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Plasma properties in high power impulse magnetron sputtering

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Abstract

The work presented in this thesis involves experimental and theoretical studies related to plasma properties in high power impulse magnetron sputtering (HiPIMS), and more specifically plasma transport. HiPIMS is an ionized PVD method based on conventional direct current magnetron sputtering (dcMS). In dcMS very little of the sputtered material is ionized since the plasma power density is not high enough. This is not the case for HiPIMS, where a substantial part is ionized, and thus presents many new opportunities for thin film growth. Understanding the dynamics of the charged species in the HiPIMS discharge is therefore of essential value when producing high-quality thin film coatings.

In the first part of the work a new type of anomalous electron transport was found. Investigations of the transport resulted in the discovery that this phenomenon could quantitatively be described as being related and mediated by highly nonlinear waves, likely due to the modified two-stream instability (MTSI), resulting in electric field oscillations in the MHz-range (the so-called lower hybrid frequency). Measurements in the plasma confirmed these oscillations as well as trends predicted by the theory of these types of waves. The degree of anomalous transport in the plasma could also be determined by measuring the current density ratio between the azimuthal current density (of which the Hall current density is one contribution) and the discharge current density, J_φ / J_D. The results provided important insights into understanding the mechanism behind the anomalous transport.

It was furthermore found that the current ratio J_φ / J_D is inversely proportional to the transverse resistivity, $\eta_\perp$, which governs how well momentum is transferred from the

electrons to the ions in the plasma. By looking at the forces involved in the charged particle transport it was expected that the azimuthally rotating electrons would exert a volume force on the ions tangentially outwards from the circular race track region. The effect of having an anomalous transport would therefore be a large fraction of highly energetic ions being transported sideways and lost to the walls. In a series of experiments, deposition rates as well as incoming ion energy distributions were measured directly at the side of the magnetron. It was found that a substantial fraction of sputtered material is transported radially away from the cathode and lost to the walls in HiPIMS as well as dcMS, but more so for HiPIMS giving one possible explanation to why the deposition rate for substrates placed in front of the target is lower for HiPIMS compared to dcMS. Furthermore, the recorded, incoming ion energy distributions confirmed theoretical estimations on this type of transport regarding energy and direction.

Preface

The work presented in this licentiate thesis constitutes the first part of my PhD studies conducted since May 2006 in the Plasma & Coatings Physics Division at Linköping University. The goal of my doctorate project is to gain insight into the physics of HiPIMS plasmas as well as thin film growth using HiPIMS. The research is financially supported by the Swedish Research Council (VR) and by the European Commission within the 6th framework (integrated project: InnovaTiAl). The results are presented in two appended papers, which are preceded by an introduction giving an overview of the research field and describing the methods used in the research.

Papers included in the thesis

1. **"Anomalous transport in high power impulse magnetron sputtering"**
   D. Lundin, U. Helmersson, S. Kirkpatrick, S. Rohde, and N. Brenning
   Plasma Sources Sci. Technol. 17, 025007 (2008)
   Selected for inclusion in the IOP Select collection

2. **"Cross-field ion transport during high power impulse magnetron sputtering"**
   D. Lundin, P. Larsson, E. Wallin, M. Lattemann, U. Helmersson, and N. Brenning
   Submitted for publication

In the first paper I was involved in the planning, performed the characterization and analysis, and wrote a major part of the paper. In the second paper I was responsible for the planning, performed a large part of the characterization and analysis, and wrote the paper.

Related publications not included in the thesis

1. **"A bulk plasma model for DC and HIPIMS magnetrons"**
   N. Brenning, I. Axnäs, M. Raadu, D. Lundin, and U. Helmersson
   Submitted for publication

Acknowledgements

This one goes to the greatest girl in my life: **Mum**.

Thanks **dad** for giving me my first book in mathematics and convincing me that university studies rock. Big respect goes to my little brother **David** for pointing out what a nerd I am, making me realize what I should spend my life doing.

From a slightly more professional point of view I would like to express my deepest gratitude towards my two supervisors: **Ulf Helmersson**, for always asking difficult questions, making me progress, and most of all for believing in me and giving me the freedom to explore the world of plasma and thin films. **Nils Brenning**, for being the coolest scientist I have ever met. Your knowledge and crazy ideas are constantly guiding me.

I would probably end up with a too long list of colleagues and friends in the **Plasma & Coatings Physics** division together with the **Thinfilm Physics** and **Nanostructured Materials** divisions, but I would like to mention a few names: **Daniel Jädernäs**, for being the perfect office neighbor; always ready to take on the next experiment with great enthusiasm, **Petter Larsson**, omniscient colleague, flat mate, and super-technician: without you several experiments would most likely have blown up and not much science would have been generated, and also **Erik Wallin**, for always questioning my ideas and steering me clear of failure. In short: I definitely enjoy working with all of you people!

I am also very grateful towards **Johan Böhlmark** for taking me on as a student in plasma physics, and making me realize that graduate studies are not only performed

by people wearing frightfully thick glasses and pocket calculators strapped to their side.

During this work I have had the honor to work with several great researchers around the world, whose help are invaluable to me:

- **Martina "lill-chefen" Lattemann**, who previously worked in our group at Linköping University, and now works at TU Darmstadt and Forschungszentrum Karlsruhe, Germany
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- **Scott Kirkpatrick** and **Suzanne Rohde** at the University of Nebraska, USA
- **Ingvar Axnäs**, **Michael Raadu** and **Jan Wistedt** at the Royal Institute of Technology, Sweden

Last, but not least, big shouts go to all my **friends** out there – without you this adventure would not have been the same.

Contents

Variables and constants

$\mathbf{B}$	magnetic field vector
c	speed of light
D	diffusion coefficient
$\mathbf{D}$	dielectric field vector
ε_0	permittivity of free space
$\mathbf{E}$	electric field vector
η	resistivity
$\mathbf{J}$	current density vector
k	Boltzmann's constant; wave number or wave vector ($\mathbf{k}$)
λ_D	Debye length
μ_0	permeability of free space
M	ion mass
m_e	electron mass
n	density
ω	angular frequency
p	pressure
ρ	charge density
R_c	radius of magnetic field line curvature
T	temperature
V	electric potential

1 Introduction

1.1 Thin film growth

Thin films are layers of material with a thickness ranging from a few atomic layers (~nm) to a few micrometers, and can today be found just about everywhere in our society; from anti-reflective coatings on glasses to computer chips. The advantage is the combination of the surface properties of the thin film with the bulk properties of the underlying material, leading to enhanced chemical, mechanical or electrical properties to name a few. The history of making thin films dates back to the metal ages, and particularly to the ancient craft of gold beating. The Egyptians were the first to practice this art about 4000 years ago [1], which a multitude of different jewelry bear witness about. Famous examples are the decorative gold leafs from ancient Luxor with a thickness of about 0.3 micrometer. As a reference a normal sheet of paper is about 100 micrometers. However, thin films used in other cases as for mere decorative purposes were produced much later. In the early 1800s, electroplating, the first widespread thin film deposition technique, was invented by the Italian chemist Luigi V. Brugnatelli [2]. The resulting thin films were not of great quality. Instead it was in 1852 when W.R. Grove first studied what became known as sputtering [3] (a way of depositing thin films, which will be discussed in more detail later on). Grove used a tip of wire as the coating source and sputtered a deposit onto a highly polished silver surface held close to the wire at a pressure of about 0.5 Torr. In 1858 A.W. Wright of Yale University published a paper in the American Journal of Science and Arts on the use of an "electrical deposition apparatus" that he used to create mirrors [4]. At about the same time the famous T. Edison filed a patent application for vacuum coating equipment to deposit coatings on wax cylinder phonographs [5]. Since it could not be proven certain that Wright had used sputtering to produce these

thin film mirrors, it meant that Edison won in court on being the inventor to thin film deposition through sputtering. Edison could therefore be said to be the first person to make commercial use of sputtering.

1.2 Thin film deposition

There are numerous ways of producing thin films, such as electroplating, evaporation, sputter deposition, chemical vapor deposition and combinations of these methods. Here only the most commonly used methods will be discussed followed by a brief description of a recently developed technique. The interested reader is referred to reference 6 for more information on thin film deposition.

Electroplating is very common within industry. Here, the object to be coated is lowered into a solution (for example an acid), into which a metal is dissolved. By applying a negative charge to the object, positive metal ions are attracted, and a coating forms on the surface. Unfortunately high-quality, dense, defect-free films are hard to achieve using this method.

Two other widespread methods, known to produce thin films of greater quality are chemical vapor deposition (CVD) and physical vapor deposition (PVD). For CVD, volatile gases (precursors) are let into a deposition chamber, which is under vacuum conditions. By adding heat, the gas will start to react and form a coating on any surface present in the chamber. The technique is widespread within industry, since it does not require a complex deposition system with high vacuum conditions and advanced power supplies. One major drawback in CVD is that very high temperatures are needed to evaporate the different constituents and make them react in the gas phase on a surface. This means that several applications are excluded due to the risk of melting and/or damaging the object to be coated (in thin film deposition we usually call this a *substrate*). For example, different thermal expansion coefficients between the coating and the substrate make CVD less suitable for coatings on steel, plastics and electrical components. In some cases this problem can be solved by using a *plasma*[1] instead of heating, to activate the process (so called plasma-enhanced CVD).

[1] A plasma is defined as a collection of freely moving charged particles that is in average electrically neutral. We will learn more about plasmas in the next chapter.

PVD is a general term describing how films are deposited by the condensation of a vaporized form of a material onto various surfaces. The vapor of the thin film material is created by physical means from a solid deposition source, often called a *target*. One such PVD method is called *sputter deposition*. Here, target atoms are, by physical bombardment of particles from a plasma[2] inside the deposition system, made to eject. These atoms are then transported through the deposition chamber and condensate at the substrate, forming a film. The whole process requires some kind of electrical discharge in order to be sustained.

The most common PVD methods are arc evaporation (see for example reference 7 for more details) and magnetron sputtering. Strictly speaking, sputtering is not the mechanism used in arc evaporation. Instead an extreme discharge is used to melt the target material in a small spot and eject it out into the chamber. In magnetron sputtering an external magnetic field is used to better confine the plasma close to the sputtering region. Films deposited by conventional PVD methods can sometimes be porous, amorphous or polycrystalline since the deposition flux contains mostly neutral atoms, and the ion bombardment of the growing film is provided from inert gas ions, which are usually not incorporated into the resulting film. Since a dense film, free of micropores (pinholes) is desired for certain applications, this can be a problem. Still, thin films made by PVD techniques can be very smooth and dense compared to other techniques used in industry today. In general, magnetron sputtering is better at producing smooth films on complex surfaces, but sometimes with low adhesion. Arc evaporation gives very good adhesion, but a much rougher film surface.

In 1999 a new PVD technique, called *high power impulse magnetron sputtering* (HiPIMS) was invented by Dr. Kouznetsov [8], building on previous work by Mozgrin *et al*. [9]. It used high-power pulses to ionize more of the sputtered material. Dr. Kouznetsov owns several HiPIMS patents [10], which he put into his company Chemfilt AB (today called Chemfilt Ionsputtering AB). There are many advantages inherent to the HiPIMS process. It is very easy to set up if a conventional magnetron sputtering system is present. In principle, all you need to change is the power supply.

[2] In sputter deposition, the plasma is created by letting in a gas followed by applying an electrical discharge of hundreds of volts and at least a few amps.

Furthermore, with a large fraction of ionized sputtered material, the resulting coatings are denser and one can also control the deposition flux to a much greater extent. It is by obvious reasons very interesting to further investigate this promising technique and understand what underlying mechanisms are responsible for the change in thin film properties. Thus, it is necessary to characterize the plasma generated in the HiPIMS discharge. In doing so it has been found that the transport of charged particles is more efficient in the HiPIMS case than can be explained by standard theory [11, 12]. Understanding the mechanisms in the plasma is therefore essential and a great part of this work is dedicated to investigating the HiPIMS plasma. Both magnetron sputtering and HiPIMS will be described in more detail in the following chapters.

1.3 Purpose and outline

The purpose of this work has been to expand on existing HiPIMS studies and models of plasmas to include recent findings in the field of plasma transport. Both experiments and theory have been worked out in order to achieve a better understanding of the HiPIMS plasma and possible consequences of anomalous charged particle transport previously seen, but not fully understood [11]. Furthermore, investigations on the lower deposition rate for HiPIMS compared to conventional sputtering have been carried out. One of the main motivations for this work, besides the fundamental knowledge gained, has been to make HiPIMS an industrially attractive thin film deposition technique.

The outline of the introductory chapters preceding the papers is as follows. First a general overview of plasma physics used in thin film growth, and sputtering in particular, is given. This is followed by a chapter on the plasma dynamics in order to understand the principles behind the transport of charged particles. After this, the basic principles of the analysis techniques used are presented. Magnetron sputtering and particularly HiPIMS are then developed in the chapters that follow. The thesis is concluded with a summary of the results and a short outlook, where a selection of ongoing and planned work is discussed.

2 Plasma for material processing

2.1 Background

Historically the term 'plasma' was introduced by Irving Langmuir in 1928 [13] when he investigated oscillations in an ionized gas. He used the word to describe a region containing balanced charges of ions and electrons. Today we define a plasma as a collection of freely moving charged particles that is in average electrically neutral [14], and we often refer to it as the "Fourth State of Matter" because of its unique physical properties, distinct from solids, liquids and gases. Examples of plasmas include the sun (and other stars), fluorescent light bulbs and the aurora borealis (northern light), making up about 99% of our known universe[3] [15]! A plasma is sometimes erroneously called an extremely hot gas, but by heating up a gas it is possible to create a plasma. At a sufficiently high temperature the gas molecules will decompose to form freely moving gas atoms. If the temperature is further increased these gas atoms will release some of their electrons resulting in free, randomly moving electrons and ions. A plasma has been generated if enough gas atoms are ionized making the collective motion controlled by electromagnetic forces. In this thesis we have worked with both weakly ionized plasmas in which only a small fraction of the atoms are ionized, as well as highly ionized plasmas, in which nearly all atoms are ionized. Even in a weakly ionized plasma, the dynamics of the system may be dominated by effects caused by the small number of relatively strongly interacting ions and electrons, as opposed to the large number of relatively weakly interacting neutrals.

[3] The discussion on dark matter is here disregarded.

2.2 Plasma for thin film deposition

The common way of generating a plasma for material processing by PVD is to use two metal electrodes: a cathode and an anode (usually the grounded chamber walls) enclosed in an evacuated vacuum chamber. Some kind of power supply, like a conventional direct current (dc) supply, is connected to the setup, see Figure 1.

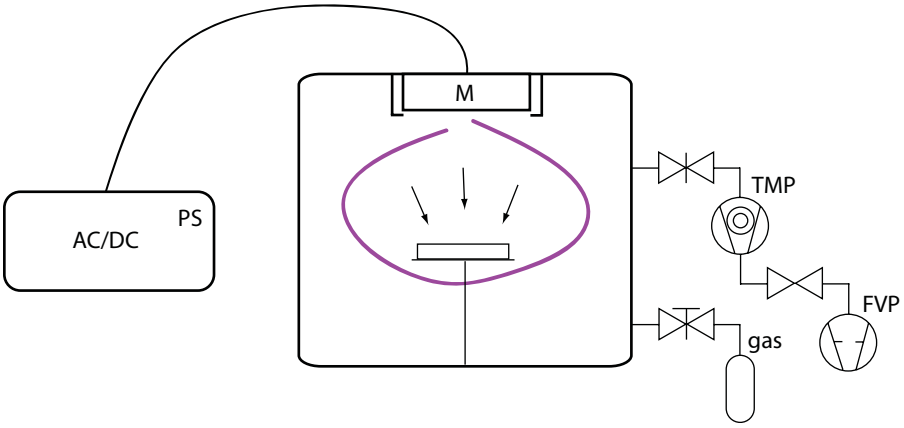

Figure 1. Schematic drawing of a simple sputter deposition system showing a deposition chamber connected to a power supply (PS). The deposition chamber consists of a top-mounted magnetron and target (M). A turbo molecular pump (TMP) and a fore vacuum pump (FVP) are also connected to the chamber. A substrate is placed in the center on a substrate table and is immersed in the plasma (sketched below the magnetron). Through a gas inlet (lower-right in the system) a working gas, such as argon, is let in.

A working gas like argon (Ar) is introduced into the chamber. The gas serves as the medium where the electrical discharge is initiated and sustained. The pressure used is around 1 mTorr - 1 Torr. By applying a few hundred volts to the cathode there will be a visible glow between the cathode and the anode, and a plasma is being maintained from this so-called *glow discharge*. The mechanism of transferring the working gas to a plasma can be seen as the analog of dielectric breakdown in an insulating solid, where the dielectrics will start conducting current at a critical voltage. In the case of the gas it starts with a free electron, caused by *e.g.* cosmic radiation or thermal energy, being accelerated towards the anode by an electric field, created by the voltage difference applied between the electrodes. The accelerated electron will gain energy and eventually collide with a neutral gas atom and ionize it. Due to charge conservation the following reaction will take place:

$$e^- + Ar \rightarrow 2e^- + Ar^+.$$

The resulting two electrons can now bombard two other neutrals, while the Ar ion will be accelerated and collide with the cathode releasing, among other particles, secondary electrons. This regime is called the *Townsend discharge* [6], and very little current is flowing due to the small amount of charge carriers (see Figure 2).

The cascade of ionizing collisions will ultimately result in a large current causing the gas to break down, and eventually the discharge becomes self-sustaining, meaning that enough secondary electrons are generated to produce the required amount of ions to regenerate the same number of electrons. The gas begins to glow and there is a sharp voltage drop, and we are now in the *normal glow* regime. The current density is here rather evenly distributed over the entire cathode surface. If one increases the power even further the *abnormal discharge* regime will be reached. Here, the ion bombardment already covers the whole cathode surface and the increased power results in both an increase in voltage as well as current density. The resulting charge carrier density (plasma density) is found in the range from 10^{15} m^{-3} to 10^{19} m^{-3}, mostly depending on what type of discharge applied. Here is where plasma processing, such as sputtering and etching, takes place. If increasing the applied power even further it results in a second avalanche due to thermionic electrons. The voltage drops sharply, but the current density is very high. This is an *arc discharge* and is the regime used for cathodic arc deposition.

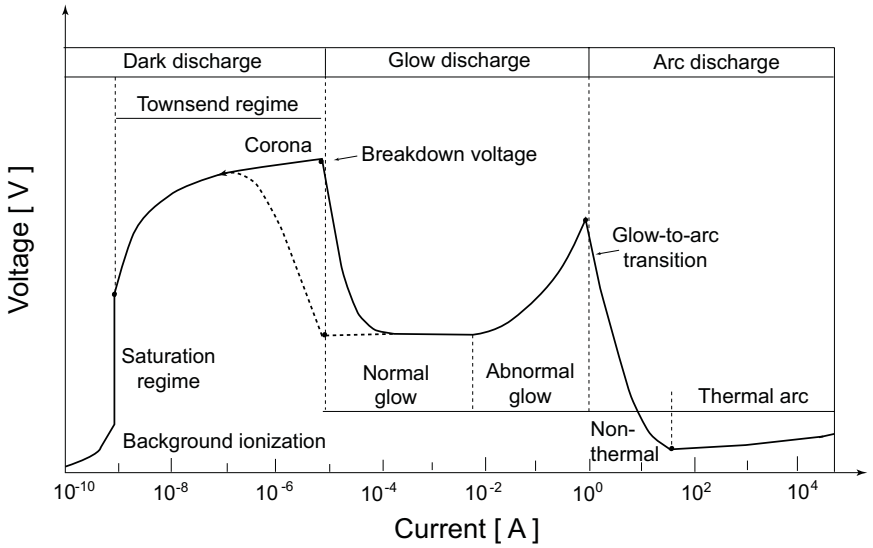

Figure 2. Different plasma discharge regimes. (After Roth [16].)

The plasma used for material processing is called a cold plasma, although it is far from cold in the more everyday use of the word. The reason for this is that this type of plasma can be treated as a fluid (we don't have to keep track of the individual particles) in thermal equilibrium, which means that different charged species have Maxwellian (Gaussian) velocity distributions, $f(v) = Ae^{-\frac{1}{2}\frac{mv^2}{kT}}$. Hot plasmas have non-Maxwellian distributions and have to be treated with kinetic theory instead. A cold plasma still has an electron temperature of at least 10 000 K, or a few electron-volts (eV), where 1 eV = 11 600 K. This means that the electrons in the tail of the distribution still have enough energy to overcome recombination of ions and electrons back into neutrals, meaning that the plasma is sustained [17]. In other words, the ion loss rate is balanced by the rate of ionization. An ion energy distribution for HiPIMS is shown in Figure 3 (see **Paper 2** for an investigation on ion energy distributions).

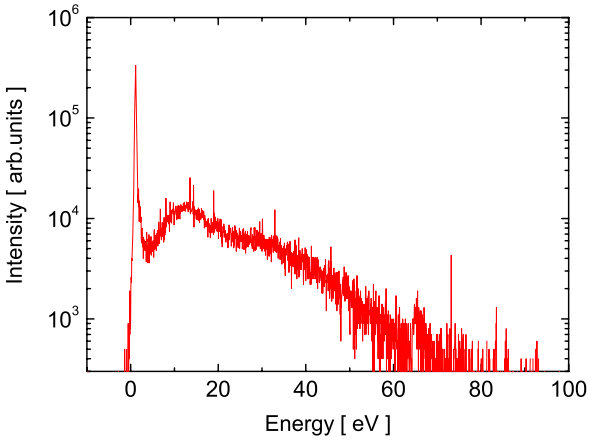

Figure 3. Time-averaged Ti^+ ion energy distribution in a HiPIMS discharge.

A common misunderstanding is that a high temperature is connected to great heat transfer. The reason why the hot electrons do not melt the whole system is because there are so few of them inside the chamber, which means that the heat conduction is very low.

2.3 Plasma fundamentals

Now we have come to a situation where a plasma is maintained in the vacuum chamber. Since plasmas can be considered as charged fluids, they will obey *Maxwell's equations*, meaning that electromagnetic forces will govern the particle motion in a rather complex way[4]. Later on a more detailed study of the particle orbits will be presented. For the moment let us have a look at how the plasma interacts with the wall of the chamber by investigating one of Maxwell's equations called the Poisson equation (or Gauss' law),

$$\nabla \cdot \mathbf{D} = \nabla \cdot \varepsilon_0 \mathbf{E} = e(n_i - n_e)\,, \tag{2.1}$$

[4] As will be shown in the next chapter, the particle motion is described by Maxwell's equations coupled with the Lorentz force equation. Another aspect of the plasma is the fluid character, meaning that fluid equations will come into play. This will not be discussed here.

where n_i and n_e are the positive ion and electron densities respectively. The equation relates the electric field to the charge balance at a certain point. By using the fact that the electric field can be derived from a potential according to

$$\mathbf{E} = -\nabla V\,, \tag{2.2}$$

the following expression can be derived

$$\nabla^2 V = (e/\varepsilon_0)(n_i - n_e)\,. \tag{2.3}$$

Equation (2.3) can be solved using the so-called Boltzmann relation ($n_e = n_0 e^{V/T_e}$), the approximation $n_i \approx n_0$ and the boundary conditions $V = 0$ when $x \to \pm\infty$. In 1D this results in $V = V_0 e^{-|x|/\lambda_D}$, where

$$\lambda_D = \left(\frac{\varepsilon_0 T_e}{e n_0}\right)^{1/2} \tag{2.4}$$

is called the *Debye length*. It is the length scale on which charge densities can exist; on greater distances charge imbalances do not affect the plasma. In the case of processing plasmas λ_D usually amounts to a few tens of μm. This is indeed a very important finding, because it leads to the notion that in the bulk of the plasma there are more or less equal amounts of negative and positive particles ($n_i \approx n_e = n_0$) making the plasma *quasineutral*, a very important characteristic of a plasma. Here n_0 is the *plasma density*. The only place where the quasineutrality can be violated is in the sheath between the plasma and another boundary such as the chamber walls. In reality the thickness of the sheath is about $5\lambda_D$ due to large potential drops. In the sheath the ions outnumber the electrons, or $n_i > n_e$. The potential of the wall is negative relative to the plasma due to fact that the electrons move faster than the ions and therefore leave the plasma to a greater extent. This process goes on until a large enough potential difference between the plasma and the walls has been built up resulting in a negative, repelling sheath drop. Thus the *plasma potential* is often positive (usually a couple of V) relative the walls, see Figure 4. It is important to remember that

electrons are fed into the plasma through secondary electron emission and ionization processes in order to sustain the plasma. Worth mentioning is that objects not connected to ground, introduced in the plasma will take on a slightly negative potential with respect to ground. This is known as the *floating potential* and is also due to the higher mobility of the electrons.

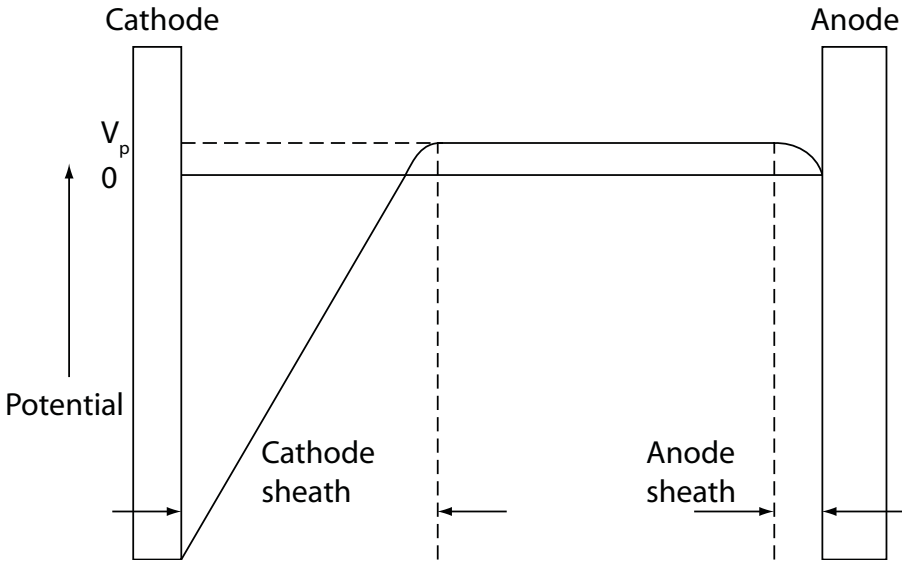

Figure 4. Potential distribution from a dc discharge. Here the cathode is the negatively biased magnetron and the anode is the chamber walls. V_p is the plasma potential. The fall in potential is indicated for each sheath region. (From M. Ohring [6].)

Regarding material processing, the discussion on sheaths become very important, since the ions naturally gain a directed velocity when coming close to and eventually strike the chamber wall or a substrate placed in the chamber ([17], p 9). The reason for this is the imbalance $n_i > n_e$ found in the sheath, which leads to the *Bohm sheath criterion* ([14], p 169), stating that ions will stream into any sheath with a velocity, u_s, at least as large as the ion acoustic velocity, c_s:

$$u_s > \left(\frac{eT_e}{M} \right)^{1/2} = c_s \tag{2.5}$$

The obvious question is then why the ions get a much larger, directed velocity compared to the thermal velocity one would expect them to have? The answer is that

there is a small electric field in the so-called *presheath*, between the plasma and the sheath, which accelerates ions to an energy of at least ½(eT_e). Thus, the plasma can exist with a material boundary (such as a chamber wall) only if there is an isolation consisting of a sheath and a presheath. In the sheath there is a potential drop repelling electrons and at the same time attracting ions to the boundary. This potential drop adjusts itself automatically so that an almost equal flux of ions and electrons are leaving the bulk plasma and thereby preserving quasineutrality.

2.4 Sputtering

A phenomenon that is not part of the discharge dynamics, but important for applications, is cathode sputtering, which is a process where material from the cathode is knocked away by impinging positive gas ions from the plasma[5]. In more detail, the gas ions found in the discharge cross the sheath region while gaining energy, strike the cathode surface and physically eject (or sputter away) cathode atoms through momentum transfer. In 1852 W.R. Grove was the first to study what became known as "sputtering" although others had observed the effect while studying glow discharges [3]. Besides sputtering, incoming ions can also stick to the surface (adsorb), scatter, or get implanted in the first few atomic layers of the cathode. A few other events can also take place, such as surface heating[6] and alteration of the surface topography, making ion bombardment into something we can see as playing a round of "atomic pool". What will actually happen when an incoming ion breaks up the close-packed atoms in the cathode material is highly dependent on the ion energy. It is therefore meaningful to introduce the concept of *sputter yield*, *S(E)*, as number of sputtered atoms per incident particle. For the most commonly used materials (such as Cu, Ti and Cr) the sputter yield is in the range of 0.5 – 2. It is in general good to have as high sputter yield as possible, since this means a higher deposition rate of sputtered material.

[5] This is true in the case of thin film deposition using magnetrons, but other types of bombarding particles can be used.
[6] A substantial fraction of the kinetic energy of the ion is used for heating up the target.

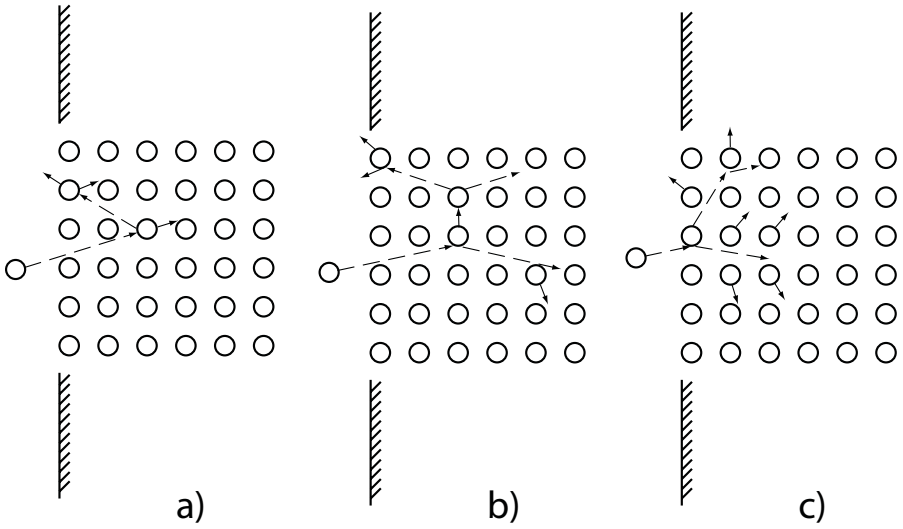

Figure 5. Energy regimes of sputtering: a) Single knock-on (low energy), b) linear cascade, and c) spike (high energy). (After P. Sigmund [18].)

In Figure 5 the main events of sputtering have been identified: a) Single knock-on (low energy), b) linear cascade, and c) spike (high energy). In principle one can summarize it as the higher the incoming ion energy, the greater the chance to affect several atoms in the bulk material resulting in more collisions and more sputtered atoms. A very important fact, pointed out by Emmerlich *et al*. [19], is that there is a non-linear energy dependence of the sputter yield, meaning that the applied voltage is not linearly proportional to the amount of sputtered particles. Finally, after an atom has been sputtered it is available to interact with the plasma.

3 Plasma dynamics

3.1 Particle motion

Although the underlying equations governing plasmas are relatively simple, the plasma behavior is extremely varied and subtle, making it a very complex system to analyze. Such systems lie in some sense on the boundary between ordered and disordered behavior, and cannot typically be described either by simple, smooth, mathematical functions, or by pure randomness. Still we can try to find a way to see what is happening inside the plasma, the so-called plasma dynamics, by studying some simple cases of particle motion. Maxwell's equations describe the behavior of electric and magnetic fields.

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{3.1}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t} \tag{3.2}$$

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \tag{3.3}$$

$$\nabla \cdot \mathbf{B} = 0\,. \tag{3.4}$$

They contain very important information in the field of electromagnetism, which have helped us to understand a great part of the physics in today's modern society: from radio and TV communication to various space phenomena. Here **E** is the electric field, **B** the magnetic field and ρ the charge density. Equations (3.1) (Faraday's law of induction) and (3.2) (Ampère's circuital law) relate the spatial and temporal behavior of the electric and magnetic fields to each other. They can be combined to form a wave equation, telling us how electromagnetic waves propagate (more about waves in

plasmas in **Paper 1**). Equation (3.3) (Gauss' law) states that an electrical charge will give rise to a divergent electric field, and equation (3.4) (Gauss' law for magnetism) tells us that there are no magnetic monopoles. This means that cutting a magnetic compass needle in two will not result in one piece pointing north and the other pointing south, but instead two smaller, ordinary compass needles. Another, often used equation is the continuity equation,

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{u}) = 0\,, \tag{3.5}$$

which states that matter is not created out of nothing (conserved). **u** is the particle velocity and *n* the particle density.

Now we return to the matter of trying to describe the behavior of the plasma. Fortunately it is possible to look at single particle motion and thereby get a feeling for the plasma dynamics. The equation that describes the motion of a charged particle under the influence of electric and magnetic fields is called the *Lorentz force equation*:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{u} \times \mathbf{B}) \tag{3.6}$$

Here **F** is the force acting on a particle of charge *q* and velocity **u** in the presence of an electric field **E** and a magnetic field **B**. This equation states that a positively charged particle will be accelerated along the direction of the electric field (in the opposite direction had it been a negatively charged particle), and it will move in circles around a guiding center in a plane perpendicular to the magnetic field. The resulting total motion (or drift velocity), $\mathbf{u}_{E/B,}$ will be directed perpendicular to both **E** and **B**, as displayed in Figure 6.

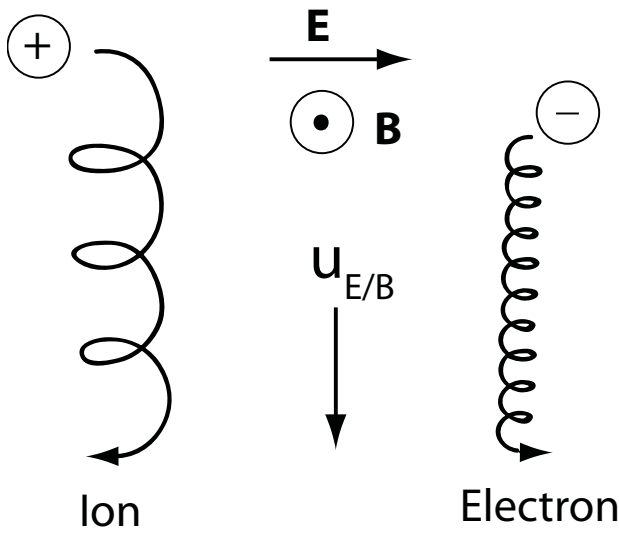

Figure 6. Single particle motion in combined electric and magnetic fields. B points out of the plane of the paper. (After F. F. Chen [15].)

The drift is usually called Hall drift or *E*/*B* drift, due to the fact that the drift velocity for both particles is $u_{E/B} = |\mathbf{E}|/|\mathbf{B}|$. Note that two particles with opposite charges will drift in the same direction. Furthermore, the radius of the gyrating motion is called the *Larmor radius* and is roughly about 1 mm for an electron and on the same scale as the vacuum chamber (tens of cm) for an ion. The electrons are well confined in the plasma due to the small gyration radius. The ions on the other hand, having a much larger gyration radius, can more or less freely cross the magnetic field lines and are therefore weakly confined.

In PVD plasmas, the plasma dynamics consists of more than the *E*/*B* drift. The most important drifts (which are more thoroughly described in **Paper 1**) are: (1) the curved magnetic vacuum field gyro centre drift $u_{e,R}$, which, for an isotropic Maxwellian distribution, can be written as [15, p 30]:

$$\mathbf{u}_{e,R} = \frac{2kT_e}{e}\frac{\mathbf{R}_c \times \mathbf{B}}{R_c^2 B^2}, \tag{3.7}$$

and (2) the pressure gradient (or diamagnetic drift) drift, $u_{e,\nabla p}$ [15, p 69]:

$$\mathbf{u}_{e,\nabla p} = \frac{\nabla p \times \mathbf{B}}{e n_e B^2}. \tag{3.8}$$

Here $\mathbf{R}_c$ is the curvature radius of the magnetic field lines and ∇p is the pressure gradient. What is interesting is that all three drift contributions are in the same direction, and are of significant amplitude. This results in a net force on the electrons moving them away from the cathode (in **Paper 2** an investigation has been carried out to describe the consequences of the force drift).

3.2 Plasma oscillations

So far we know that a plasma for material processing, such as thin film deposition, is a cold plasma, but still can have a temperature of tens of thousands of Kelvin (a few eV). The charged particles in this type of plasma also have a tendency of moving around quite a lot. A question that arises is what happens when there is a small separation of charge, *i.e.* that the electron cloud is slightly displaced from the cloud of positive ions at a certain moment. The situation would look somewhat like in Figure 7.

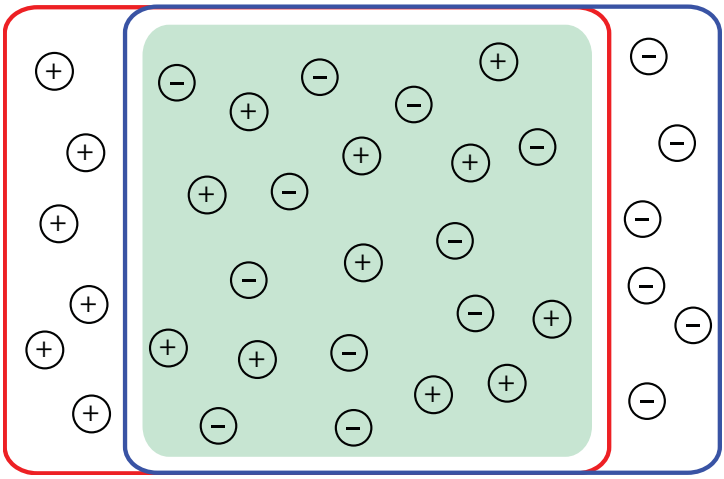

Figure 7. Electron cloud slightly displaced from the cloud of positive ions. In the middle the quasineutral plasma.

This problem can be solved using Maxwell's equations together with the Lorentz force equation, and the result is that the displacement of the much faster electrons disturbs the charge balance, and thereby an electric field is set up to attract the

electrons back again. When moving back, the electrons overshoot and pass the ion cloud due to their smaller mass, and once more there is a need to compensate for the displacement. In this way an oscillating motion arises. The frequency of these oscillations is called the *electron plasma frequency*. When taking into account that the ions are not immobile, it becomes clear that the ions also oscillate. This is called the *ion plasma frequency*, and the two oscillations combined are the *plasma frequency*, which is somewhere in the range of 10^{12} -10^{13} Hz for the plasmas considered here. As we shall see there are other types of oscillations, which will be important for the transport properties in the plasma (see also **Paper 1**).

3.3 Plasma transport

Plasmas are in reality never homogenous, and they will always have a variation of density (density gradient). To equalize this difference in density, plasma in high density regions will diffuse towards regions with lower densities. As the plasma diffuses (transport of charged species) there will be a large amount of collisions. The simplest ones to consider are between ions or electrons and neutrals causing ionization of the neutrals[7]. When, say an electron, hits a neutral it will most of the time bounce away from it. It is therefore a good idea to assign to the neutral an effective cross sectional area, or *momentum transfer cross section*, σ, which means that when an electron hits such an area its momentum will change and the change should be comparable to the size of the original momentum ([15], p 155). In general the cross section depends on the energy of the incoming particle, as displayed in Figure 8.

[7] In reality, elastic collisions are even more simple to treat, but they are of less interest here.

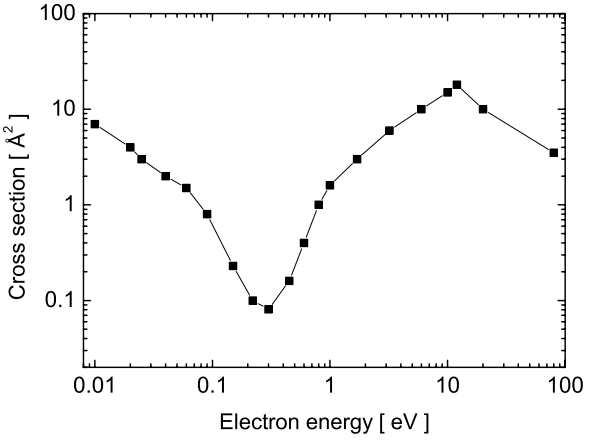

Figure 8. Momentum transfer cross section for argon, showing the so-called Ramsauer minimum. (After [17, 20].)

Argon is a noble gas and is most often used as a chamber gas for material processing plasmas. The most important events for electron collisions in argon are: (1) electron impact excitation, (2) elastic scattering and (3) electron-neutral ionization [21]. If the incoming electron has enough energy it can disturb the electrons orbiting the argon atom, causing an inelastic collision. Sometimes only the outermost electron is pushed to a higher energy level, thus leaving the atom in an excited state. Eventually the atom decays into a metastable state or back to the ground level, emitting a photon of certain energy. The elastic scattering process is called Rutherford scattering and happens when an electron is diffracted in the Coulomb potential of atoms and molecules. Rutherford scattering is used in many electron diffraction techniques, such as reflection high-energy electron diffraction (RHEED). If the incoming particle has enough energy it will (as hinted in the last type of electron collision above) tear off an electron of the neutral and thus ionize it. The *ionization cross section*, σ_{ion}, is very important in thin film processing, since it gives an idea of how ionized the plasma is. It usually starts at a threshold energy, which is the minimum energy required to ionize one specific neutral, and then it increases rapidly up to around 50-100 eV, where it starts to decrease. This is because the electrons have too high energies, and thereby too high velocities, to be able to interact long enough with the neutrals and ionize them.

3.4 Diffusion

Now we will use our knowledge about collisions and particle motion to look at the overall behavior of plasma motion, or diffusion. Diffusion of plasma in a magnetic field is rather complicated, because the particle motion is anisotropic (not homogenous). If both ions and electrons had had Larmor radii smaller than the chamber dimensions, then all the charged particles would be frozen into the plasma, meaning that they would gyrate around the magnetic field lines. In reality ions have a much larger Larmor radius leading to ions and electrons colliding with one another or with a neutral, which might lead to a shift of their guiding centers and diffusion across magnetic field lines as displayed in Figure 9. This is the case with processing plasmas where electrons are strongly magnetized and ions weakly magnetized. The result is that collisions will prevent diffusion along **B**, but increase the diffusion across **B**, and scaling as $\mathbf{B}^{-2}$.

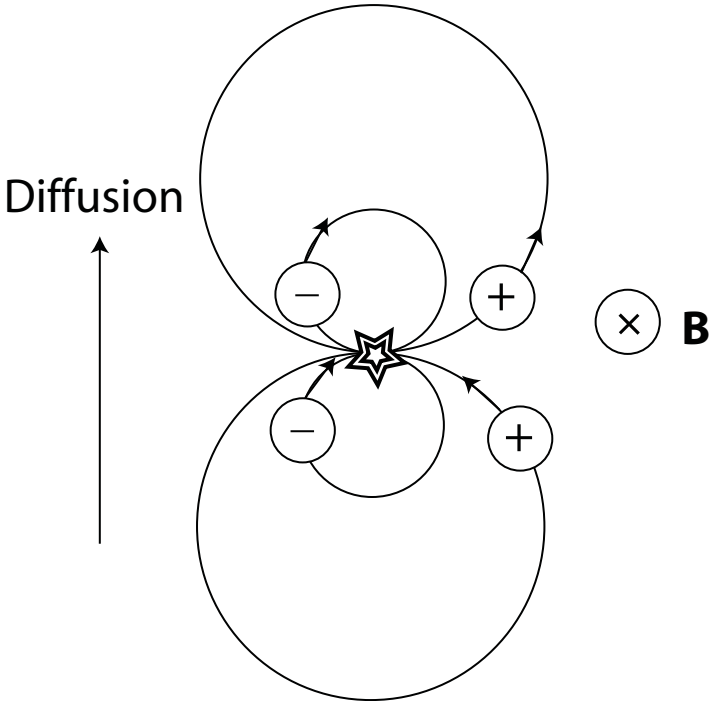

Figure 9. Collision between an electron and an ion resulting in a shift of the guiding centers and a cross-field diffusion. The magnetic field line is here directed into the plane of the paper. (After F.F. Chen [17].)

Electrons do not always follow this classical picture based on collisions, but instead work out new ways of diffusing in the plasma. Several plasma experiments on diffusion in the first half of the 20th century were not able to confirm the $\mathbf{B}^{-2}$ dependence expected from classical theory of collisions. Instead the measured cross-field diffusion, $D_{\perp}$, scaled as $\mathbf{B}^{-1}$ leading to a faster transport of charged particles [15]. This anomalous type of transport was first discovered by Bohm, Burhop and Massey [22] and Bohm gave the semiempirical formula

$$D_{\perp} = \frac{1}{16}\frac{kT_e}{eB} \equiv D_B . \tag{3.9}$$

The value 1/16 has no theoretical justification, but the Bohm diffusion is obeyed in many experiments.

Another type of diffusion is in **Paper I** found to be caused by instabilities in the plasma. The electrons generate plasma oscillations of high enough frequency, which sets up an electric field, and thereby they are moved across the magnetic field lines. This will be dealt with in some detail in the next two sections.

3.5 Resistivity

Classical *resistivity*, η_c, is defined as the momentum exchange between charged particle species (usually electrons and ions), in the direction of the current, which means that the resistivity in the plasma is related to collisions, so called *Coulomb collisions*. This way of defining the resistivity is called the *Spitzer resistivity*[8] written as,

$$\eta_c = \frac{m_e}{2n_e e^2 \tau_{SP}}, \tag{3.10}$$

where τ_{SP} is the Spitzer collision time,

[8] Note that the plasma resistivity is independent of density, which is not so intuitive (one would probably expect that more particles lead to more collisions, and thereby a higher resistivity.

$$\tau_{SP} = 1.09 \times 10^{14} \frac{T_e^{3/2}}{n_e \ln \Lambda}. \quad (3.11)$$

Here ln Λ is the Coulomb logarithm and can in almost all situations be approximated by 10. The resistivity is important, since it tells us about the momentum transfer between ions and electrons mediated by a wave field, meaning that with a higher resistivity there will be a much greater force transferred to the ions from the electrons and thereby increasing the energy of the ions.

In this work the classical resistivity has been slightly modified due to the existence of a plasma instability exciting a wave (see the next section). The macroscopic transverse resistivity [9] over the wave structure can then be rewritten as $\eta_\perp = < n_e E_\phi > / J_\phi < n_e >$, where the time average of the density and the electric field result in a net force if there exists a correlation between the two[10]. This is a new type of friction between waves in the plasma that we can call a *wave resistivity*. The effective momentum transfer time, often called the effective electron collision time τ_c, is related to this resistivity through

$$\eta_\perp = \frac{m_e}{\tau_c e^2 n_e} = \frac{B}{\omega_{ge} \tau_c e n_e}, \quad (3.12)$$

where the last step is made using the electron angular gyro frequency $\omega_{ge} = eB/m_e$. In order to relate the wave resistivity to the plasma transport it is necessary to calculate a value of $\eta_\perp$. This is possible through the product $\omega_{ge}\tau_c$ (seen in the equation above), which can in the bulk plasma of magnetrons, where the current is carried mainly by the electrons, be directly obtained from a macroscopic measurement of the current density ratio as $\omega_{ge}\tau_c = J_\phi / J_D$ [23] (this very fundamental conclusion is exploited in **Paper 1-2**). J_φ is the azimuthal current density and J_D is the discharge current density, due to the current directed perpendicular from the cathode surface.

[9] The word 'transverse' here refers to the fact that it is a resistivity perpendicular to the magnetic field.
[10] The φ direction of the electric field and the current density is the azimuthal direction around the circular magnetron (see chapter 5 for more information on magnetrons).

3.6 Plasma instabilities

Plasma instabilities are generally characterized by a growth of some of the internal states of the plasma, which makes it leave its equilibrium state. An analogy would be a marble balancing on a ledge. Here, a small perturbation would make it fall off and completely lose its equilibrium, as seen in Figure 10. In the case of the plasma this could mean that confinement is lost and the plasma drifts away.

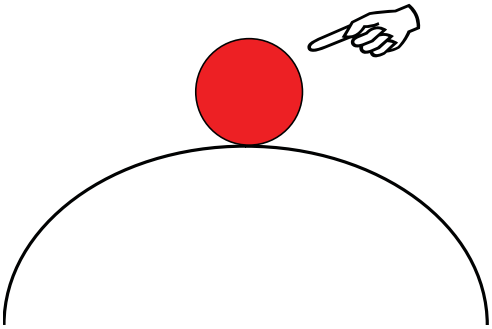

Figure 10. A ball resting in an unstable equilibrium. A small perturbation will make it fall.

The most central part of this work is related to *anomalous transport* (a fast transport of charged species) related to plasma instabilities. This is because the instabilities can affect the resistivity in the plasma and thereby the momentum transfer between electrons and ions, which ultimately will affect the transport properties of the charged species in the plasma. In a series of measurements with different types of electric field probes (presented in **Paper 1**) it was found that the so-called *modified two-stream instability* (MTSI) can grow in the HiPIMS plasma. This is why it is worth spending some time investigating the matter.

The modified two-stream instability is a special case of the two-stream instability, which is taken as a good starting point for our discussion. The two-stream instability grows in a non-magnetized plasma provided that the relative drift between electrons and ions exceeds the electron thermal velocity, *i.e.* $U = u_e - u_i > u_{e,th}$. This relative motion results in a Doppler shift between the plasma frequencies of the electrons and ions. If the wave vector[11], k, of the oscillations fulfills the condition $\omega_{pe} - kU = \omega_{pi}$, oscillations in the two distributions of particles will enhance each other and the

[11] A wave vector specifies the direction of the propagating wave. It is also related to the wavelength.

instability will start to grow exponentially [24]. One way of looking at this is by considering a region of the plasma where there is a small depletion of ions. The much faster electrons will respond to a difference in charge density according to the continuity equation (equation (3.5)), by moving faster across this region in order to keep the quasineutrality. This can only be achieved by setting up an electric field around the depletion zone, which on a longer timescale leads to an acceleration of ions out of the region, and thus even greater ion depletion and larger electron acceleration. The instability starts to grow.

The modified two-stream instability is derived assuming existence of a magnetic field component perpendicular to the relative drift of particles. This is the situation in the HiPIMS discharge [11]. Furthermore it is safe to assume that the ion gyration radius (the Larmor radius previously discussed) is much larger than the spatial dimension of the plasma. If the electric field is at an angle with respect to the magnetic field the electrons will not only move transverse to the two fields (as indicated in Figure 6), but also be accelerated along the magnetic field. Following the work of Buneman *et al*. [25], Ott *et al*. [26] and later Hurtig *et al*. [27] it is found that the electrostatic dispersion relation [12] for a homogeneous plasma in a constant magnetic field $\mathbf{B}_0 = B_y$ can be written

$$1 - \frac{k_z^2}{k^2}\frac{\omega_{pe}^2}{\omega_{ge}^2} - \frac{\omega_{pi}^2}{(\omega - k_z U_z)^2} - \frac{k_y^2}{k^2}\frac{\omega_{pe}^2}{\omega^2} = 0\,, \tag{3.13}$$

where ω_{pe} and ω_{pi} are the angular electron and ion plasma frequencies and ω_{ge} is the so-called angular electron gyration frequency (sometimes called the cyclotron frequency). U_z is the relative velocity and k_i is the wave vector along i. The dispersion relation can be solved exactly at the so-called angle of equal effective mass. It is the angle between the relative velocity and the wave vector where the ion and electrons appear to have the same mass when subjected to an electric field, or written as

$$\sqrt{m_e / m_i} = \sin\theta\,. \tag{3.14}$$

[12] Dispersion relations describe how electromagnetic waves propagate depending on the wavelength. Think about how the sunlight is split up into different colors when passing a prism. The dispersion relation is the key to understanding how energy is transported in any medium.

The maximum growth rate of the instability has been found to be $\gamma_{\max} = \omega_{lh} / 2$, where $\omega_{lh} = eB / \sqrt{m_e m_i}$ is the *lower hybrid frequency*. This is another type of plasma oscillations, which is usually in the MHz regime for HiPIMS plasmas (see **Paper 1**). The instability gives rise to a sheared drift of electrons across the magnetic equipotential lines (violating the frozen-in condition on very short timescales) directed momentarily by the direction of the oscillating electric field. Thus, MTSI would be the driving mechanism behind this drift generating electric field oscillations in the lower hybrid regime.

We are now ready to connect the two parts on resistivity and transport together. The modification of the classical resistivity by a wave resistivity is possible due to the existence of the modified two-stream instability exciting a wave. The possibility of estimating this wave resistivity can be done by investigating the current density ratio $\omega_{ge}\tau_c = J_\phi / J_D$. In HiPIMS and mid-frequency pulsed magnetrons, recent measurements in different devices (see **Paper 1** and references 11 and 28) agree on a value close to $\omega_{ge}\tau_c = 2$, which is roughly an order of magnitude lower than what is expected from classical theory of diffusion and electrical conductivity using collisions to move electrons across the magnetic field, or Bohm diffusion [11, 12]. Thus, a low ratio of azimuthal current density to the discharge current density (or equivalently $\omega_{ge}\tau_c$), increases the transverse resistivity and thereby the force on the ions, making electron and ion transport across the magnetic field lines more efficient in the HiPIMS case than can be explained by standard theory.

4 Plasma Analysis

4.1 Background

This chapter introduces the fundamentals of plasma diagnostics used in this work. It will by no means be a complete description of all techniques available, but rather a summary on electrostatic probe theory and mass spectrometry. These two techniques were used in **Paper I** and **Paper 2** in order to characterize the plasma regarding dynamics and composition. Thus, they constitute a link between theory and experiments, and as such they are invaluable tools in any plasma based process. In thin film growth the information extracted from analyzing the plasma is important, since it tells us about the properties of the material flux transported in the plasma. There is a clear need to investigate the plasma in order to understand why coatings have certain properties [29, 30].

4.2 Electrostatic probes

For investigations of electric fields and oscillations in the plasma, electrical probe arrays of different geometries were used in **Paper I**, as seen in Figure 11.

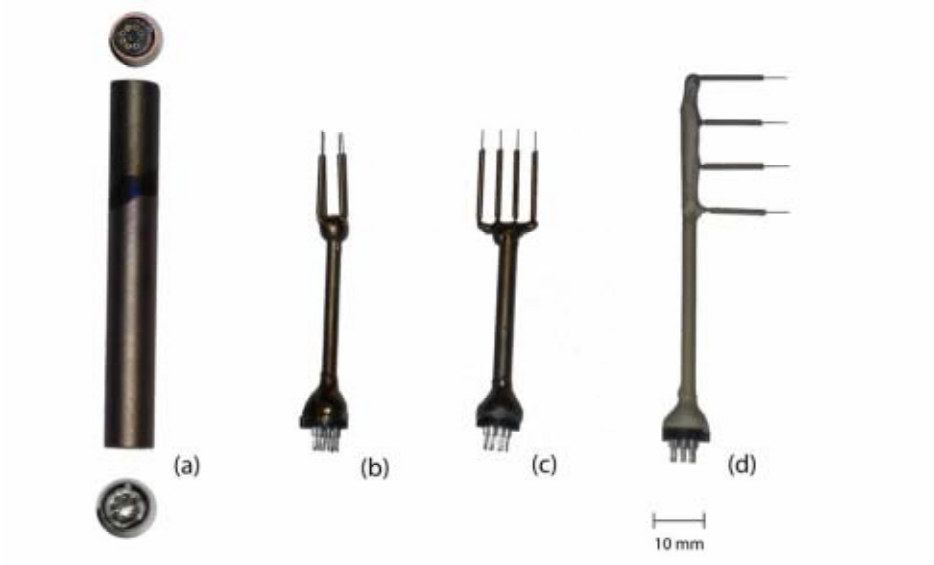

Figure 11. Electric field probes and transformer used for measuring oscillations. (a) Impedance matching unit with connector sides. (b) Four-pin probe measuring E_ρ and E_φ. The distance between the probe tips is 6 mm. (c) Fork-probe measuring azimuthal phase velocity, v_φ. The distance between the probe tips is 4 mm. (d) Probe measuring E_z oscillations. The distance between the probe tips is 10 mm.

The electric field is obtained from the difference in floating potential between pairs of cylindrical probe tips in the arrays. For accurate measurements, appropriate impedance matching is needed [31] and thus, two different impedance matching circuits, mounted inside the ceramic shaft of the probe, were used. The reason for this is that oscillations in the MHz-range should be detected while filtering out the influence of the voltage pulse produced by the power supply[13]. It is easy to see how complicated this is by the following calculations: the amplitude of the electric field in our measurements is approximately 100 V m^{-1} and the distance between two probe tips is roughly 10 mm, resulting in a measured signal of 1 V. At the same time the HiPIMS voltage pulse might be up to 1 kV, which complicates matters substantially. For frequencies above 300 kHz a 40:1 transformer, wound on a ferrite toroid which

[13] Another feature is that this setup suppresses so-called common-mode interference, which is a type of disturbance affecting both the signal and the signal return.

transforms the 50 Ω of the oscilloscope to 80 kΩ was connected to the probes. For frequencies from tens of Hz up to a hundred kHz, this transformer has too low sensitivity and also too large phase shifts, so a conventional resistive divider of 10 kΩ/50 Ω was used instead. It has lower sensitivity at higher frequencies, but a flat low-frequency response (see **Paper I** for more details on the use of these probes).

4.3 Mass spectrometry

In order to characterize the different species in the deposition flux other techniques than using electrostatic probes are needed. In this work, a method known as mass spectrometry has been employed to look at the energy distributions of different ions present in the plasma. The technique is widely used within all kinds of areas, both in industry and academia. The setup is as follows: An extraction probe with a small orifice is inserted into the plasma, into which gas atoms and ions enter. The mass spectrometer uses both electric and magnetic fields to filter incoming ions with respect their mass-to-charge ratio. This means that when studying neutrals, they first have to be ionized. By activating an ionization stage situated inside the extraction orifice consisting of a hot filament ejecting electrons, the neutral atoms become ionized through impact ionization. All ions then pass a series of filters; first energy-dependent followed by mass-dependent filtering.

There are different types of filters used to filter out ions depending on their energy. The instrument used in **Paper 2** was an energy-resolved mass spectrometer and a so-called Bessel box was utilized. It is a rather simple construction, which consists of electrodes that retard and focus the incoming ions, and thereby letting ions of a certain energy pass [32].

The final stage in the filtering process is a mass filter, and the most commonly used type is called a *quadrupole mass filter*. It uses four parallel electrodes onto which a constant (dc) plus a time-varying (ac) potential are applied. For given dc and ac values the ion trajectories through the electrodes will vary depending on the mass-to-charge ratio, in a way that only the desired ions will pass the filter while the others will be deviated from their original path. Finally the ions will be detected with a

secondary electron multiplier (or a Faraday cup) and counted for in the included software.

5 Magnetron sputtering

5.1 Background

In the late 1930s Penning invented a way to better confine electrons near a surface by using electric and magnetic fields, resulting in increased ionization of the plasma in the vicinity of the surface. The Penning Discharge was a first step towards the construction of a magnetron[14] [33]. In the 1970s and 1980s variations of the Penning's invention was developed by several researchers, notably Penfold and Thornton [34] and later on Mattox, Cuthrell, Peeples and Dreike [35]. These new magnetrons were placed inside deposition chambers (as previously seen in Figure 1) and allowed sputtering at lower pressures (~ mTorr) and lower voltages (~ 500 V), while having higher deposition rates than what had previously been attained using dc sputtering without magnets.

The reason for the magnetron being excellent in confining the plasma is the magnetic field configuration combined with an electric field, such as the one generated by applying an electrical voltage. One example is where the magnets are placed with one pole positioned at the central axis of a circular magnetron, and the second pole placed in a ring configuration around the outer edge, as displayed in Figure 12.

[14] Actually the first types of magnetrons were not used for material processing, but instead for generating microwaves in radars. These were the so-called cavity magnetrons developed in the 1920s. Today we find these magnetrons inside all microwave ovens.

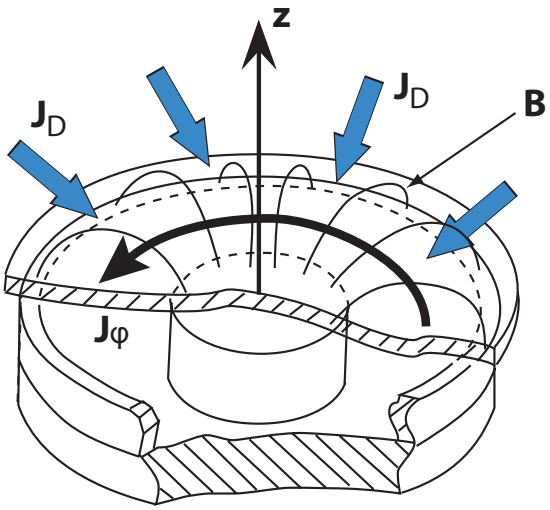

Figure 12. A circular planar magnetron cathode, showing the shape of the magnetic field, the current densities and the resulting drift path.

It results in crossed E and B fields, which generates a Hall drift of the electrons (discussed in 3.1) and effectively traps them in a torus above the so-called target race track, which is a zone where the erosion of the target is particularly effective, as shown in Figure 13. The reason for this erosion is that the better confined electrons increases the plasma density, which in turn increases the probability of ionizing collisions leading to an increased ion bombardment creating a race track. The race track is radially located where the electric field and the magnetic field are perpendicular to each other, which is somewhere between the inner magnet and the outer magnet ring.

One of the disadvantages of these early magnetron sources was that the plasma was too effectively trapped near the surface of the sputtering target due to the magnetic field emerging and reentering the target in a closed loop type of pattern. This is called a balanced magnetron and is displayed in Figure 13.

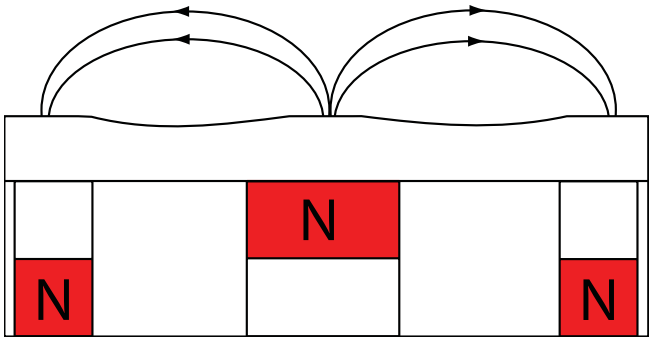

Figure 13. Schematic drawing of a cross section of a balanced magnetron, displaying the magnetic field lines as closed loops above the target surface. Between the inner and outer magnetic rings the target displays an erosion track, or the so-called race track.

Instead it was the invention of the unbalanced magnetron by Windows and Savvides in 1986 that offered a better solution [36]. The unbalanced magnetron allows some electrons to escape from the confining **E**×**B** field and create plasma in regions away from the target surface, which ultimately leads to a better transport of material to the substrate. A sketch of an unbalanced magnetron is shown in Figure 14. An additional feature with this configuration is that when the escaping magnetic field is linked to other unbalanced magnetron sources (north to south poles) the plasma generation area can be significantly increased.

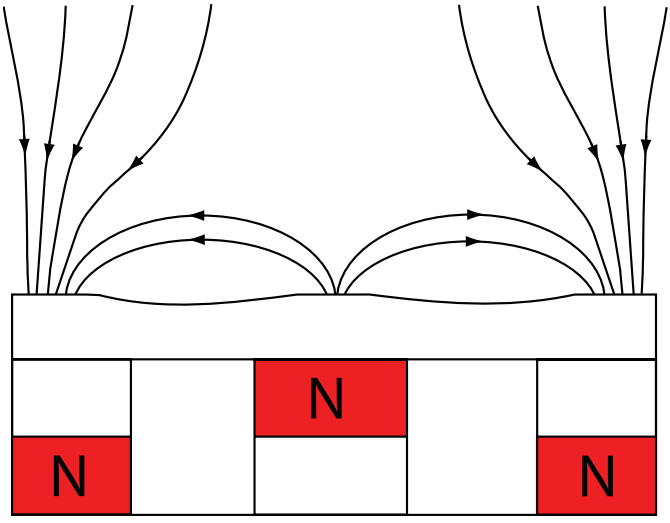

Figure 14. Schematic drawing of a cross section of an unbalanced magnetron, displaying the magnetic field lines as only partially closed loops above the target surface. Here, the electrons can more easily escape and travel towards the substrate region.

5.2 Ionized PVD

As we have come to understand, magnetron sputtering is an important industrial process for many applications ranging from deposition of hard coatings to deposition of functional coatings for electronic applications. Due to increasing demands from industry there is a constant need for improved coatings, which has led to a continuous effort in developing new and better sputtering techniques. This is so that producers of thin films can tailor and enhance properties like hardness, wear and corrosion resistance, as well as specific electrical and optical behavior. One such possibility is direct control over the sputtered flux through increased ionization of the sputtered material by using a substrate bias (see below). Another advantage is that bombarding ions can transfer momentum to the surface atoms on the coating, which in turn leads to increased adatom mobility. This has beneficial consequences for microstructure of the thin film regarding enhanced mechanical and chemical properties. However, in glow discharge processes such as magnetron sputtering it is relatively easy to achieve a large fraction of working gas ions (like Ar^+), whereas ions from the sputtered material are rare. For many applications it is desired to increase the fraction of the latter type of ions. The reason for this is that ions contrary to neutrals from the sputtered material can be controlled by an electric field in terms of both direction and energy. With the use of a negative potential (bias voltage) on the substrate it is possible to deposit material into vias and trenches, where a neutral flux would tend to cover the upper part of the walls while leaving the bottom only partly covered.

When the deposition flux reaching the substrate consists of more ions than neutrals the process is referred to as ionized PVD, or IPVD. There are many different IPVD-techniques available today. Some techniques increase the ionization of the atoms by post-vaporization ionization using plasmas and magnetic coils to generate ions that can be accelerated to the substrate surface when applying a negative bias [37]. Another technique is the previously mentioned cathodic arc evaporation (see for example reference 38), which uses the fact that very localized; extremely high current discharges can create a dense plasma resulting in a high degree of ionization around a particular spot. Still, the drawback of dealing with microdroplets persists. A third possibility is the use of hollow cathode magnetron sputtering [39, 40]. The hollow cathode traps electrons in a cup-shaped geometry or between two parallel plates and

working like two electrostatic mirrors, and thus increasing the plasma density and the probability of ionizing any material passing through. The technique is not that easily upscaled to industrial dimensions, and also introduces additional complexity in the deposition process, which has prevented it from commercial success.

Still the perspective of having advantages like: improvement of the film quality by denser films [41] and enhanced adhesion, decreasing the deposition temperature [42], and better control over the deposition flux, is more than enough to continue developing new IPVD techniques. It is in this light that high power magnetron sputtering (HiPIMS) has become so interesting, and is used as the main process in this thesis.

5.3 High impulse power magnetron sputtering (HiPIMS)

High power impulse magnetron sputtering (HiPIMS), or sometimes referred to as high power pulsed magnetron sputtering (HPPMS), is an ionized PVD method based on conventional direct current magnetron sputtering (dcMS). In dcMS very little of the sputtered material is ionized since the plasma power density is not high enough (or simply speaking that the electrical discharge power is not high enough). Increasing the power density will on one hand increase the plasma density and ionize more of the sputtered material, but on the other hand eventually melt the target, which of course is a less desirable effect. Instead, by applying very high power in repeated, short pulses, the average power is kept low enough for the cooling system to keep the target temperature below the melting point. The high power (up to MW in the pulse peak) within each pulse is enough to create a dense plasma in front of the target to ionize a large fraction of the sputtered material.

The technique was described by Dr. Kouznetsov in 1999 [8], who most likely was inspired by previous work from Mozgrin *et al*. [9], and furthermore patented by himself and his company Chemfilt AB (today Chemfilt Ionsputtering AB, which manufactures HiPIMS power supplies) [10]. There are many advantages inherent to the HiPIMS process. It is very easy to set up if a conventional magnetron sputtering system is present. In principle, all you need to change is the power supply. Furthermore, a large fraction of the sputtered material is ionized (30-90 % depending

on material [43]), resulting in denser films [44, 45]. By varying the substrate bias voltage the energy of the deposition flux can be tailored for certain purposes. The film growth will be perpendicular to the substrate surface even in the case of substrates of complex geometries [44] making the technique suitable for *e.g.* trench filling applications in the semiconductor industries [8]. Another advantage of generating a large fraction of ions in HiPIMS is the possibility of using it for surface pretreatment. Here bombarding ions sputter away oxide layers existing on most material surfaces and thereby cleaning the substrate prior to deposition. During the process some ions are also implanted in the substrate. This results in a gradual change in composition between the substrate and the film grown on top. Pre-treatment of surfaces in this way has been shown to improve adhesion [45, 46] and thus enhanced wear and corrosion properties [47].

The lower deposition rate for HiPIMS compared to dcMS for the same average power is a major drawback[15]. In a review on HiPIMS by Helmersson *et al*. [48] it was found that the rates are typically in the range of 25-35 % compared to dcMS, which makes the technique less attractive for industrial use. A reason for this, as suggested by Christie [49], is the back-attraction of metal ions to the target followed by self-sputtering. Konstantinidis *et al*. [50] pointed out the importance of the plasma conductivity, while Bugaev *et al*. [51] and Bohlmark *et al*. [52] showed that the magnetic confinement of the sputtered material affected the deposition rate. Recently Emmerlich *et al*. [19] identified a non-linear energy dependence of the sputtering yield, meaning that it does not make sense to compare HiPIMS and dcMS deposition rates for the same average power if not taking this dependence into account. When comparing with experimental results they saw trends confirming their experiments, but it could not fully explain the differences. It is most likely a combination of the factors mentioned above, and possibly others, that affects the deposition rate. The study in **Paper 2** also highlights the importance of looking into the particle transport in order to better understand the differences in deposition rates.

[15] One could also mention the risk of arcs, ejecting microdroplets out into the deposition chamber. With modern arc suppression units this is not considered to be a problem anymore.

6 Summary of results

6.1 Paper 1

In section 3.6 a new type of anomalous transport operating in the HiPIMS regime was discussed in connection to changes in resistivity and plasma instabilities. It all started with measurements of magnetic field changes in HiPIMS by Bohlmark *et al*. [11] done on the same experimental setup as used in this work. They found that a surprisingly large amount of electrons were transported across the magnetic field lines during the HiPIMS discharge, which could not be explained by classical theory of diffusion and electrical conductivity, moving electrons across the magnetic field lines using collisions, or Bohm diffusion (described in section 3.4). A good way of characterizing the transport properties are by measuring the azimuthal current density, J_φ, which are confined electrons rotating in the vicinity of the target race track, and the discharge current density, J_D, generated by cross-field-transported electrons. By doing so, it is possible to calculate the current density ratio. In dcMS, measurements of J_φ / J_D give typical values in the range $8 < J_\varphi / J_D < 30$ [23, 53]. In HiPIMS and mid-frequency pulsed magnetrons, recent measurements in different devices [11, 28]) agree on a value close to $J_\varphi / J_D = 2$, which is roughly an order of magnitude lower than for dcMS.

An important part of this work was dedicated to verifying the current density ratio $J_\varphi / J_D = 2$. It was found that the previously used Hall current was only one contribution out of three to the total azimuthal current density in HiPIMS. A more detailed analysis of the J_φ / J_D ratio showed that the value $J_\varphi / J_D = 2$ was indeed attained, in agreement with Bohlmark's investigation on anomalous electron transport in HiPIMS plasmas.

Further investigations of the anomalous transport resulted in the discovery that this phenomenon could quantitatively be described as being related and mediated by highly nonlinear waves, likely due to the modified two-stream instability (MTSI), resulting in electric field oscillations in the MHz-range (the so-called lower hybrid frequency, see section 3.6). Measurements in the plasma confirmed these oscillations as well as trends predicted by the theory of these types of waves. The results provided important insights into understanding the mechanism behind the anomalous transport.

6.2 Paper 2

An important result of the anomalous transport is that the current ratio J_φ / J_D is found to be inversely proportional to the transverse resistivity, $\eta_\perp$, which governs how well momentum is transferred from the electrons to the ions. By looking at the forces involved in the charged particle transport it becomes clear that the azimuthal force on the ions, $\mathbf{F}_{i\varphi} = -\eta_\perp e n_e \mathbf{J}_\varphi$, exerts a volume force on the ions tangentially outwards from the circular race track region. If the anomalous transport caused a decrease of J_φ / J_D by an order of magnitude, then $\eta_\perp$ would be expected to increase by an order of magnitude and thus increase the azimuthal force. It is therefore expected that the ions would be transported across the magnetic field lines and to a larger extent be deflected sideways, instead of solely moving from the target region towards a substrate placed in front of the target some distance away.

The above presented theory was verified in two separate experiments consisting of: (1) a comparison between deposition rates on substrates placed perpendicularly near the side of the target surface and a reference substrate placed parallel in front of the target, and (2) an investigation of the ion energy distributions of the side-deposited ions. The measurements were performed for both HiPIMS and dcMS.

It was found that a substantial fraction of sputtered material is transported radially away from the cathode and lost to the walls in HiPIMS as well as dcMS, but more so for HiPIMS giving one possible explanation to why the deposition rate on substrates placed in front of the target is lower compared to dcMS. Furthermore, ion energy distributions of sideways transported Ti^+ measured in the HiPIMS plasma at different z distances from the target race track clearly showed a high energy tail with ion

energies above 20 eV. These results were only seen in the HiPIMS pulses and not in the conventional dcMS discharge, as expected, since there are no reports on this type of anomalous cross-field transport in dcMS. Important conclusions from this work were that the ion energy distribution measurements confirmed the theoretical model on anomalous transport, resulting in a previously neglected cross-field side-transport.

7 Ongoing and future research

The world of plasma still remains partly (or largely) undiscovered, and so the combination of thin film deposition, HiPIMS and plasma definitely leaves a few questions left to be solved. This is rather fortunate for me, since I have reached only halfway in the pursuit of my PhD degree.

From the material presented so far it is clear that there is a gap between the theoretical understanding and experimental results of HiPIMS. One way of bridging this would be through better models. At the moment our colleagues at the Royal Institute of Technology in Stockholm are working on a new HiPIMS model. The results generated until now are very promising, and it is now time to take predictions on particle transport, gas rarefaction, electrical field and potential distributions etc. and experimentally verify them. One such ongoing study is the transition from HiPIMS mode to dcMS mode when applying long discharge pulses.

When investigating transport properties in HiPIMS plasmas, rotating spoke formations were discovered. This has previously been detected in other plasma experiments outside the field of thin film deposition [54, 55]. It would be highly interesting to investigate this matter further and physically being able to characterize what happens. This could be another clue to the charged particle transport in HiPIMS.

The possibility of additional plasma probing is far from exhausted. There is still a need to do correlated density and electric field measurements as well as exploiting magnetic probes in order to measure the degree of anomalous transport in the whole geometry. Together with our German colleagues at the University of Kiel there will

be additional probe measurements using thermal probes to spatially resolve the ion energy distributions.

Finally there are some other ideas, but in case of patents they will have to remain secret for the time being…

8 References

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