is the identification of some parameters of a

magnetron sputtering chamber that are essential for its actual operation in DC mode and which offer a basis for the design of a pulsed DC converter.

The main aspects are related to the ignition of the plasma and current control based on well-known switched mode converter topologies [117].

The Chapter is structured as follows: in section 5.2 various plasma ignition techniques are presented. In section 5.3 a current control structure and topology is proposed that is also suitable for plasma ignition. The results obtained with the help the practical implementation are presented in section 5.4. The conclusions and the relevance of the Chapter are presented in section 5.5.

5.2 Plasma ignition procedures

5.2.1 Plasma ignition by pressure control

In case of the presently used DC magnetron sputtering operation mode of the equipment described in [90], the plasma ignition procedure takes advantage of the reduction of the breakdown voltage with the increase of the argon gas pressure. The pressure range for sputtering is 0.26...0.39 Pa. Due to the fact that the voltage limit of one of the DC power supplies used is only $U_{\max} = 800$ V, and a voltage ramp is implemented at start-up, it was necessary to use pure argon for ignition at an increased pressure of 0.66 Pa. These parameters have been supported by the measurements presented in section 5.2.2.

The Matlab Simulink® simulation results of the start-up algorithm are shown in Fig. 5.1. The model makes use of the results presented in [33], while the practically proven ignition procedure has been presented in [91]. The actuator for this operation is a throttle valve placed at the inlet of the turbomolecular pump.

Even if a relatively fast pressure control is possible by this means, it is evident that in case of pulsed power mode the power electronic converter has to deal with the task of plasma ignition.

5.2.2 Identification of the V-I characteristics of the discharge

The transition between the dark and glow discharge phases is characterized by a voltage drop and a current increase [92]. In order to identify the V-I characteristics of the vacuum chamber in discussion, the parameters of the load line defined by the circuit from Fig. 5.2, have been modified with the help of a variable resistor and a variable voltage supply. The operating points are obtained by manually sweeping the output voltage of a decadic voltage source

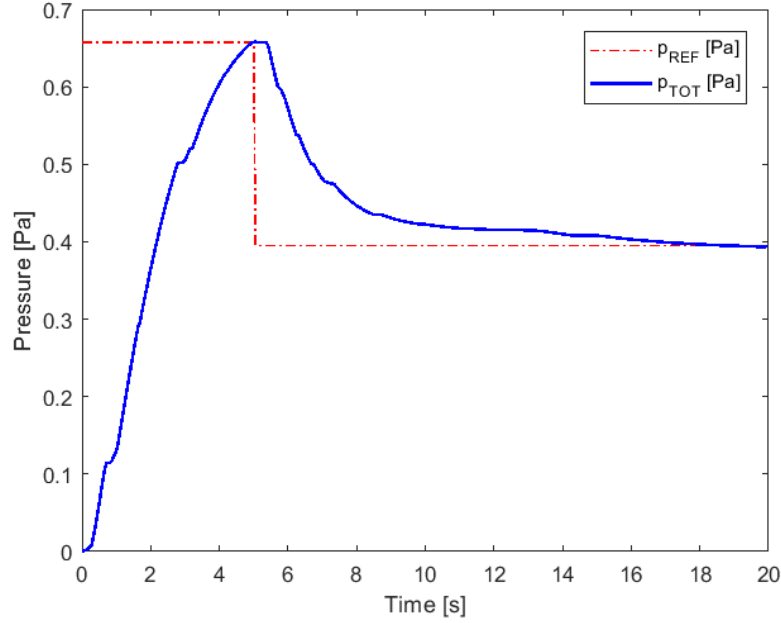


Figure 5.1: Simulation results of the pressure control algorithm used for plasma ignition in case of a DC magnetron sputtering application [117].

type Fluke 410B (10 kV, 10 mA) (in the usable power limited range), as seen in Fig. 5.3. Despite the low current limit of the available voltage source, it was possible to identify the voltage range of interest to ignite and sustain the glow discharge. In Fig. 5.3 it can be observed that certain operating points (ex. point no. 8) can be reached only on the decreasing slope of the supply voltage.

Fig. 5.4 shows the measured operating point sets with the use of different gases and gas mixtures at different chamber pressures. It can be observed that the ignition voltage is substantially higher in case of nitrogen (up to 1.6 kV), a fact that supports the procedure of ignition in pure argon, presented in section 5.2.1.

5.2.3 Plasma ignition by voltage impulses

Pulsed mode magnetron sputtering requires repeated ignition of the glow discharge. In order to study the transient response of the system, a 1 kV voltage

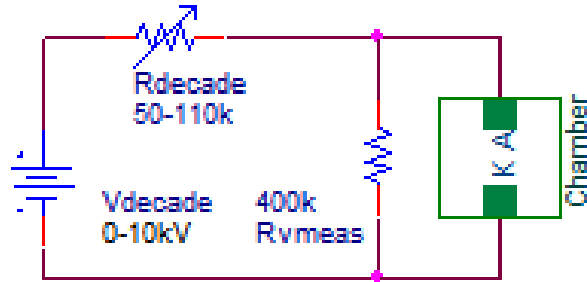


Figure 5.2: The circuit used to establish the load line for the identification of the discharge characteristics [117].

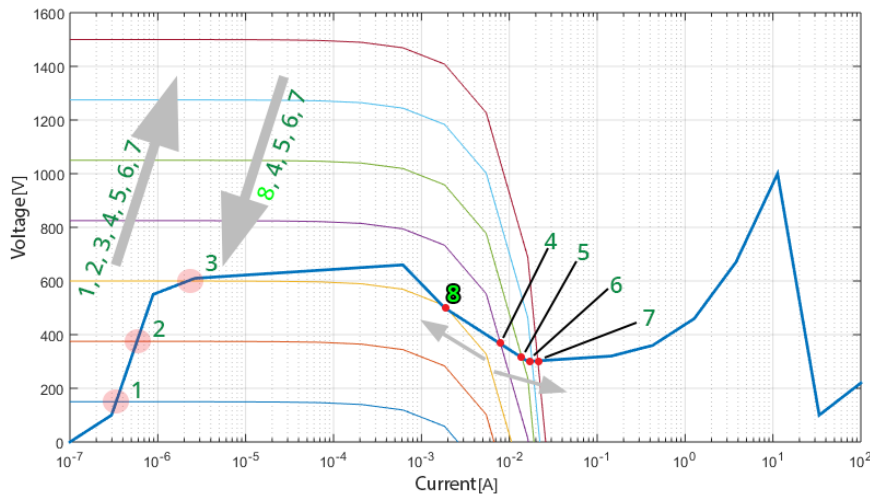


Figure 5.3: The principle of the identification of the discharge characteristics by means of the operating points established using the circuit from Fig. 5.2 [117].

source has been used. The voltage source charges a buffer capacitor which is switched onto the load with the help of an IGBT transistor (see Fig. 5.5). All current measurements in this article were undertaken with the help of a 0.25 Ω coaxial shunt. Measurements with this coaxial shunt have a transformation ratio of 4 A to 1 V.

Since the dark to glow transition requires an ionization effect to take place (the Townsend avalanche), there is a noticeable time delay between the ap-

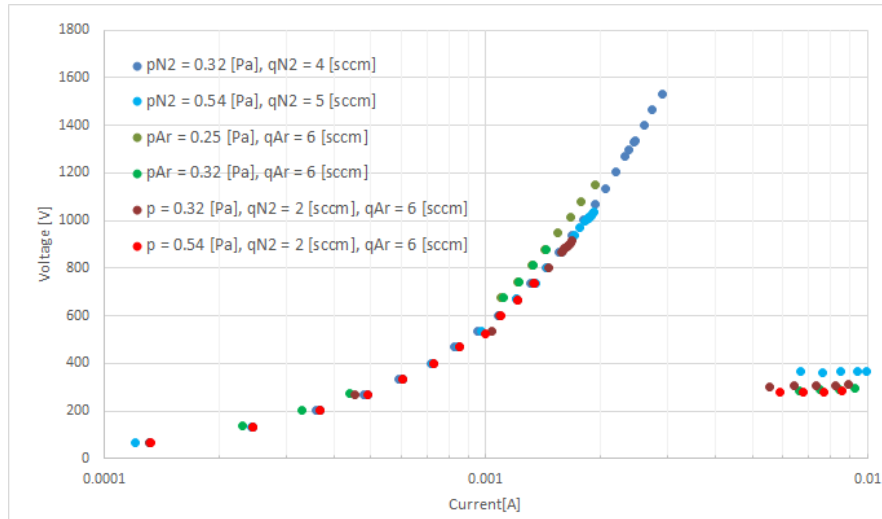


Figure 5.4: The dark and normal glow regions of the discharge characteristics determined using the circuit from Fig. 5.2 for different pressures and gases [117].

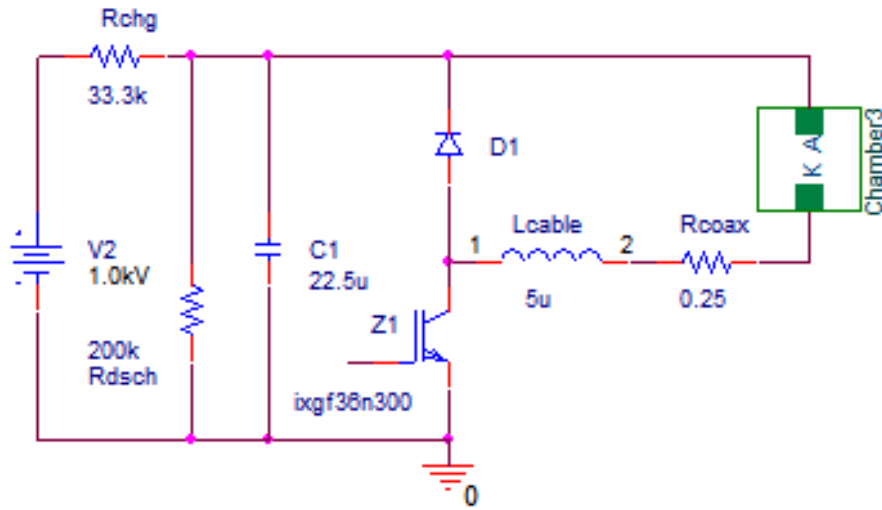


Figure 5.5: The circuit used for the voltage impulse test of the sputtering chamber [117].

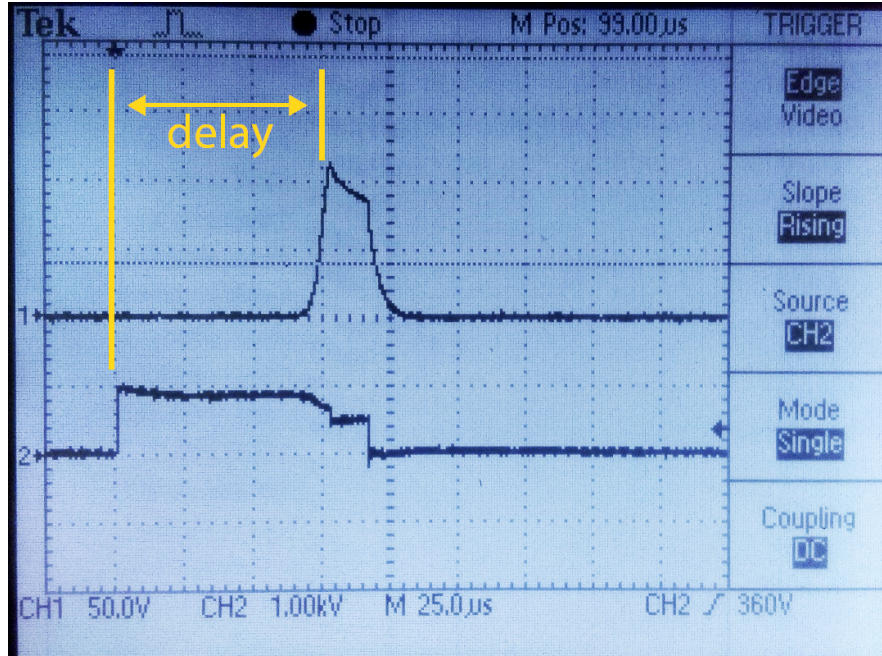


Figure 5.6: Voltage pulse (CH2) applied to the sputtering chamber and the delayed discharge current (1 V $\equiv$ 4 A). The arc is turned off after a controlled delay [117].

plication of the voltage and the occurrence of the chamber current (see Fig. 5.6). It is important to note that direct application of an ideal voltage source to a vacuum chamber results in arc discharge (see the current spike $I_{\text{peak}} = 400$ A in Fig. 5.6). This time delay has been examined and mathematically modelled in [93]. Similar results, shown in Fig. 5.7 have been obtained by practical measurements with the help of the circuit from Fig. 5.5.

This large delay time necessary for the build-up of the plasma represents one of the difficulties to be handled in case of the pulsed power magnetron sputtering.

5.2.4 Plasma ignition by current impulses

The desired glow discharge regime can be obtained using controlled current impulses. Fig. 5.8 presents a circuit suitable for the generation of a series of impulses, illustrated by Fig. 5.9. The increased ignition voltage resulted by the application of the current impulse to the sputtering chamber contributes

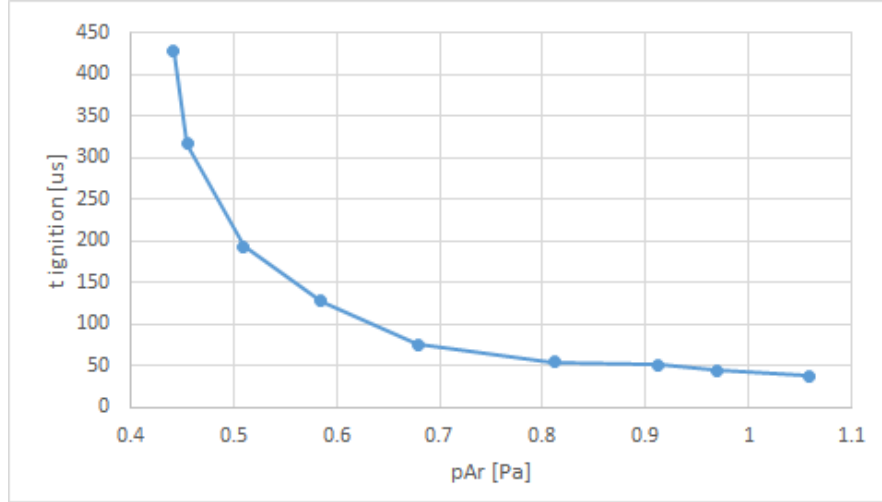


Figure 5.7: The delay of the discharge current pulse versus the chamber pressure in the presence of argon gas at $q_{\text{Ar}} = 6$ sccm [117].

to the reduction of the chamber current delay explained in section 5.2.3.

Since the vacuum chamber does not provide any instant current path for the Boost converter inductor, the switching device used must be protected from overvoltages by either a snubber [94] or a transient voltage suppressor network. As a first test, its switching device has been driven with 5 impulses (see Fig. 5.9). The aftermath of the first impulse is a 1.8 kV voltage spike that is limited only by the transient voltage suppressor network. The following 4 impulses almost instantly ignite the plasma without any long duration high voltage spike. This phenomenon can be explained with the presence of positive ions in the chamber, that are left over from the first ignition. The presence of these ions contribute to easier further plasma ignitions [95].

5.3 Control of the discharge current

Once the plasma has been ignited, control of the discharge current is the main control task for the converter. The fast transient behavior of the converter is largely influenced by its passive components, while its steady-state characteristics can be established by the control mode. The control structure shown in Fig. 5.10 has been proposed for this task. Fig. 5.11 presents a converter topology based on the topology from Fig. 5.8 that has been extended with

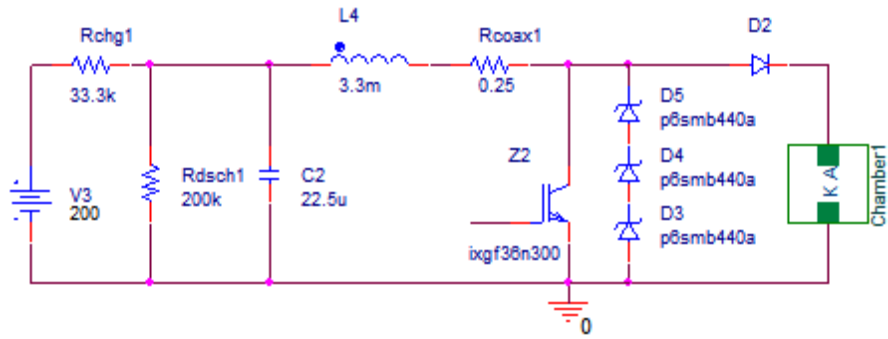


Figure 5.8: The boost converter used for controlled amplitude discharge current pulse generation [117].

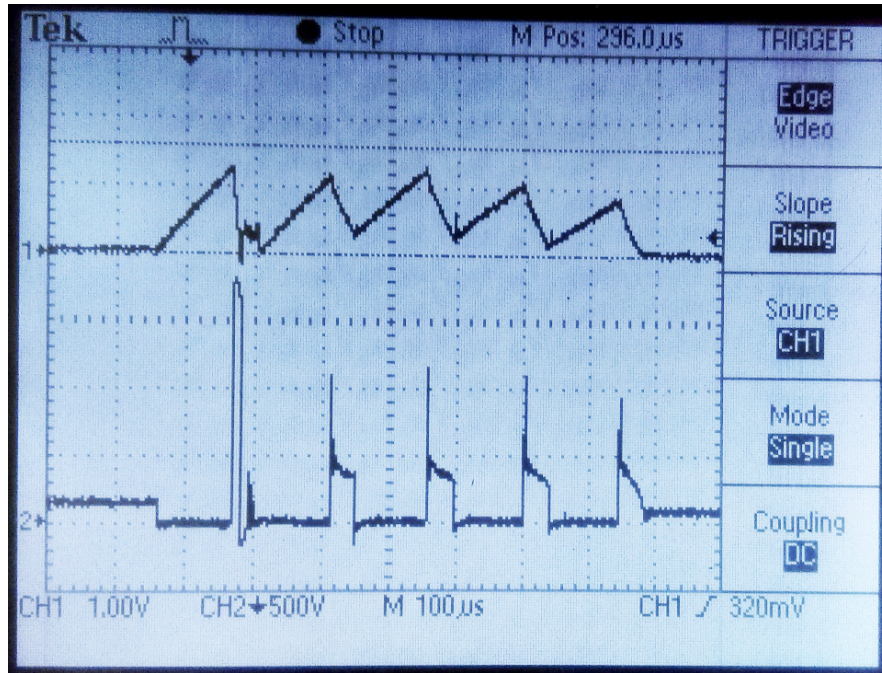


Figure 5.9: The inductor current (CH1, 1 V $\equiv$ 4 A) and the sputtering chamber voltage (CH2) in case of repetitive ignition using the circuit from Fig. 5.8 [117].

a chopper. The inductor current is controlled by a hysteresis current controller, both during the energy accumulation phase that precedes the ignition

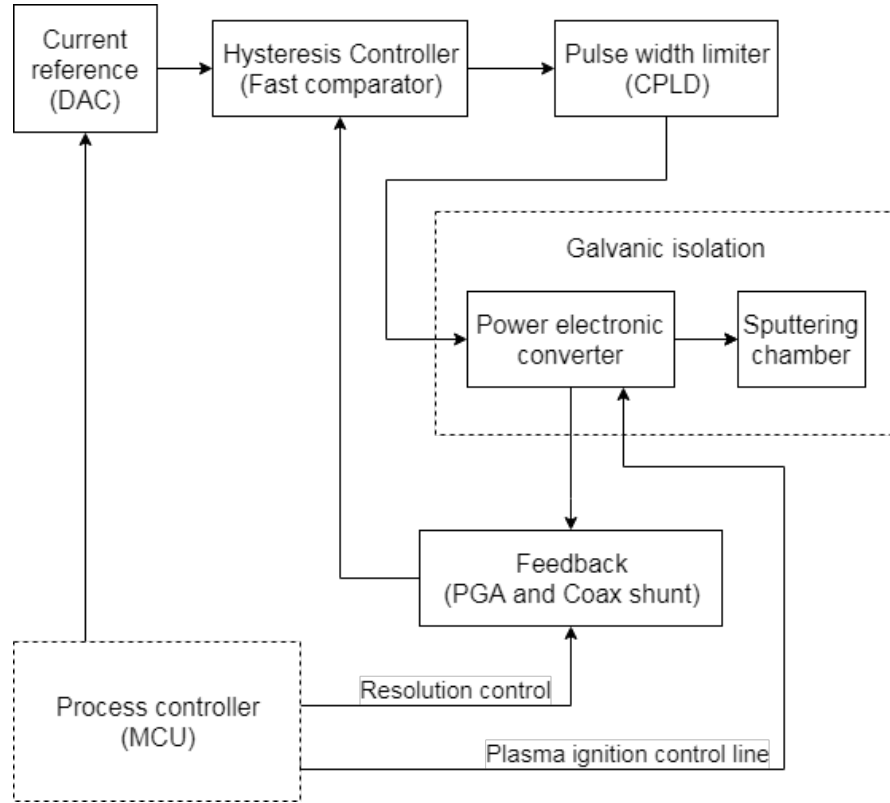


Figure 5.10: The block diagram of the control structure [117].

and during the glow discharge phase. The current is measured using a coaxial shunt. The voltage of the coaxial shunt is amplified with the help of a Micro-Controller Unit (MCU) driven Programmable Gain Amplifier (PGA). This amplified voltage, in turn, is compared to a reference voltage provided by the MCU driven Digital to Analog Converter (DAC). The output of the comparator is fed into a pulse width limiting block, which provides a lower limit for the time between transitions (see Fig. 5.12). The pulse width limiter has been implemented in VHDL and runs on a Xilinx Complex programmable logic device (CPLD). The output of the CPLD drives a couple of optical fiber links that control the driving units of the Z_{ch} and Z_{cs} transistors.

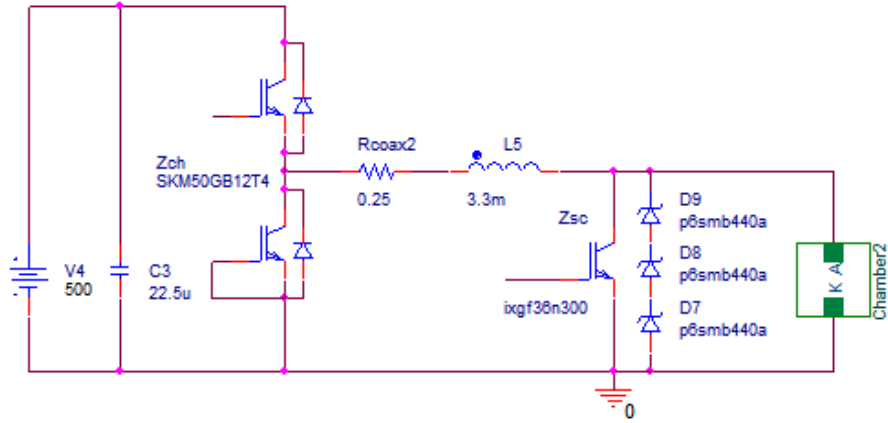


Figure 5.11: The converter topology applied for discharge ignition and current control [117].

5.4 Results

The proposed topology has been built and tested on a vacuum chamber with a supply of $q_{Ar} = 6$ sccm argon gas at a controlled chamber pressure [90] of $p_{Ar} = 1.04$ Pa.

The practical implementation ramps up the inductor current to 2.5 A in 150 ms (see Fig. 5.13).

The Z_{SC} transistor turns off using 25 $t_{per} = 600$ μ s impulses with a duty cycle of $d_{imp} = 50\%$ in order to ignite the plasma (see Fig. 5.14).

After ignition, the initial 2.5 A current reference is lowered to 0.5 A (see Fig. 5.15).

All measurements presented have been undertaken with the help of a Tektronix TDS 210 oscilloscope, a 15 kV 1:1000 high voltage probe and with the help of a coaxial shunt.

5.5 Overview

Pulsed mode magnetron sputtering puts special conditions on the applied power supply. These include the ability for repeated and fast ignition of the gas discharge, fast current control and arc handling.

A magnetron sputtering chamber has been investigated in order to establish the specific design criteria needed for the implementation of a pulsed mode

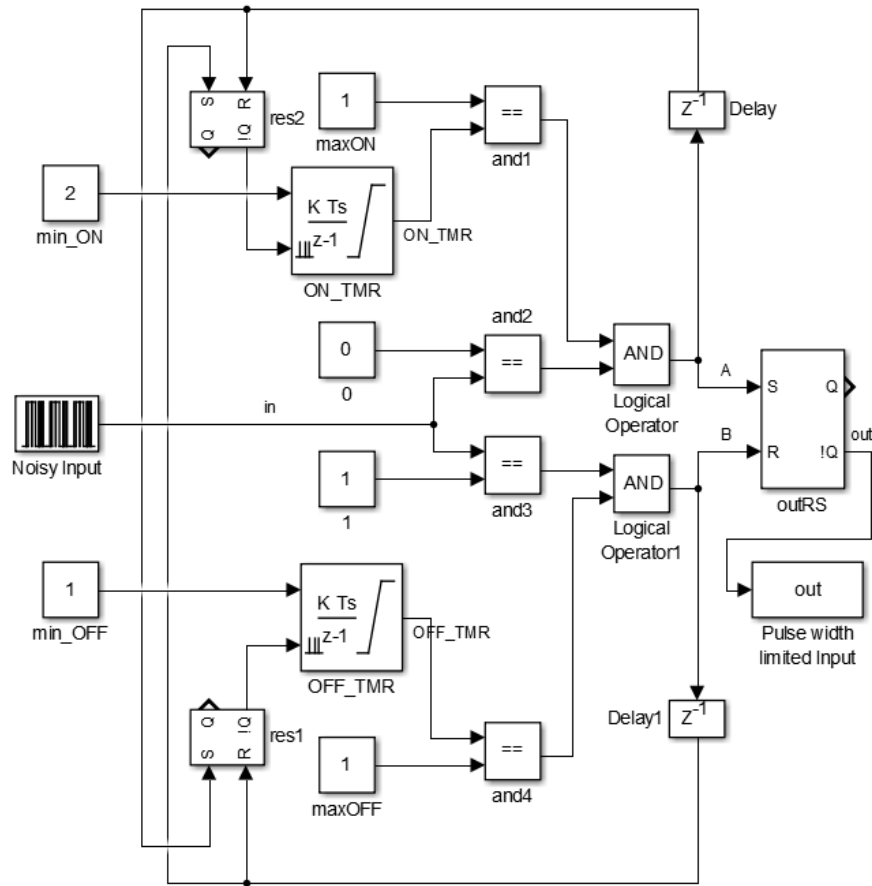


Figure 5.12: The structure of the pulse limiter block implemented in the CPLD [117].

power supply. The investigation includes the study of the current-voltage characteristics, the determination of the ignition voltage and the measurement of the current impulse delay for different gases and pressures.

A current controlled power supply has been presented that is suitable for use with both high impedance and low impedance loads, characteristic for different states of the plasma in magnetron sputtering applications.

The presented power electronic converter has been implemented and tested on a vacuum chamber where it has been demonstrated to be suitable for plasma ignition and current control of the glow discharge.

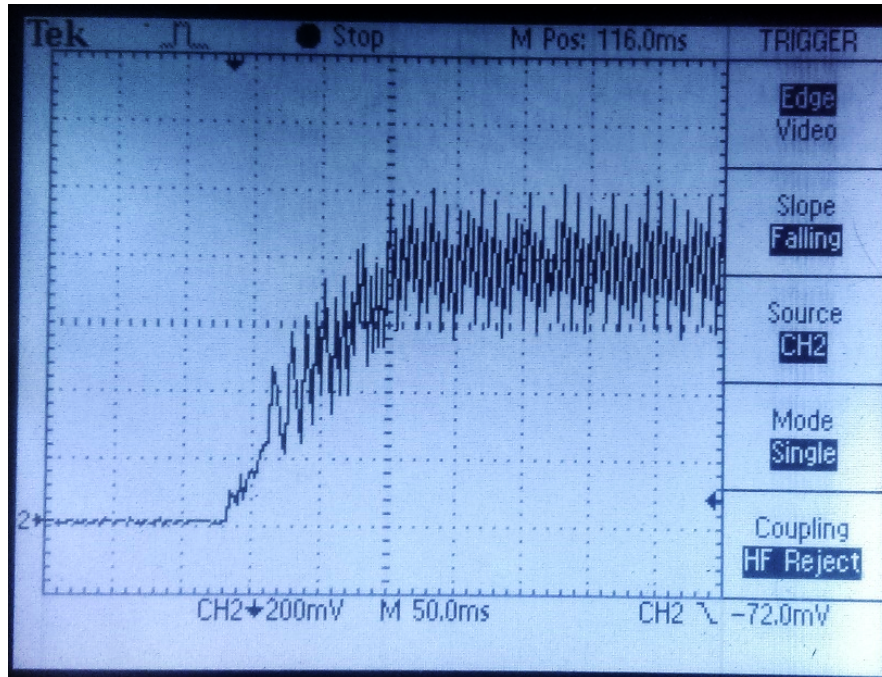


Figure 5.13: Current ramp-up during the magnetization of the inductor preceding the discharge ignition ($1 \text{ V} \equiv 4 \text{ A}$) [117].

Arc handling can be solved in a straightforward manner, based on the current design.

Thesis 4. A current controlled power supply has been presented that is suitable for use with both high impedance and low impedance loads, characteristic for different states of the plasma in magnetron sputtering applications.

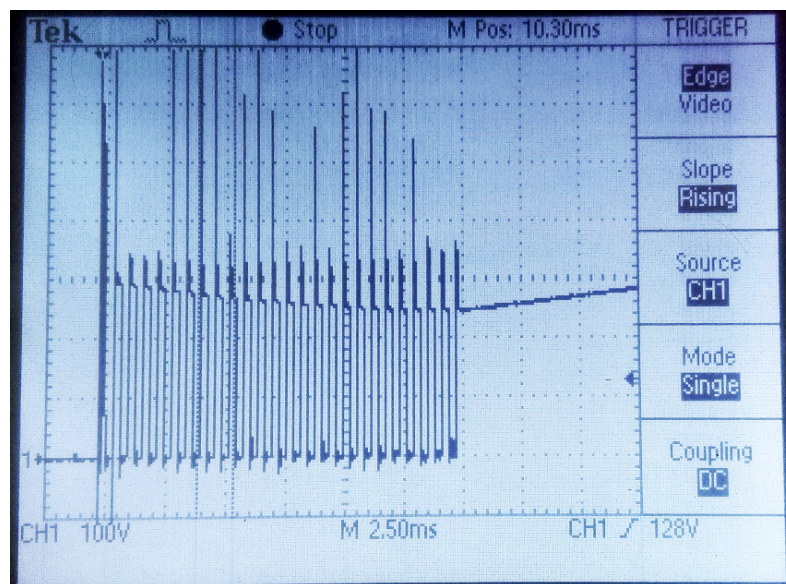


Figure 5.14: The voltage of the sputtering chamber (CH1) during the ignition pulse set [117].

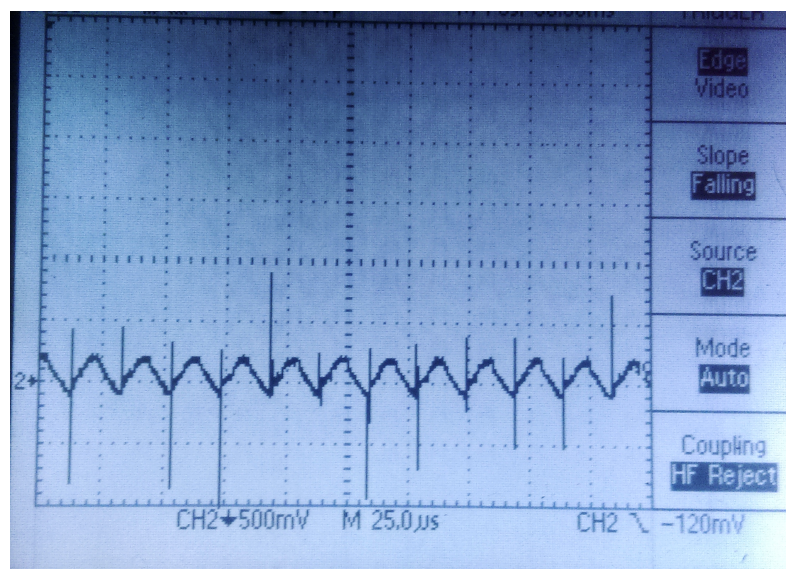


Figure 5.15: The controlled sputtering chamber current (CH2, 1 V $\equiv$ 4 A) [117].

Chapter 6

Behavioral modeling

6.1 Introduction

Materials coated with thin films combine the ease of machining and the low cost of the coated material with the special characteristics and benefits of the coating material. These thin films can be produced from a few atom layers to a few tens of microns in thickness.

Due to their special physical and chemical characteristics, they have been widely applied as wear-resistant, self-lubricating, anticorrosive, optical, photocatalytic, decorative, or other type of coatings in many areas ranging from the semiconductor technology and biomedical applications to manufacturing of hard-coated machining tools, low-friction bearings and high-performance valve trains.

The special crystallographic structures found in thin film applications can't be manufactured in bulk form, whereas their production as thin layer coatings is relatively straightforward using Physical Vapor Deposition (PVD).

A traditional physical vapor deposition method is the DC magnetron sputtering [96]. In the last decades the sputtering deposition technologies have been significantly advanced by the application of pulsed discharges, which can overcome the disadvantages of the reactive DC magnetron sputtering and open new perspectives due to the increase of the ionization level in the discharge plasma.

These pulses can be supplied by special converters, which have to be designed taking into account the characteristics of the discharges in pulsed mode. The aim of this study is the synthesis of a simple behavioral model that can represent the interaction between a magnetron sputtering chamber and the

power electronic converter used as electrical energy supply.

There can be identified a multitude of factors that influence the behavior of the interconnected system formed by the converter and the magnetron discharge, such as:

- Non-electrical parameters such as the pressure of the inert gas used for sputtering, the partial pressure and type of different reactive gases, the material properties and temperature of the target, and the mechanical layout of the sputtering chamber;
- The layout of the magnetron system and the spatial distribution of the magnetic field;
- The presence of independent electron sources, ionizing fields or radiation;
- The method used for discharge ignition;
- The state of the target, of the substrate, and of the plasma, in correlation with the process control method;
- The circuit parameters of the power supply;
- The parasitic electrical parameters of the sputtering chamber and of the interconnection network;
- The arc handling circuit and method;
- The parameters of the supplied energy (frequency, voltage and current magnitude and pulse shape, the output current-voltage characteristics and limits of the power supply).

In case of the DC magnetron sputtering, the power electronic converter plays the role of a controlled current source with voltage and power limitation, and the main issues are the sputtering process control, and the arc handling, with apparently less influence of the converter topology.

On the other hand, AC and pulsed sputtering processes rise more problems of impedance matching, and there exists a strong interaction between the driving circuit topology and control strategy, and the magnetron discharge.

This chapter presents considerations regarding the pulsed magnetron discharge that influence the behavior of the driving converter, and which influence the feasibility of a proposed topology, with operation based on magnetic energy storage [129].

6.2 Pulsed power applied in the magnetron sputtering process

The pulsed power discharge technology is used in plasma-based physical vapor deposition (PVD) for at least two reasons. First, the deposition of dielectric films is made possible by the so-called pulsed DC magnetron sputtering. In case of this technology, arcing accompanying the reactive DC magnetron sputtering process is prevented by asymmetric bipolar pulsing, i.e. by the insertion of discharging time periods between the active sputtering voltage pulses, which are necessary to neutralize the positive charges accumulated on the dielectric layer formed on the target surface [97, 98, 99]. It is also shown, as explained in [100], that the use of bipolar pulsing results in preferential sputtering of the insulating layer, thus reducing the target poisoning.

The second reason for using pulsed power is related to the desire to increase the ionization level in the magnetron discharge, thus influencing the formation of the deposited film on the substrate. Several effects result in the possibility of technological enhancement in case of increased ionization level. These range from the possibility of controlled ion bombardment of the substrate surface to the influences on the microstructure of the deposited thin film [101].

The increased ionization (leading to the so-called Ionized Physical Vapor Deposition- IPVD, when the ions are preponderant in the deposition flux) can be obtained in a couple of ways. A secondary discharge can be applied to the magnetron discharge by radiofrequency inductive coupling or using a microwave field [102]. Increased plasma density can be obtained also using a special magnetic geometry (Hollow Cathode Magnetron- HCM) [103], and an extreme density of the sputtered target material ions is obtained in case of the Self-Sustained Sputtering (self-sputtering) [104]. There exist also technologies, which use an independent electron source to increase the ionization level inside the sputtering chamber [105].

A relatively recent method of increasing the discharge ionization level is the High Power Impulse Magnetron Sputtering (HiPIMS) [106], mentioned also as High-Power Pulsed Magnetron Sputtering (HPPMS). The HiPIMS process itself can result in self-sputtering “runaway” [107].

6.3 Characteristics of the pulsed magnetron discharge

In this Chapter I attempt to derive a simple model of the magnetron discharge, which can support the design of the power supply unit. From this perspective,

knowledge of the current- voltage characteristics of the magnetron sputtering discharge is required.

The classical DC magnetron sputtering operates in the abnormal glow discharge region, at current densities below $1 \frac{\text{A}}{\text{cm}^2}$ [108]. In this region, the discharge voltage increases with the discharge current, and proper conditions for the ion bombardment of the target can be obtained.

It is clear, that the discharge voltage depends on several factors, among which the layout of the magnetron system, the magnetic field parameters, the gas pressure, and the material properties of the target. It is also known that in case of the reactive magnetron sputtering, the discharge voltage depends on the state of the target due to its influence on the secondary electron emission yield [109].

In this study, it is considered, that these conditions are represented by the model parameters of the current-voltage characteristics.

In case of the steady-state magnetron discharge, besides detailed physical modeling, attempts have been made to empirically fit the experimental voltage-current data of the magnetron discharge to characteristics described by relations type

$$i_d = k u_d^n \quad (6.1)$$

where $n \in (1 \dots 10)$ is considered to describe the trapping efficiency of the electrons by the magnetic field [110]. For example, [111] found a good fitting by interpolation for $n = 4.7$ in case of a discharge operating at $p_{Ar} = 0.5 \text{ Pa}$. However, due to the fact that this relation overestimates the current at low voltage [110], relations type

$$i_d = \beta (u_d - U_0)^m \quad (6.2)$$

have been considered, with best fit for $m = 2$. In the above relation, U_0 is the minimum voltage for which the discharge is sustained, and is similar to the current-voltage characteristic of the diode sputtering systems.

In the behavioral model presented in this study the discharge voltage is generated by a controlled voltage source according to a relation derived from the above one, for the parameter set

$$\begin{cases} U_0 = 480 \text{ V} \\ \beta = 1 \cdot 10^{-4} , \\ m = 2 \end{cases} \quad (6.3)$$

thus

$$u_d = u_0 + \sqrt{\frac{i_d}{\beta}} . \quad (6.4)$$

However, in pulsed mode, the time dimension is added to the problem, and the evolution in time of the discharge voltage and current can be determined by numerical simulation based on the mathematical model of the discharge (ex. on a fluid model [112]).

It has been shown, that commonly used current-voltage characteristics are not adequate in case of high-power impulse magnetron sputtering, and complex time-dependent phenomena take place such as the transition in time of the discharge from the inert gas ion sputtering towards a significant contribution of self-sputtering [113].

In the perspective of a behavioral modeling, at least the following aspects have to be considered [114, 115, 116]:

- The influence of the applied voltage on the delay of the current pulse onset;
- The influence of the residual charge on the current onset delay;
- The influence of the residual charge on the ignition voltage.

It has been shown by a number of studies that there can exist a delay of up to a couple hundreds of microseconds between the voltage pulse and the onset of the discharge current (Fig. 5.6 [117]), influenced by the ignition voltage level, the gas composition (and partial pressures of the components), and the initial plasma density from the sputtering chamber [106, 107]. For this reason it can happen that a very short voltage pulse can't ignite the discharge at all [100].

It has been shown that pre-ionization can reduce the delay by ten times [113]. In case of the medium-frequency pulsed DC sputtering it has been observed, that the shorter off-times, and the corresponding increased availability of the residual charges result in the decrease of the ignition voltage peak [118].

A similar effect can be observed in the simulation results from [112].

It is generally accepted that the ignition delay is composed of a so-called statistical time lag and a formative time lag. The first one corresponds to the apparition of the initial electrons between the electrodes, while the second one is necessary for the development of the discharge [107, 100, 119]. It is

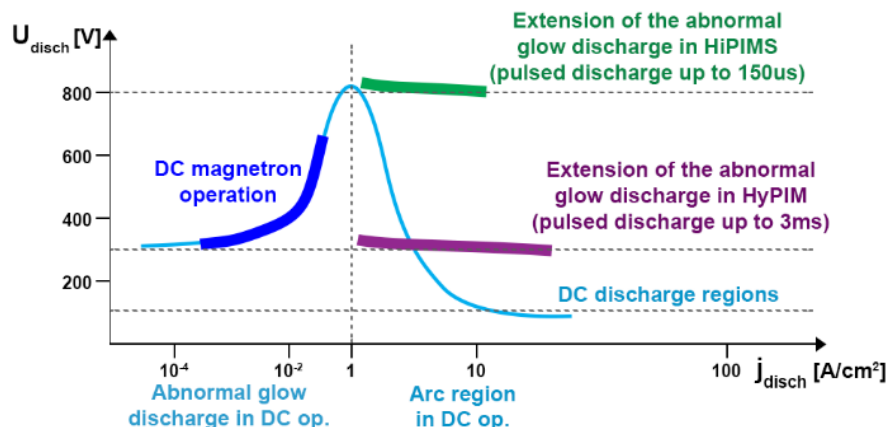


Figure 6.1: Examples for the different types of pulsed power operation, overlaid on the classical V-I characteristic of a gas discharge in DC operation [129].

shown in [120] that the delay is a function of the applied voltage, and that the statistical time lag is negligible in comparison with the formative time lag, which is mainly determined by the inertia of the ions. In [107] it is declared that also the formative time lag can be “practically eliminated” in case of the existence of a substantial initial plasma density. This is the case of the pre-ionization, and this effect should be taken into account also in case of repetitive pulses.

Recent research works have shown that different regions of the well-known current-voltage characteristic of the stationary plasma discharge can be extended well beyond their stationary limits [102, 109] (Fig. 6.1 [108]).

6.4 Characteristics of the applied pulses

In case of the pulsed DC magnetron sputtering process, medium-frequency asymmetric bipolar pulses are applied to the target. The negative active pulse is followed by a low magnitude (below 100V) “discharging” pulse. Sufficient length of these time periods with voltage reversal is necessary for the residual electrons from the plasma to discharge the dielectric layer, otherwise a gradual charge accumulation causes arcing. At the same time, the length of a single active pulse has to be limited to prevent the volume or surface creepage breakdown of the dielectric film. It results, that in this process there exists a

critical lower limit of the pulsing frequency ($20 - 350\text{kHz}$) and a critical upper duty cycle of the pulses ($0.5 - 0.9$) [98], with higher duty factors possible at higher frequencies [121].

Various methods have been explored to produce high-voltage discharges necessary for sputtering, producing in the same time a high level of ionization, while avoiding the transition of the discharge into an arc.

It has to be mentioned that, cathodic arc deposition is also a Physical Vapor Deposition (PVD) method widely used in industrial applications, which assures a high level of ionization of the evaporated metal particles, but the magnetron sputtering is a “gentler” process, which provides better stoichiometry control, with fewer defects [123]. The cathode hot spots formed in an arc discharge emit droplets that compromise the deposited layer obtainable by sputtering.

In case of the HiPIMS, short ($100 - 150\mu\text{s}$), very high power pulses (in the MW range) are applied to the target, but with a low repetition frequency ($< 500\text{Hz}$) in order to limit the average power. The large specific power ($1...3\text{kW}$) on the target surface results in significant ionization of the sputtered particles, which in turn results in the improvement of the deposited film properties [121, 124].

The low repetition frequency is explained by the fact that the average target power has to be kept at low level, despite of the huge instantaneous target power during the active pulse (two orders of magnitude larger [125, 100]).

Intensive research work has been invested to push the limits of the pulse length, keeping the discharge in a quasi-steady state of high current and high voltage, without transitioning into the arc discharge regime. This is made possible by the delay of the cathodic hot spot formation [107].

Hyper Power Impulse Magnetron (HyPIM) glow discharge has been reported by [11], with 1 ms pulse length and above $30\frac{\text{A}}{\text{cm}^2}$ current density. The voltage of this type of discharge is in the range of $300 - 400\text{V}$, well above the voltage of an arc, but below the discharge voltage in case of DC magnetron sputtering, as shown in Fig. 6.1.

Further development of the HiPIMS technology has been made by pre-ionization preceding the high-power impulse. This can be obtained either by superposition of the high-power impulse on the DC magnetron discharge, or by first producing a weak ionization pulse segment, followed by the strong ionization pulse segment, called Modulated Pulsed Power Magnetron Sputtering (MPP). This pulse shaping can be obtained by pulse width and pulse frequency modulation of the voltage micro-pulses applied to the sputtering chamber. By the application of the MPP technology, very high power im-

pulses of $3000\mu\text{s}$ pulse width can be obtained without transitioning into an arc discharge (Fig. 6.1). The deposition rate can become higher, than in case of DC sputtering, and it can even reach the rate of the cathodic arc deposition [124, 126, 107].

6.5 Pulse shaping principles, and circuit topologies

In principle, the pulse energy can be delivered to the magnetron discharge from an inductive or capacitive storage by power electronic converters capable of shaping the voltage and current waveform in the desired manner. Initially, waveform shaping limitations had been experienced due to the limitations of the available power switches. Based on the thyristor technology, the pulsed discharge for magnetron sputtering was produced using “pulser” circuits known from other pulsed power applications. In this case, the semi-controlled nature of the thyristor set limitations on the instants and frequency of switching. For instance, high power impulse could be produced by fully discharging a capacitor with moderate capacity on the magnetron sputtering chamber. This resulted in a variable pulse voltage with the pulse length imposed by the parameters of the circuit components [100].

With the advent of the IGBT technology, which provides high voltage, high current, and sufficiently fast switching devices, the versatility of these circuits has been increased significantly.

The magnetron discharge is initiated by an overvoltage generated by a transient circuit process.

In case of a capacitive storage, the ignition can be obtained by the resonant charging of the sputtering chamber capacitance [100].

In case of an inductive storage, it's straightforward to produce the ignition voltage by interrupting the inductor current. Magnetically coupled inductors can be used to increase the ignition voltage, and to generate the “discharging” voltage in case of the asymmetric bipolar magnetron sputtering [100].

It's a major requirement to the power supply that the arc regime is avoided in order to prevent the deterioration of the deposited film properties. Thus, efficient detection and suppression of the arc is additionally required in cases when its formation can't be prevented [121].

In pulsed operation the beginning ($\sim 100\mu\text{s}$) of the pulse is not critical from this point of view, as a highly ionized state can be reached without transitioning to the arc regime.

The arc energy has to be reduced as much as possible by shunting the power

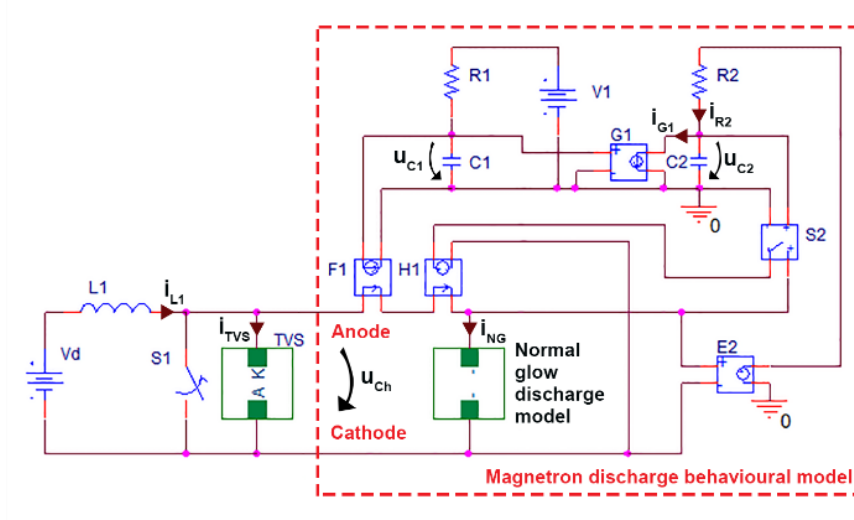


Figure 6.2: Simplified diagram of the behavioral model of the magnetron discharge supplied by a pulse generator with inductive energy storage [129].

delivery to the chamber, and even applying a reversed polarity voltage to sweep out the residual charge carriers [127, 100].

6.6 The converter discharge interaction

In order to study the interaction between the power electronic converter and the sputtering chamber in pulsed discharge mode, I propose a behavioral model implemented in pSpice.

The converter topology proposed in this Chapter resembles the “chopper” pulser with inductive energy storage. Its topology, along with a behavioral model of the magnetron discharge, is shown in Fig. 6.2. I used a chain of transient voltage suppressor (TVS) diodes (7x1N6071) to limit the CE voltage of the IGBT transistor (IXGF36N300) represented in Fig. 6.2 by the ideal switch S1.

After a magnetization period of the L_1 inductor (3.3mH), when the current supplied by V_d (100V) increases linearly, S_1 is turned off, and a negative voltage larger than the ignition voltage of the magnetron discharge is produced between the cathode (the target) and the anode of the sputtering chamber. As explained in the previous sections, the voltage magnitude and the pre-

ionization are taken into account in this behavioral model, as factors that influence the delay of the discharge current after the application of the voltage. After turning off S_1 , it can be considered that the TVS voltage represents a well-defined ignition overvoltage, which persists until the ignition of the magnetron discharge. For the period of the current delay, the i_{L_1} inductor current mainly flows through the TVS chain, excepting a small fraction that represents the initial phases of the discharge current, denoted by i_{NG} in the behavioral model of the normal glow discharge [122]. The ignition lag is modelled by the time necessary for the u_{C_2} voltage to reach the turn-on voltage of the switch S_2 . This charging time is influenced by the initial value of the u_{C_2} voltage, the i_{R_2} charging current through R_2 , and the discharging current i_{G_1} , generated by the voltage-controlled current source G_1 . The higher the voltage applied to the chamber, and the higher the initial voltage of C_2 , the shorter the time delay until S_2 is turned on. The discharge current generated by G_1 decreases if u_{C_1} decreases due to the current supplied by the current-controlled current source F_1 , and thus, the ignition lag is shortened. This models the effect of the residual plasma on the current onset delay. Repeated magnetron current pulses, i.e. increased average output current of F_1 keeps C_1 discharged, while the deionization periods allow its charging via R_1 , thus increasing the discharge current of C_2 . The ignition of the discharge is modelled by closing the S_2 switch. From that moment, the chamber voltage u_{Ch} is determined by the current-controlled voltage source H_1 according to the relationship 6.4.

6.7 Results and discussion

Results obtained in pSpice using the above model are shown in Fig. 6.3 In this case it can be observed that the first, unsuccessful ignition is followed by a pulse with shorter discharge current lag, while the delay of the third discharge current pulse disappears almost entirely due to the simulated residual charge accumulation. A similar result shown in Fig. 6.4 has been obtained by practical measurement.

Fig. 6.6 shows the simulated evolution of the TVS junction temperature due to repeated unsuccessful ignition of the magnetron discharge, similar to the experimental results shown in Fig. 6.5 Here, the ignition voltage has been assumed higher than the breakdown voltage of the 7x1N6071 TVS chain (i. e. $7 \times 180 = 1260V$). This can be the situation in case of low Ar pressure.

The equivalent thermal circuit model that could be directly applied in pSpice modeling is usually not specified in the data sheet of the TVS devices. In

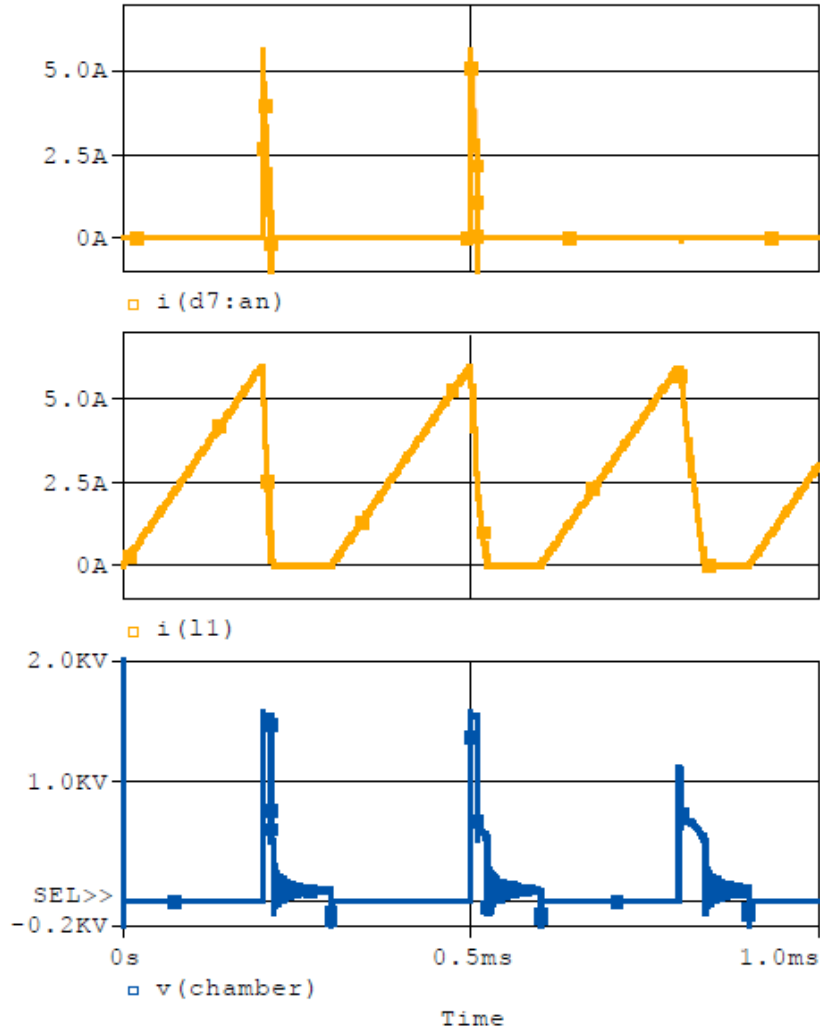


Figure 6.3: The TVS diode current (top), the L_1 inductor current, and the chamber voltage (bottom) obtained by simulation using the model presented in Fig. 6.2 [129].

case of the 600 W Littelfuse P6SMB series, the transient thermal impedance is given for $T_p \in (1\text{ms} \dots 1000\text{s})$, while in case of the 1500 W Microchip 1N6036A-1N6072A series, the reverse peak pulse power (P_{pp}), specified for

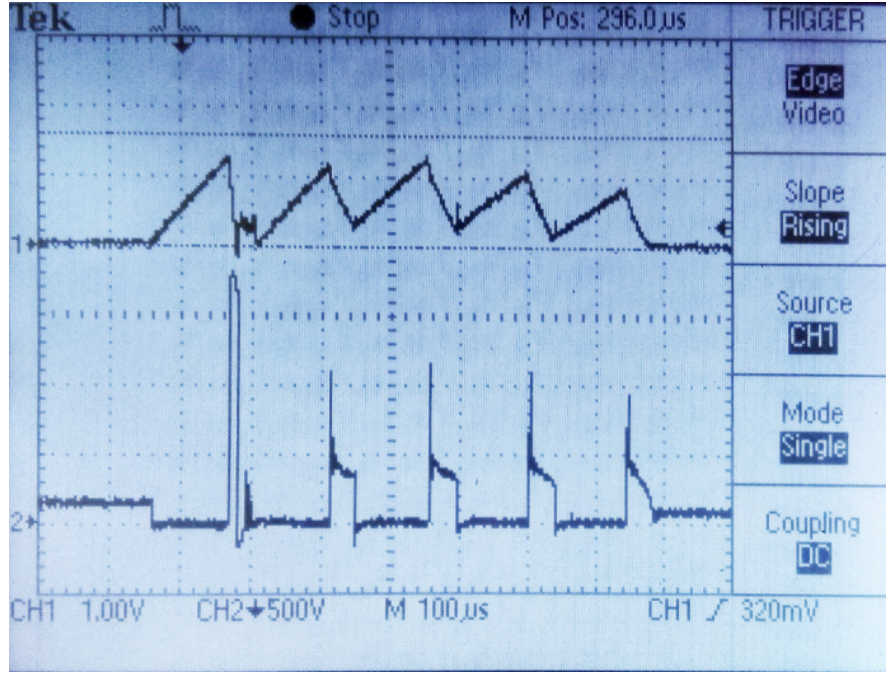


Figure 6.4: The inductor current and the chamber voltage: practical measurement results in case of a pulser connected to a sputtering chamber with Ti target and Ar gas ($p = 0.5\text{Pa}$) [129].

$T_p \in (100\text{ns} \dots 10\text{ms})$, can be used to derive the transient thermal model. In case of the above study, the transient thermal impedance of the 1N6071 TVS has been derived from the $P_{pp}(T_p)$ characteristic considering $T_{j_{\max}} = 175^\circ\text{C}$. From the $Z_{th}(T_p)$ thermal impedance characteristic, the parameters of a Foster network can be derived by step-by-step linear fitting.

Once the values of R_1, C_1, R_2, C_2, V_1 , and the gains of F_1, H_1, G_1, E_2 are fitted/determined such that the behavior of the model closely represents the measured data in a given a system, the usefulness of the proposed model becomes apparent, since one can tune the parameters of the discharge process, can choose the appropriate values of V_d and L_1 , and can dimension S_1 and the TVS chain that are suitable for magnetron discharge ignition via current impulses. With the help of the simulated TVS junction temperature one can determine the maximum number of successful and unsuccessful ignition impulses that the converter can handle, without its TVS diodes reaching their maximum junction temperature.

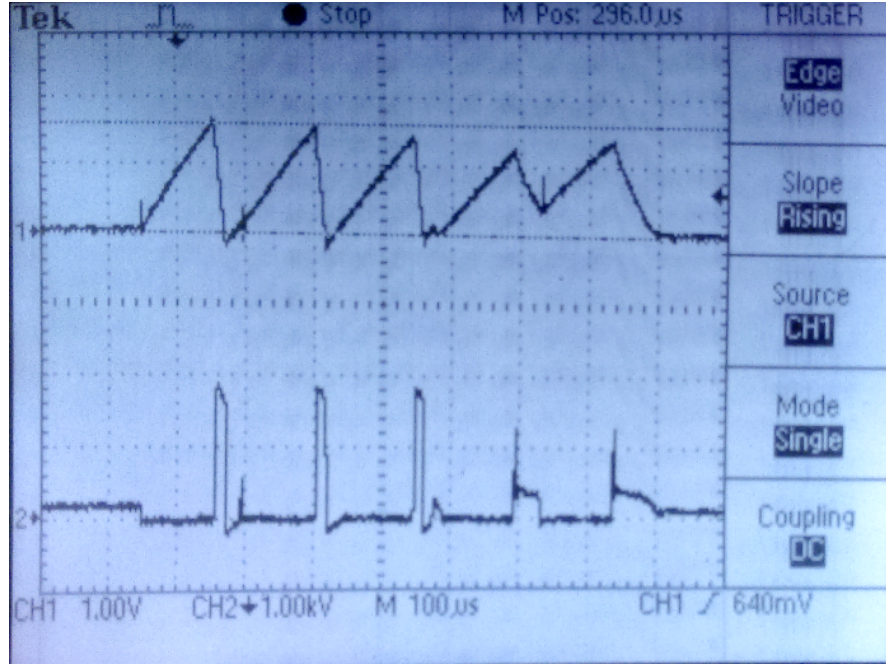


Figure 6.5: A series of unsuccessful ignitions in the experiment from Fig. 6.4, repeated for lower Ar pressure [129].

The fact that the number of unsuccessful ignition impulses must be limited to 6 in order to avoid reaching $T_{j_{\max}} = 175^{\circ}\text{C}$, provides a clue for the adopted discharge ignition strategy for the case presented in Fig. 6.6.

6.8 Overview

A simple behavioral model implemented in pSpice has been demonstrated to be suitable for the qualitative reproduction of measurement results associated with physical phenomena characteristic for the pulsed magnetron discharge. The delay of the current pulse onset after the application of the voltage pulse has a strong impact on the thermal stress of the transient voltage suppressors applied in the converter investigated in this Chapter. Despite the complex behavior of the plasma in pulsed mode, assuming abnormal discharge mode, the converter-discharge interaction can be reproduced acceptably well for converter dimensioning purposes.

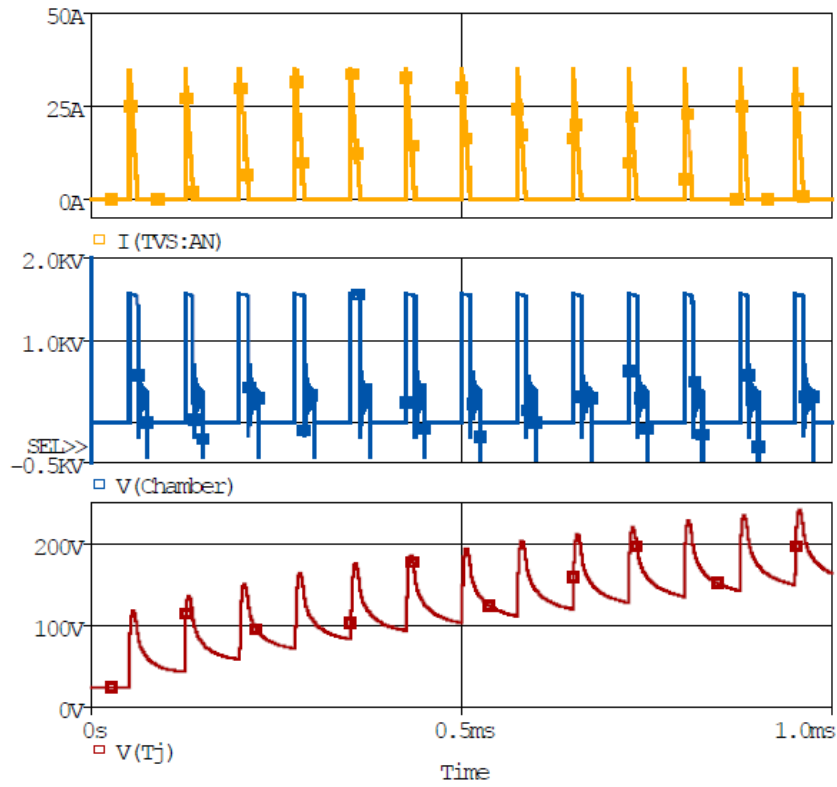


Figure 6.6: The TVS current, chamber voltage, and TVS junction temperature in case of a pulse train with unsuccessful ignition. $V(Tj)$ in the bottom diagram represents the junction temperature in °C [129].

Thesis 5. A simple behavioral model implemented in pSpice has been demonstrated to be suitable for the qualitative reproduction of measurement results associated with physical phenomena characteristic for the pulsed magnetron discharge.

Chapter 7

Results and contributions to the field of study

In this final Chapter, I will conclude by summarizing the results obtained throughout my work. In Chapter 1 the state of the art in the modeling of reactive magnetron sputtering has been surveyed, covering different techniques ranging from discharge modeling to particle in cell simulations, and beyond. The surveyed concluded that the main topics I should focus on are the following: parameter identification, control structure synthesis for stoichiometric sputtering, practical implementations of pulsed mode power supplies, and behavioral modeling of such compound systems.

In Chapter 2 I focused on developing a graphical identification method suitable for determining the main parameters of the Berg Model so that they can be used for fine-tuning a control algorithm. This has been accomplished by simplification of the analytically determined gas flow-pressure relation in both the metallic and the poisoned operation modes in order to provide a support for the graphical determination of the reactive gas sticking coefficient on the condensation surface and of the sputtering yield of compound molecules. The sputtering yield of the target metal and of the reactive gas sticking coefficient on the target surface is determined using both an analytical and a least squares curve fitting method.

In Chapter 3 an analytical study is undertaken in order to determine the conditions needed for stoichiometric layer growth on the substrate surface. I have shown that there is a monotonic relationship between the target coverage

and the partial pressure of the reactive gas. Results from the literature show that the target voltage, along with state estimation, can be used to calculate the target coverage. I have combined these findings in a method that facilitates stoichiometric film growth on the substrate surface. I have proposed a control structure employing two control loops, that can keep the system stable whilst controlling the sputtering power, that in the end leads to stoichiometric film growth on the substrate surface.

In Chapter 4 a new control algorithm and a corresponding control structure is proposed that provides stable operation of the process using two continuously supplied reactive gases. The novelty of the proposed algorithm consists in the extension of reactive magnetron sputtering control algorithms to the two-gas reactive magnetron sputtering process, and the definition of current-dependent monotony domains in the space of the partial pressures. The stoichiometry of the deposited film is influenced by controlling the amount of coverage of the ternary compound TiO_xN_y on the substrate. By implementing the proposed limiting algorithms, the trapped state of the target can be avoided. Implementation in engineering practice is conditioned by the successful state-identification of the substrate surface coverage by the desired compound, and fast partial pressure measurement of the two reactive gases.

In Chapter 5 a current controlled power supply has been proposed and built that is suitable for use with both high impedance and low impedance loads, characteristic for different states of the plasma in magnetron sputtering applications. I determined the specific design criteria needed for the implementation of the pulsed mode power supply by taking into account the current-voltage characteristics, the ignition voltage and the current impulse delay for different gases and pressures. The presented converter has been tested on a vacuum chamber where it has been demonstrated to be suitable for plasma ignition and current control of the glow discharge, providing a straightforward approach for arc handling.

In Chapter 6 a simple behavioral model implemented in pSpice has been demonstrated to be suitable for the qualitative reproduction of measurement results associated with physical phenomena characteristic for the pulsed magnetron discharge. The delay of the current pulse onset after the application of the voltage pulse has a strong impact on the thermal stress of the transient voltage suppressors used in the investigated converter. Despite the complex behavior of the plasma in pulsed mode, assuming abnormal discharge mode,

the converter-discharge interaction can be reproduced acceptably well for converter dimensioning purposes.

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