Thèse n°10204

EPFL

Plasma-Assisted Hybrid Vapour Deposition Technology for Thin Film Fabrication

Présentée le 4 mai 2023

Faculté des sciences et techniques de l'ingénieur Laboratoire de photovoltaïque et couches minces électroniques Programme doctoral en science et génie des matériaux

pour l'obtention du grade de Docteur ès Sciences

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2023

To Isabella and Alexander Hain

[...] as we know, there are known knowns; there are things we know we know. We also know there are known unknowns; that is to say we know there are some things we do not know. But there are also unknown unknowns—the ones we don't know we don't know. [...] it is the latter category that tends to be the difficult ones.

– D. H. Rumsfeld

I would like to extend a huge thank you to my supervisors Dr Thomas Nelis and Dr Aïcha Hessler-Wyser. The support and knowledge I have received from both of them has been outstanding, from Thomas's whips and barks to Aïcha's constructive comments and attention to detail.

Thanks to the joint supervision of Thomas and Aïcha, and collaborations with Prof. Johann Michler (to whom I also extend my thanks), I have been very fortunate to have had access to the infrastructure of BFH's group for Plasma Surface Engineering, EPFL's PV-Lab and Empa's for Mechanics of Materials and Nanostructures. Not only did that mean access to a wide range of equipment, but, more importantly, I had the opportunity to meet and work with many fantastic people. Without all of you, work would not have proceeded half as well and for sure it would not have been nearly half as fun as it has been. Thanks to you all!

To Luisa, you've been such a wonderful friend and I am so glad to have met you. Without your constant encouragement,"manifesting" and Elton John singing sessions, I doubt that everything would have gone **EXACTLY** to plan. Chaaaaaaarge!

To the gorgeous Boyos group consisting of Daniele, Petai and Patrik, you guys are the best! Thanks for all the crazy, fun and weird moments we've spent together, from the multiple coffee and beer sessions and collective screaming on discord to just chilling dressed as a dragon, Scooby Doo, a lobster and minestrone soup.

To Carlos, Gaby and Pretzel, thanks for being there for me, for all the games and movies nights (especially *The Room*) and for adopting me into the Swiss Cluster team.

To Krzysztof and Maria, from Poland to Switzerland we've stuck together and you've always been around to provide a helpful hand or a kind word. Dzięki wielkie!

To the BFH and Empa peeps: Léo (plasma survivor), Tanya (you have my shoulder), Cinzia (lockdown), Alex (embracing the Scottishness), Peter (the Godfather), Kuba (his gaze), Nicoló (jam sessions), Enrico (amazing!), Bryan (cocktail master), Angelos and Eleni (attack!), Amit (boss), Annalena (banter), Mathieu and Alex (the happy couple).

To my collaborators: Janos, Patrick, Ben, Helen, James, Chanel, Sean, Thomas, Louis, Paul. To Prof. Agnieszka Kopia and Prof. Piotr Bała for their guidance and support from the very beginning of my scientific journey. Wiele Wam zawdzięczam.

Finally, to my parents, friends and family, thank you for your continuous support throughout this time.

ABSTRACT

Continuous development of thin film deposition technologies is essential for the fabrication of films that meet the specific requirements of their target applications and Therefore, it is necessary to increase the number of accessible working conditions. and tuneable process parameters, which can be achieved by venturing into the field of hybrid techniques. Among a variety of available deposition techniques, the focus of this work is on physical vapour deposition magnetron sputtering (PVD MS) methods, with the addition of microwave (MW) plasma. The main advantage of this work is its generalised approach to examining the "big picture" not only of film deposition itself, but also of the phenomena occurring at the material source, how they affect the deposition environment and the nature of the decoupled effects, and how they relate to film characteristics. With this in mind, the reader is first guided through selected plasma physics concepts necessary to follow the proposed hybrid vapour deposition The validity of this methodology is examined on the example of (HVD) processes. three material case studies, namely diamond-like carbon (DLC), indium nitride (InN) and zinc tin nitride (ZTN). Each case study explores the influencing factors of MS, starting with pulsed direct current magnetron sputtering (p-DCMS) through high power impulse magnetron sputtering (HiPIMS) and reactive HiPIMS (R-HiPIMS). Furthermore, the effects of incorporating the volume MW plasma (which fills the entire vacuum chamber) are investigated in the context of improving process control through tailored phenomenological decoupling, i.e. separation of otherwise interdependent effects. A range of *in situ* diagnostic techniques are used, including studying the obtained HiPIMS I(V,t) curves, time-resolved optical emission spectroscopy (OES), time-of-flight mass spectrometry (ToF-MS) and Langmuir probe measurements. The fabricated films were characterised in terms of the material's structure, micro- and nanostructure, as well as application properties. The obtained results highlight the significant contribution of MW plasma for enhancing phenomenon control during sputtering for all studied material cases.

Keywords: thin films deposition; HiPIMS; microwave plasma; plasma diagnostics; DLC; nitrides;

ZUSAMMENFASSUNG

Die kontinuierliche Weiterentwicklung der Dünnschichttechnologien ist entscheidend für die Herstellung von Schichten, die den spezifischen Anforderungen ihrer Zielanwendungen und Arbeitsbedingungen entsprechen. Dazu ist es notwendig die Anzahl der zugänglichen und einstellbaren Prozessparameter zu erhöhen, was durch den Einsatz von Hybridtechniken erreicht werden kann. Unter den verschiedenen verfügbaren Abscheidungstechniken konzentriert sich diese Arbeit auf die physikalische Gasphasenabscheidung Magnetronsputtern (PVD MS) unter Zusatz von Mikrowellenplasma (MW). Der Hauptvorteil dieser Arbeit ist der allgemeine Ansatz, nicht nur die Schichtabscheidung selbst zu untersuchen, sondern auch die Phänomene, die an der Materialquelle auftreten, wie sie die Abscheidungsumgebung und die Art der entkoppelten Effekte beeinflussen und wie sie mit den Schichteigenschaften zusammenhängen. Vor diesem Hintergrund wird der Leser zunächst durch ausgewählte plasmaphysikalische Konzepte geführt, die für das Verständnis der vorgeschlagenen Verfahren zur hybriden Gasphasenabscheidung (HVD) notwendig sind. Die Gültigkeit dieser Methodik wird anhand von drei Materialfallstudien untersucht, nämlich diamantartigem Kohlenstoff (DLC), Indiumnitrid (InN) und Zinkzinn-Nitrid (ZTN). In jeder Fallstudie werden die Einflussfaktoren des MS vom gepulsten DC-Magnetronsputtern (p-DCMS) über das HochleistungsImpulsmagnetronsputtern (HiPIMS) bis hin zum reaktiven HiPIMS (R-HiPIMS) untersucht. Darüber hinaus werden die Auswirkungen der Einbeziehung des MW-Volumenplasmas (das die gesamte Vakuumkammer ausfüllt) im Zusammenhang mit der Verbesserung der Prozesskontrolle durch massgeschneiderte phänomenologische Entkopplung, d.h. Trennung ansonsten voneinander abhängiger Effekte, untersucht. Eine Reihe von in situ Diagnoseverfahren wird eingesetzt, einschliesslich der Untersuchung der erhaltenen HiPIMS I(V,t)-Kurven, der zeitaufgelösten optischen Emissionsspektroskopie (OES), der FlugzeitMassenspektrometrie (ToF-MS) und Langmuir-Sondenmessungen. Die hergestellten Schichten wurden hinsichtlich Materialstruktur, Mikro- und Nanostruktur sowie Anwendungseigenschaften charakterisiert. Die erzielten Ergebnisse unterstreichen den signifikanten Beitrag des MW-Plasmas zur Verbesserung der Phänomenkontrolle während des Sputterns für alle untersuchten Materialfälle.

Stichworte: Dünnschichtabscheidung; HiPIMS; Mikrowellenplasma; Plasmadiagnostik; DLC; Nitride;

RÉSUMÉ

Le développement continu des méthodes de dépôt de couches minces est essentiel pour la fabrication de films avec des exigences spécifiques à chaque application et à leurs conditions d'utilisation. Afin de pousser les limites de ces développements, il est nécessaire d'augmenter le nombre de paramètres de processus accessibles et réglables, ce qui peut être réalisé par des techniques hybrides. Parmi une variété de techniques de dépôt disponibles, ce travail se concentre sur les méthodes de dépôt physique en phase vapeur par pulvérisation cathodique (PVD MS), avec l'ajout d'un plasma micro-ondes (MW). L'originalité de ce travail réside dans son approche généralisée et la «vue d'ensemble», non seulement du dépôt de film lui-même, mais aussi des phénomènes qui se produisent à la source du matériau, de la façon dont ils affectent l'environnement du dépôt et la nature des effets découplés, ainsi que de la façon dont ils sont liés aux caractéristiques du film. Dans cette optique, le lecteur est d'abord guidé à travers certains concepts de physique des plasmas nécessaires pour appréhender les processus proposés de dépôt hybride en phase vapeur (HVD). La validité de cette méthodologie est examinée pour trois études de cas de matériaux, à savoir le carbone de type diamant (DLC, aussi appelé le carbone adamantin), le nitrure d'indium (InN) et le nitrure de zinc-étain (ZTN). Chaque étude de cas explore les facteurs d'influence du MS, en commençant par la pulvérisation cathodique à courant continu pulsé (p-DCMS), en passant par la pulvérisation cathodique à impulsions à haute puissance (HiPIMS) et la HiPIMS avec une espèce réactive (R-HiPIMS). En outre, les effets de l'incorporation du plasma MW volumique (qui remplit toute la chambre à vide) sont étudiés dans le contexte de l'amélioration du contrôle du processus par un découplage phénoménologique adapté, c'est-à-dire la séparation d'effets habituellement interdépendants. Une série de techniques de diagnostic in situ sont utilisées, notamment l'étude des courbes HiPIMS I(V,t) obtenues, la spectroscopie d'émission optique résolue dans le temps (OES), la spectrométrie de masse à temps de vol (ToF-MS) et les mesures par sonde de Langmuir. Les films ont ensuite été caractérisés, en particulier leur structure, de micro- et nanostructure du matériau, ainsi que leurs propriétés optiques et électriques. Les résultats obtenus montrent clairement l'importance considérable du plasma micro-ondes pour améliorer le contrôle des phénomènes apparaissant lors du dépôt par pulvérisation pour tous les cas de matériaux étudiés.

Mot-clés : déposition couches minces; HiPIMS; plasma micro-ondes; analyse du plasma; DLC; nitrures;

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LIST OF ABBREVIATIONS

a-C	amorphous carbon
a-C:H	hydrogenated amorphous carbon
Arc-PVD	cathodic arc deposition
BF-TEM	bright-field transmission electron microscopy
CFE	cold field emission
COF	coefficient of friction
CVD	chemical vapour deposition
DC	direct current
DFT	density functional theory
DLC	diamond-like carbon
ECR	electron cyclotron resonance
EDX	energy dispersive X-ray spectroscopy
FNS	first negative system
FPS	first positive system
FWHM	full width at half maximum
HAADF	high-angle annular dark field
HiPIMS	high power impulse magnetron sputtering
HVD	hybrid vapour deposition
InN	indium nitride
MA-HiPIMS	microwave plasma assisted high power impulse magnetron sputtering
MA-pDCMS	microwave plasma assisted pulsed-direct current magnetron sputtering
MAR-HiPIMS	microwave plasma-assisted reactive high power impulse magnetron sputtering
MBE	molecular beam epitaxy
MEMS	microelectromechanical systems
MPPMS	modulated pulse power magnetron sputtering
MS	magnetron sputtering
MW	microwave
nc-graphite	nanocrystalline graphite
NEMS	nanoelectromechanical systems

xvi Abbreviations

OES	optical emission spectroscopy
pDCMS	pulsed-direct current magnetron sputtering
PVD	physical vapour deposition
R-HiPIMS	reactive high power impulse magnetron sputtering
RF	radiofrequency
RFA	retarding field analyser
SAED	selected area electron diffraction
SE	secondary electron
SEM	scanning electron microscopy
SPS	second positive system
STEM	scanning transmission electron microscopy
SZD	structure zone diagram
ta-C	tetrahedral amorphous carbon
ta-C:H	tetrahedral amorphous carbon
TEM	transmission electron microscopy
ToF-MS	time-of-flight mass spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectometry
ZTN	zinc tin nitride

1

INTRODUCTION

Thin films, classified as low-dimensional materials fabricated via condensing atomic, molecular and/or ionic species, have become almost a necessity in many scientific and industrial fields, due to possibility of accessing a wide range of materials and These include obtaining various chemical compositions (e.g. metals, functionalities. alloys, compounds), structures (mono- and polycrystalline, amorphous), morphologies (e.g. rough, smooth, densely packed, porous), and applicational properties (hardness and wear resistance, corrosion resistance, optical, electrical, magnetic), among many others [1–8]. There is a variety of fabrication processes from which to choose from, mainly classified into wet (e.g. electro- and electroless plating) and vacuum (e.g. evaporation, sputtering, atomic layer deposition) methods [9, 10]. It is important to highlight that there is no single "best" method, with process selection depending on a number of factors, such as process scale, applicational requirements, technological and automation possibilities and/or operation costs, therefore each case should be considered individually. However, in the scope of this thesis, we will be focusing on a group of vacuum techniques referred to as vapour deposition methods. Often, this group is divided into two extremes, namely chemical vapour deposition (CVD) and physical vapour deposition (PVD). CVD consists of depositing solid materials in the form of thin films, as a result of chemical reactions of gaseous species on the substrate's surface initiated by high substrate temperatures. In PVD, thin films are fabricated through atomic material deposition. The material is vapourised from a solid or liquid source in the form of atoms or molecules and transported through a vacuum/ low pressure gaseous/ plasma environment towards the surface of the substrate, where they then condensate, initiating film growth. Regardless of the selected variant, the fabrication procedure follows the same three steps, as described in [11]:

- synthesis/ creation of depositing species: the material can be transformed into vapour phase through evaporation, sputtering or chemical vapours and gases;
- *transport from source to substrate*: this may occur under line-of-sight, thermal scattering, molecular flow conditions or ionisation;
- *deposition onto the substrate and subsequent film growth*: once the atoms/ ions/ molecules are deposited, the film nucleates on the substrate and grows as a result of various mechanisms.

Considering the ever increasing requirements of current technological developments, e.g. in the fields of electronics (MEMS, NEMS) or photovoltaics (solar cells), it starts to become more interesting to combine these film fabrication approaches, opening up to a plethora of hybrid vapour deposition (HVD) opportunities [12–19]. In turn, we give ourselves more parameters, with which we can steer the deposition process in the desired direction. Once

again, there are different technologies to choose from, such as the incorporation of lasers, electron and ion beam sources, or, as was selected for this work, plasma.

In the presence of plasma, it is possible to produce various energetic species (Figure 1), such as charged particles (electrons, ions and radicals), and highly reactive neutral species (reactive atoms, reactive molecular fragments, photons, excited atomic states) [11, 20]. With respect to the conditions of vapour deposition techniques, often the plasma will be considered to be in non-equilibrium state [21, 22], which is interesting for decoupling phenomena that would otherwise be dependent on one another.



Figure 1 Graphical overview of possible plasma species and occurring phenomena;

In non-equilibrium state, energy transfer from an applied electric field to the electrons proceeds considerably quicker than through electron-heavy particle collisions, as a result of which the gas temperature is lower than the electrons' kinetic energy ($T_q < T_e$). Subsequently, rather than the plasma's chemistry being thermally driven, energetic electrons are responsible for initiating chemical processes. This provides the option for tuning the plasma's reactivity, while maintaining low gas and substrate temperatures. Furthermore, it provides possibilities for dissociating thermally stable gas precursors or evaporating materials with high melting points without resulting to high process temperatures. Additional strategies for limiting gas temperatures include using noble gases as plasma gas and adjusting gas flows, reducing plasma dimensions, i.e. surface to volume ratio, and operating in short-discharge modes. Furthermore, these plasma characteristics enable modifying the energy and amount of incoming deposition material, in turn, providing control over the structure and properties of the growing film, including degree and direction of orientation, grain size, texturing, film density and film stress [23]. Within the scope of this thesis, the means for tuning the plasma behaviour and composition were evaluated based on the material case studies of diamond-like carbon (DLC), indium nitride (InN) and zinc tin nitride (ZTN) thin films. A range of technologies were combined to provide decoupling capabilities for attaining different atom and ion sources

and manipulating their deposition and growth mechanisms. A short description of the possibilities each of the listed technologies may provide are given below:

- high power impulse magnetron sputtering (HiPIMS): generates large quantities of highly energetic ions as a result of high pulse power densities (leading to highly compact film structures), accompanied in some cases by directed flux of charged species, decouples e.g. plasma power from plasma density or high current from arcing (linked in traditional DC magnetron sputtering discharge);
- *unbalanced magnetrons*: changing the strength distribution of the magnets within the magnetron affects the produced electromagnetic field, in turn, modifying the plasma and its location in relation to the magnetron;
- *solid-state microwave generators*: modifies plasma temperatures and enables species ionisation/ post-sputtering ionisation, produces a volume plasma that fills the entire vacuum chamber (influence over plasma chemistry and chemical reactions);
- *substrate biasing*: attracting positively charged species and influencing their impact energy, where pulsed biasing synchronised with the magnetron discharges facilitates ionic species selection;

STATEMENT OF PROBLEM

Although there are many detailed studies related to individual technologies or phenomena mentioned in the introductory chapter, there are few works that take a more generalised approach to determine mutual relations between different plasma-based technologies that create the deposition environment, the overall system configuration, and their effect on the resulting fabricated film. This methodology facilitates identifying key parameters of a given process for obtaining thin films targeted for specific applications. Following the previously mentioned process steps, three main issues regarding the deposited material can be formulated (Figure 2):

- *substrate-film interface*: substrate damage/ changes being temperature-induced and/or brought upon impact of deposited material species, initial nucleation of deposited material on the substrate's surface, diffusion, geometry conformation;
- *growth and structuring of film*: film growth mechanism, growth homogeneity, growth rate, interaction depth with already deposited material, microstructure;
- surface quality of fully deposited film: surface roughness, morphology, chemistry;



Figure 2 Schematic depiction of film fabrication concerns;

With the above in mind, the general challenges concern proposing a deposition procedure for a wide range of films in a reproducible manner, while maintaining a relatively simple setup configuration, as well as characterising the deposition environment within the vacuum chamber as a function of deposition parameters and generated environment, while correlating the obtained information with the characteristics of the final product. Combining plasma-based technologies would enable accessing a much wider range of parameters through phenomenon decoupling. However, as plasma environments are often highly complex (as will be shown in the following chapters), many assumptions are made, therefore, reflecting the reality is far from straight forward. Nevertheless, through this generalised approach it is possible to establish trends by coupling *in situ* deposition environment diagnostics with deposited material characterisation. To validate the HVD approach, three different material case studies were selected and investigated within the scope of this work, performed with increasing system complexity:

- DLC: investigating the influence of pulsed-direct current MS (pDCMS), high power impulse magnetron sputtering (HiPIMS) and their microwave plasma-assisted (MA-pDCMS, MA-HiPIMS) variants on the properties of the fabricated DLC films. Here, the challenge consists of evaluating the effect of the two sputtering modes, while determining the role of substrate biasing and microwave plasma source positioning in obtaining hard films of low surface roughness.
- InN: low temperature fabrication of InN thin films via microwave plasma-assisted reactive high power impulse magnetron sputtering (MAR-HiPIMS). The main issues addressed here is related to mitigating indium discharge instabilities during reactive sputtering, while providing means for obtaining stoichiometric nitrides.
- ZTN: low temperature co-sputtering of zinc and tin during MAR-HiPIMS, where the effect of substrate biasing and microwave power on the crystallographic structure of ZTN films of similar chemical compositions and thicknesses is studied.

THEORY REVIEW

[...] a plasma does not tend to conform to external influences; rather, it often behaves as if it had a mind of its own.

– F. F. Chen

Plasma is a rich and highly complex field of studies, often combining concepts from classical mechanics, electro-, thermo- and fluid-dynamics, solid state and statistical physics, quantum chemistry and mechanics. With the estimation that up to 99 % of the visible universe consists of plasma, we benefit from its many forms, from the life-sustaining Sun to the magnificence of polar lights. We can therefore expect there to be multiple factors influencing its properties, with one type of plasma system classification shown in Figure 3. Here, the plasma density and electron energy are used as classification parameters, however, there are many others: natural vs technical, hot vs cold, thermal vs non-thermal, magnetised vs non-magnetised, and many more. In view of all these possibilities to both achieve and characterise plasma, the aim of this review section is neither to provide nor explain all potential plasma phenomena. Only concepts explicitly used within the frame of this thesis will be presented, all of which will be related to low pressure gas discharge plasmas. This will serve as a guide to understand the underlying principles of plasma-assisted vapour deposition processes and their relevance in the context of the performed experimental work. For more detailed descriptions on plasma-related topics, the reader is referred to the following dedicated "plasma physics" books [21, 24–28]. In the light of this work being focused on understanding the interplay of combined microwave plasma and magnetron sputtering processes for tailored thin film fabrication, this review chapter will discuss the following topics

- plasma fundamentals: plasma conditions, parameters and basic behaviour principles,
- *microwave plasma*: plasma-electromagnetic wave interactions, electron cyclotron resonance effect and its relevance during low pressure plasma processing,
- magnetron sputtering: magnetron design, target sputtering,
- *high power impulse magnetron sputtering*: parameter decoupling and control, reactive sputtering,
- *surface processes*: deposition conditions vs material development.



Figure 3 Electron density vs electron temperature ranges of typical plasma phenomena found in nature or used for technological applications, grey dashed lines mark the Debye lengths (λ_{De}), adapted from [26];

3.1 PLASMA FUNDAMENTALS

3.1.1 Definition and general conditions

Plasma, first coined by Langmuir in the 1920s, is considered as the fourth state of matter and is a term used to describe a *quasineutral gas*, *consisting of charged and neutral particles exhibiting collective behaviour* [25, 26]. We shall now delve into the physical meaning behind this definition and provide the main conditions, which must be met to classify an ionised gas as a plasma.

First, we will consider the notion of *quasineutrality*. Plasma is a collection of free positively (q_{+}) and negatively (q_{-}) charged species, where, within the context of this work are mainly considered to be positively charged ions and electrons (generated when sufficient energy is introduced into a system). The charge densities will remain approximately equal (Eq. 3.1.1) at any given point in space, i.e. remain electrically neutral:

$$n_e \simeq n_i$$
 (3.1.1)

where: n_e and n_i are the densities (m⁻³) of electrons and ions, respectively. To highlight plasma's complex nature, already this equation only approximates reality. Under many experimental conditions, positive doubly charged ions, and in some cases (e.g. oxygen

plasma) negative ions are generated and will contribute to the negative electron balance [21]. Therefore, the following description (Eq. 3.1.2) is more detailed:

$$q_{+} - q_{-} = \sum_{z} z \cdot e \cdot n_{z+} - e \cdot n_{e} - e \cdot n_{-} = 0$$
 (3.1.2)

where: *z* is the charge number for positive ions, *e* is the elemental charge (1.602×10⁻¹⁹ °C), and n_{z+} , n_{-} are the densities of positive ions with charge number *z*, and singly-charged negative ions, respectively.

The second term mentioned in the plasma definition is *collective behaviour*. Overall plasma has a neutral charge, however, local variations can occur. This leads to the generation of electric fields, in turn giving rise to long-range interactions within the plasma between the charged regions via Coulomb forces. Therefore particle motions are not only influenced by local conditions, but also by the state of remote plasma regions. An extreme case of such behaviour is so-called collisionless plasmas, where these forces are much greater than those induced via local collisions.

With the above in mind, it can be said that plasmas will continuously adapt in an attempt to protect themselves from factors leading to electrical neutrality deviations. To better imagine this behaviour, we can compare this "defence mechanism" to that of a stressed hedgehog. When threatened, a hedgehog will roll itself into a tight ball, exposing its sharp spikes in a shield-like manner to protect itself from harm. Similarly, strong electrostatic forces will act to shield the bulk (body) plasma against even slight charge imbalance "threats", whether they be electric interactions between the charged species within the plasma, system components (e.g. vacuum chamber walls), or electrodes and probes (e.g. biased substrates or diagnostic devices). With plasma consisting predominantly of electrons and positive ions, we need to consider their significant mass difference. Often their mass ratio $\frac{m_i}{m_e}$ is assumed as infinite, indicating that it is the electron that is fast enough to react to the generated electric imbalance and move accordingly to provide an excess or deficit of negative charges. By following the relationship shown in Eq. 3.1.3 (under thermal equilibrium conditions, where $T_i = T_e$), the electron velocity (v_e) would be almost 250 times greater than the ion velocity (v_i) of Ar⁺:

$$\frac{1}{2} \cdot \mathbf{m}_{e} \cdot \overline{\mathbf{v}_{e}}^{2} \,\overline{\mathbf{v}_{e}^{2}} = \frac{1}{2} \cdot \mathbf{m}_{i} \cdot \overline{\mathbf{v}_{e}^{2}} \overline{\mathbf{v}_{i}}^{2} = \frac{3}{2} \cdot \mathbf{k}_{B} \cdot \mathbf{T}_{e,i}$$
(3.1.3)

where: m_e – electron mass (9.1×10⁻³¹ kg), m_i – ion mass (approx. 6.6×10⁻²⁶ kg for Ar⁺), k_B – Boltzmann's constant (~1.38×10⁻²³ J· K⁻¹), $T_{e,i}$ – electron/ion temperature (K). As the electrons move to maintain charge neutrality in the bulk plasma, a so-called *Debye sheath* of an opposing charge adjacent to the disrupting surface is generated. The thickness of the sheath is referred to as the *Debye length* (λ_D , Eq. 3.1.4) and under non-equilibrium conditions ($T_e \gg T_i$) the ionic component can be neglected, simplifying λ_D to the *Debye electronic length* (λ_{De} , Eq. 3.1.5). This length is used as a plasma reference screening scale, where λ_{De} must be considerably smaller than all other physical dimensions (*L*) of the studied system to conserve plasma quasineutrality. Furthermore, for the Debye sheath to form and be statistically valid, there need to be enough charged species (N_D , Eq. 3.1.6)

present within the *Debye sphere* (with a radius of λ_{De}), much like there must be enough trees grouped together to collectively refer to them as a forest. Additionally, the relationship shown in Eq. 3.1.6 needs to be met to fulfil the condition for collective behaviour:

$$\lambda_{\rm D} = \sqrt{\frac{\varepsilon_0 \cdot k_{\rm B} \cdot T_e}{n_e \cdot e^2 \cdot \left(1 + \frac{z \cdot T_e}{T_i}\right)}}$$
(3.1.4)

$$\lambda_{\rm De} = \sqrt{\frac{\varepsilon_0 \cdot k_{\rm B} \cdot T_e}{n_e \cdot e^2}} \ll L \tag{3.1.5}$$

$$N_{\rm D} = n_e \cdot \frac{4\pi}{3} \cdot \lambda_{\rm De}^3 \gg 1 \tag{3.1.6}$$

where: ε_0 – permittivity of vacuum (~8.85×10⁻¹² C²·m·J⁻¹).

The next step consists of understanding plasma's temporal behaviour brought on by electrostatic disruptions. If we consider that the positively and negatively charged particles are evenly distributed then there will be no net force applied to any of them, i.e. they are in equilibrium. However, as soon as even one charged particle is out of its equilibrium position, the charge distribution will be modified and electrical (Coulomb) forces will act to pull this particle back towards equilibrium (this will mostly concern electrons). The displaced particles (electrons) overshoot their equilibrium positions (relative to the positive ions) due to their lower inertia and oscillate around them at a frequency known as the angular plasma frequency (ω_v / rad s⁻¹). This phenomenon is schematically presented in Figure 4. In fact, what we can find are the conditions for defining a "relatively simple" mechanical oscillation mechanism. The plasma's reaction to local equilibrium charge distribution perturbations can be, in first approximation, treated as a simple damped oscillation (Eq. 3.1.7, also included in Figure 4). An electric field (E_x , Eq. 3.1.8) forms through the displacement of electrons from their initial position, and the strength of the field will depend on the distance of this displacement (x) and the electron density. The electrons will be accelerated back towards their equilibrium positions, driven by $-e \cdot E_x$, and oscillate (Eq. 3.1.7). Based on this relationship, it is possible to derive the ω_p , or when considering the motion of electrons, the angular electron plasma frequency (ω_{pe} , Eq. 3.1.9):

$$m_e \cdot \frac{d^2 x}{dt^2} = -e \cdot E_x = -\frac{e^2 \cdot n_e \cdot x}{\varepsilon_0} \text{ or } \frac{d^2 x}{dt^2} + \omega_p^2 \cdot x = 0$$
(3.1.7)

$$\mathsf{E}_{\mathsf{x}} = \frac{e \cdot \mathsf{n}_{e} \cdot \mathsf{x}}{\varepsilon_{0}} \tag{3.1.8}$$

$$\omega_{\rm pe} = \sqrt{\frac{n_e \cdot e^2}{\varepsilon_0 m_e}} \text{ or } f_{\rm pe} = \frac{\omega_{\rm pe}}{2\pi}$$
(3.1.9)

where: f_{pe} – numerical electron plasma frequency (s⁻¹ or Hz). It should be noted that these equations assume the presence of cold electrons. As an example, a plasma with an electron density $n_e = 10^{17}$ m⁻³ will have an f_{pe} of approx. 3 GHz.



Figure 4 Schematic representation of a plasma in an electrically neutral state and after inducing electron displacement, in turn generating plasma oscillations;

Interestingly, plasma oscillations are local in a sense that they will not pass on information via collisions like in acoustic waves, but rather through the fringing of the generated electric field to neighbouring "layers" and thermal effects. Moreover, it is important to state that plasma oscillations can only arise when the *mean time between collisions* (τ) with neutral atoms is long enough compared to the oscillation period (i.e. "weak" oscillation damping), therefore the condition shown in Eq. 3.1.10 is required. This condition must also be satisfied for an ionised gas to be classified as a plasma, i.e. charged species are controlled by electromagnetic forces:

$$\omega \cdot \tau > 1 \tag{3.1.10}$$

3.1.2 Basic collision parameters

To better understand plasma behaviour and the implications of the previously mentioned condition $\omega \cdot \tau > 1$, especially under non-equilibrium conditions ($T_e \gg T_i$), it is important to consider the nature of collisions (strong oscillation dampening). Under such conditions, plasmas are characterised by density gradients, which can be brought about by various factors, e.g. pressure gradients or electric field forces, inducing occurrences of random particle collisions. These interactions are critical in the generation of charged particles, excited species or reactive radicals, which are of interest in the context of material surface modifications or film depositions. Each particle collision (any possible electron, ion and neutral species combination) is characterised by a specific *momentum transfer collision cross-section* (σ), which can be defined as an area of interaction between the interacting particles. The distance covered by a given particle, after which a collision is highly probable, is defined as the *mean free path* (λ_{mfp} / m) and depends on σ and the density of particles

within the studied plasma volume (n_V), as seen in Eq. 3.1.11. The mean time between collisions (τ) for particles with a velocity ($\overline{\nu_p}$) is given in Eq. 3.1.12, and its inverse gives the *collision frequency* (ν_{coll} , Eq. 3.1.13), which usually accounts the average over all velocities.

$$\lambda_{\rm mfp} = n_V^{-1} \cdot \sigma^{-1} \tag{3.1.11}$$

$$\tau = \frac{\lambda_{mfp}}{\overline{\nu_p}} \tag{3.1.12}$$

$$v_{\text{coll}} = \tau^{-1} = \frac{\overline{v_p}}{\lambda_{\text{mfp}}} = n_V \cdot \sigma \cdot \overline{v_p}$$
(3.1.13)

These concepts will be further considered when discussing interactions between plasmas and external electromagnetic waves (in the context of microwave plasma generation and cyclotron motion of charged particles), as well as the confinement of electrons in the presence of magnetic fields (magnetron design).

3.1.3 Sheath formation

Having previously defined the Debye length as an important plasma reference screening scale, we will now look at the phenomenon of sheath formation in more detail. Still not accounting for all possible effects, we will consider plasma-chamber wall interactions (Figure 5A). First, we assume that the plasma potential (V_p / V) is equal to 0, meaning that there are no electric fields present within the plasma (q_+ and q_- particles are in equilibrium state). Upon impact with the walls, both ions and electrons will be lost. Remembering that electrons are much faster than ions, they will reach the wall more quickly, therefore more of them will be lost. This will induce quasineutrality perturbations by leaving the plasma with a net positive charge in respect to the walls. An electric field is generated, producing in turn a protective space-charge sheath between the wall and the plasma's bulk in an attempt to retard electron losses. This means that the space-charge sheath will self-adjust so that the electrons will be electrostatically confined and their flux reaching the walls will be approximately equal to the ionic flux. However, for the ions to continuously enter and contribute to the space-charge sheath, they need to be accelerated from the bulk plasma to the sheath's edge to a velocity $v_i(0)$ equal or greater than the so-called *Bohm velocity* (v_{Bohm}) Eq. 3.1.14), otherwise referred to as the Bohm sheath criterion [21, 29]:

$$v_{i}(0) \geqslant v_{Bohm} = \sqrt{\frac{k_{B} \cdot T_{e}}{m_{i}}}$$
(3.1.14)

The space over which the ions are accelerated is known as the *presheath* and it defines the potential drop (ΔV_{Bohm}) between V_p and the potential of the sheath's edge V(0). This entails that the presheath, although remaining approximately quasineutral, possesses a density gradient caused by electrons being repelled back into the bulk plasma. Generally, space-charge sheaths can extend over several λ_{De} , with their thicknesses (d_{sh}) subjected to variations depending on, e.g. extent of surface-plasma charge exchanges or process conditions (gas pressure/composition, power delivery type/frequency, etc.).



Figure 5 (A) Schematic of plasma behaviour and potential changes (bulk plasma \rightarrow presheath \rightarrow sheath) when in contact with a surface, e.g. chamber wall, and (B) example phenomena that can occur within the bulk plasma, sheath and at the substrate surface during processing;

When wanting to describe ongoing interactions in space-charge sheath regions more accurately, the level of complexity that we need to account for quickly escalates. Even estimating the d_{sh} is not so trivial, as there are different possibilities depending on the selected model's assumptions. For example, the matrix sheath model (Eq. 3.1.15) assumes a constant positive ion density (with electrons being strongly repelled), while the Child–Langmuir sheath model (Eq. 3.1.16) assumes ionic flux and energy conservation in the sheath, without considering the ion's energy at v_i (0).

$$d_{sh(matrix)} = \lambda_{De} \cdot \left(\frac{2 \cdot e \cdot V_{sh}}{k_{B} \cdot T_{e}}\right)^{\frac{1}{2}}$$
(3.1.15)

$$d_{sh(C-L)} = \frac{\sqrt{2}}{3} \cdot \lambda_{De} \cdot \left(\frac{2 \cdot e \cdot V_{sh}}{k_B \cdot T_e}\right)^{\frac{3}{4}}$$
(3.1.16)

where: λ_{De} is calculated at the sheath's edge, at which the plasma density is smaller compared to the bulk plasma. Similarly to the case of collisions, sheath formation and related interactions are not the principle focus of this work. However, it is important to know that many interesting phenomena can take place within space-charge sheaths in the context surface plasma applications (Figure 5B), as it serves to act as a link between processes/reactions occurring in the bulk plasma and the treated surface or plasma sources (and *vice versa*). Furthermore, the effects of sheath formation can be used for plasma characterisation, e.g. via Langmuir probe measurements, where a voltage sweep is applied to metallic probe inserted into the plasma (this device was used during the performed experimental work).

3.2 MICROWAVE PLASMA

For many surface processes, e.g. etching and film deposition methods, the use of volume plasmas (filling the entire vacuum chamber) have been of great importance to effectively ionise the working gas, as well as dissociate chemical precursors in a controllable manner. Therefore, it is necessary to gain control over selected plasma properties to achieve the most favourable processing conditions. The option that we will be considering is plasma excitation through the use of electromagnetic waves at a microwave (MW) frequency of f_{MW} =2.45 GHz and induce the electron cyclotron resonance (ECR) effect. To this end, we need to describe the nature of plasma-electromagnetic wave interactions and the means to influence them.

3.2.1 Electromagnetic wave interactions

By exposing plasma to an external electromagnetic wave, it is possible to modify and gain control over certain plasma properties. However, this is only possible under certain conditions related to the initial state of the plasma and incident wave characteristics, such as: incident wave frequency (ω_w), strength of the wave's electric field and its effect on the motion of the electrons, v_{coll} , ω_{pe} , plasma conductivity or generated electric current density. We will not consider each of these effects separately (more details can be found e.g. in the book of Meichsner *et al.* [21], however, we will examine their collective effect in defining the *dielectric permittivity* (ε_p , Eq. 3.2.1) of a plasma. This equation makes use of the previously mentioned damped harmonic oscillator model, while ε is used in the context of Maxwell's equations describing electromagnetic phenomena.

$$\varepsilon_{p} = \varepsilon_{0} \left[\left(1 - \frac{\omega_{pe}^{2}}{\omega_{w}^{2} + \upsilon_{coll}^{2}} \right) + i \cdot \frac{\omega_{pe}^{2} \cdot \upsilon_{coll}}{\omega_{w} \cdot \left(\upsilon_{coll}^{2} + \omega_{w}^{2}\right)} \right] = \varepsilon_{0} \cdot \left[\varepsilon^{'} + i \cdot \varepsilon^{''} \right]$$
(3.2.1)

It can be seen that there are three main parameters influencing ε_p , namely the frequencies of the plasma, electromagnetic wave and that of the collisions, therefore determining ε_p can quickly get complicated. What we can do is show that ε_p is comprised of two components, i.e. real (ε') and imaginary (ε''), that can be used to define the effects of plasma-wave interactions:

- the imaginary component ε'' is related to the absorption of the electromagnetic wave by the plasma and shows that absorption can only occur in the presence of collisions;
- under conditions of $\omega_w < \omega_{pe}$, then $\varepsilon' < 0$, where the electromagnetic wave will be unable to properly propagate, resulting in the wave being partially reflected and absorbed;
- under conditions of $\omega_w \ge \omega_{pe}$, then $\varepsilon_p > 0$, which means that the electromagnetic wave can propagate into the plasma and will be attenuated, the extent of which will depend on the w_w/w_{pe} ratio;

The upper limit of electromagnetic wave absorption is defined as the *critical plasma frequency* (ω_{crit}) , i.e. the frequency at which a *critical plasma density* or *cut-off density* (n_{crit}) , Eq. 3.2.2) is generated, where the wave starts to experience reflection for $\omega_w \ge \omega_{crit}$. From Eq. 3.2.2 it can be concluded that with higher incident electromagnetic wave frequencies, greater critical densities can be achieved, e.g. for radiofrequencies (RF, f_{RF} =13.56 MHz), the n_{crit} is approx. 2×10⁶ cm⁻³, whereas for MW (f_{MW} =2.45 GHz), it is approx. 7×10¹⁰ cm⁻³ [30].

$$n_{\rm crit} = \frac{\omega_w^2 \cdot \varepsilon_0 \cdot m_e}{e^2} \tag{3.2.2}$$

It should be noted that besides the ability to reach greater electron n_{crit} values via MW-excitation in comparison to RF, it is possible to gain control over certain plasma-surface interactions. One example is the decoupling of the ion energy from the ionic flux reaching the substrate, as the oscillations of the MW electromagnetic field are too fast for the ions to follow. The particle flux can be varied by changing the input microwave power and chamber pressure, while the energy of the incoming charged species can be tuned through the application of substrate biasing, e.g. direct-current (DC) or RF. This is an important feature, as the plasma ions reaching the substrate can significantly influence the deposited film's growth mechanisms (initial nucleation and further growth), chemical composition, microstructure, as well as internal stresses [31].

For many surface processes, e.g. etching or film deposition, high plasma densities ($n_e > 10^{12}$ cm⁻³) can be beneficial for efficient molecular precursor dissociation and reactive species activation. Therefore, for certain applications, it is desirable to obtain densities greater than n_{crit} by generating so-called *overcritical* or *over-dense* plasmas. It is possible to force the wave into the plasma despite reflections by applying high enough powers. This, however, may create undesirable effects depending on the experimental setup. Under conditions, such as those used within this work (laboratory-scale vacuum system, low working pressures < 1 Pa), increasing the power would bring about severe plasma gradients, with a considerable number of electrons being lost to chamber walls before they are able to participate in ionisation processes (scarcity of collisions). Therefore, to overcome these detrimental effects, additional magnetic fields are used to confine the electrons and induce the electron cyclotron resonance effect. These mechanisms will be described in the following section.

3.2.2 Electron cyclotron resonance

When charged particles are exposed to an external electromagnetic field [32], the Lorentz force is responsible for defining their motion for a given v_p (Eq. 3.2.3). If there were no electric fields present (E = 0), the Lorentz force (normally working perpendicularly to v_p) would no longer affect the particle's kinetic energy (Eq. 3.2.4). For a uniform magnetic field $\nabla B = \overleftrightarrow{0}$, the v_p parallel to *B* will remain constant ($v_{p\parallel} = \text{const.}$), i.e. the particle will be propelled along the magnetic field at a constant speed. The particle moving at a v_p perpendicular to *B* ($v_{p\perp}$, Eq. 3.2.5) will be characterised by a constant kinetic energy

(similarly to Eq. 3.2.3), bending the particle's path and inducing a circular motion at a constant velocity of $v_{p\perp}$.

$$m_{p} \cdot \frac{d\nu_{p}}{dt} = q \left(E + \nu_{p} \times B \right)$$
(3.2.3)

$$\frac{1}{2} \cdot \mathbf{m}_{\mathrm{p}} \cdot \mathbf{v}_{\mathrm{p}} = \text{constant}$$
(3.2.4)

$$\nu_{p\perp} = \sqrt{\nu_p^2 - \nu_{p\parallel}^2} \tag{3.2.5}$$

This type of motion is referred to as the *gyration* or *cyclotron motion* and is schematically depicted in Figure 6. The *cyclotron frequency* (ω_c , Eq. 3.2.6) and, in turn, *cyclotron* or *Larmor radius* (r_c , Eq. 3.2.7) are influenced by the considered particle's mass and the strength of the magnetic field. Therefore, for any given magnetic field strength, the ω_c of electrons (ω_{ce}) will be considerably higher than of ions (ω_{ci}), while the inverse trend is observed for their radii (r_{ce} and r_{ci} , respectively). Additionally, the direction of motion will vary depending on the particle's charge, while a spiral motion is achieved when overlaying the parallel and cyclotron motions.

$$\omega_{\rm c} = \frac{q \cdot B}{m_{\rm p}} \tag{3.2.6}$$

$$r_{c} = \frac{\nu_{p\perp}}{\omega_{c}} \tag{3.2.7}$$



Figure 6 (A) Direction of cyclotron motion and (B) spiral motion for an ion and electron in a magnetic field, where the dashed lines mark their corresponding cyclotron radii, r_{ci} and r_{ce} , respectively;

Now we will consider the special case when $\omega_{ce} = \omega_w$, while $\omega_{pe} \leq \omega_w$. This condition entails that the gyrating motion of the electrons and the oscillations of the electric field are in phase (resonance), inducing continuous acceleration of the electron. This phenomenon is known as the *electron cyclotron resonance* (ECR) effect [30, 33–35]. While the static magnetic

field confines the electrons to move in a spiralling manner, the resonance between ω_c and ω_w continuously accelerate them, in turn enabling them to acquire kinetic energy over several cycles until a collision occurs. Using microwaves for this purpose is particularly advantageous, as their high frequencies fully decouple electron and ion motions (ions are too heavy to follow the oscillations), with the possibility of obtaining plasma densities in the range of 10¹³ cm⁻³. The generation of an ECR MW plasma is shown in Figure 7 on the example of an *Aura-Wave* applicator [36–38] (used in the experimental part of this thesis). The plasma becomes excited through the absorption of microwave energy and the static magnetic field is ensured by permanent magnets (with a defined magnetic field strength of 0.0875 T). The electrons become trapped and accelerated at $v_{p\perp}$ until colliding with another particle. This is beneficial for many plasma-based processes, as it improves the level of control for attaining desired particle energies and chemical reactions.



Figure 7 (A) Schematic of an Aura-Wave microwave applicator, with (B) ECR effect mechanism, (C) photograph of an ignited Aura-Wave source producing an Ar plasma, as well as simulations of (D) resonance effect at a 0.0875 T maximum magnetic field strength (red line) and (E) arrangement of magnetic field lines (L. Latrasse, private communication, 2023);

As an example, ECR MW plasmas are favourable for the ionisation of molecular gases, e.g. N_2 or complex precursors [39, 40]. The highly energetic electrons in the ECR region can efficiently sever the chemical bonds of gas molecules and generate activated/reactive species and long-lived radicals, with up to several order higher reaction rates than during equilibrium reactions.

3.3 MAGNETRON SPUTTERING

Magnetron sputtering (MS) is a plasma-based film deposition method belonging to the group of physical vapour deposition techniques (PVD). Sputtering itself was first discovered in 1852 by Grove, although at the time he referred to it as "molecular disintegration" [41]. This development enabled to decouple the previously inseparable parameters of material evaporation and target temperature. The concept is that the to-be deposited material is sputtered, i.e. bombarded by ionised and accelerated inert gas particles (most commonly argon), from a so-called target. The collision between the inert gas ions and the target causes the ejection of atoms from the target's surface, which then travel through the plasma towards the substrate, where they condensate and film growth commences [42, 43]. Since then, the deposition of films via sputtering has been widely used in both academic and industrial sectors. With that, many forms for inducing sputtering now exist, providing various "time-profile" options (frequency/duty cycle, pulse shape) for voltage supplying e.g. via direct-current magnetron sputtering (DCMS), RF and pulsed variants. In the frame of this work, high power impulse magnetron sputtering (HiPIMS) was utilised. However, before describing said technique, the main principles behind the magnetron design and general implications regarding film growth will be presented within the following subsections.

3.3.1 Magnetron configuration

A crucial step in advancing sputtering technologies was the development of the magnetron. This device, first proposed by Hull in 1921 [44] and further developed by Penning from the mid-1930s [45], aims at supporting the plasma discharge via magnetic fields. The reasoning behind the addition of magnetic fields was to enable operating glow discharges at low pressures <1 Pa, where it is possible to influence the transport of the sputtered species, which in turn provides possibilities for tuning film growth mechanisms and subsequent material properties. In other words, it enables for further parameter decoupling, i.e. glow discharge operation and gas pressure. Glow discharges are primarily maintained through the continuous generation of secondary electrons (SEs), while collisions between working gas particles and the electrons can lead to the production of ions (ionisation) that will contribute to sputtering. In the case without magnetic fields, very few collisions occur at such low pressures (long λ_{mfp}), resulting in inefficient energy transfers between particles. Furthermore, the electrons are often lost to chamber surfaces (e.g. walls) before they can even participate in ionisation processes. Moving to higher pressures reduces the λ_{mfp} , therefore more collisions (potential ionisation sources) will take place, including those between ions and neutral working gas particles. Such interactions can lead to charge exchanges and momentum transfers, leading to a wide and uncontrolled energy spread of the species reaching the substrate. Therefore, the role of the magnetic field, similarly as in the case of the ECR effect, is to sufficiently confine and prolong the lifetime of electrons

at desirable low pressure ranges. In other words, the electron's path in the presence of a magnetic field is much longer than without it.

Over the years, various magnetron configurations have been designed, however, focus will be placed on the planar magnetron design, which are most commonly used under laboratory conditions and were used for the preformed studies disclosed in the experimental section of the thesis. For other configurations, the reader may consult [10, 43, 46, 47]. Figure 8 depicts a schematic of a planar magnetron with a mounted target, along with photographs of an ignited magnetron (indium target, mixed Ar/N_2 plasma atmosphere) and targets with progressively increasing race-tracks.



Figure 8 Schematics of a planar magnetron and target (left), photographs of ignited magnetron (top right) and sputtered targets (graphite and zirconium) showing the development of the race-track (bottom right);

An annular permanent magnet and magnetic pole piece are installed with opposing poles to generate magnetic field lines running parallel to the target's (cathode's) surface and perpendicular to the applied electric field. The electrons' movement is defined by the Lorentz equation of motion, where, e.g. for a cathode fall (V_p + applied voltage) of 600 V the $v_{e\perp}$ would be approx. 1.45×10⁷ m/s (assuming a collisionless space-charge sheath). As the cyclotron radius of electrons (typically in the range of 1-10 mm) is smaller than the size of the confining magnetic field structure, they become trapped, enabling to concentrate the plasma immediately above the target. A typical electron density in the region close to the target for DCMS is in the range of 10¹⁷ m⁻³, with an ionisation mean free path of approx. 50 cm [48]. Apart from exhibiting a cycloidal movement of a given r_{ce} along the magnetic field lines, the electrons will travel in a trochoidal motion perpendicular to the magnetic and electric fields, known as the $\overrightarrow{E} \times \overrightarrow{B}$ drift or Hall drift, at a given drift velocity (v_H , Eq. 3.3.1), with typical values in the range of 10⁴ m/s.

$$\overline{\upsilon_{\rm H}} = \frac{{\rm E} \times {\rm B}}{{\rm B}^2} \tag{3.3.1}$$

The generated plasma directly above the target/cathode takes on a doughnut-like shape (Figure 8), meaning that the plasma density is non-uniformly distributed over the target's surface. This will, in turn, lead to non-uniform sputtering of the target and the generations of a circular erosion zone, often referred to as the race-track. The electrons will continue to travel along their designated path until colliding with another particle. In the case of ionisation, the ions will be attracted back towards the negatively charge magnetron and bombard the target's surface, while the sputtered atoms travel towards the substrate.

It is possible to influence the behaviour of the plasma generated above the target's surface, in turn, affecting the movement of charged particles, by changing the magnetic field lines [46, 49]. This can be achieved by installing magnets of varying strengths, where classically three configurations can be distinguished (Figure 9), i.e. balanced (equal strength of both magnets) and two unbalanced modes (different magnet strengths, type I, II). Unbalancing the magnetrons serves to assist in supplying ions to the substrate region, where they participate in film growth. Throughout the performed experimental work, the magnets were arranged in type II unbalanced mode. Further effects based on magnetic field manipulation can be achieved through the use of multiple magnetrons, such as closed-field or mirrored-field configurations (see [50] for more information).



Figure 9 Overview of magnet configurations for achieving various magnetic field lines leaving the target, adapted from [46];

3.3.2 Sputtering characteristics

Having presented the concepts of magnetron design, we can now proceed to describing the act of sputtering itself. A brief overview of sputtering events is presented in Figure 10. Firstly, an ion (commonly Ar^+) is accelerated through the cathode sheath (also possible for atoms generated through charge transfer sheath reactions) and bombards the target's surface at a certain incident angle (η) and energy (E_b , Eq. 3.3.2). The ion reaches and enters into the target (where it can remain embedded) and causes a sequence of atomic collisions
within the target, which ultimately lead to the ejection of a particle (often atom) of the target material [43].

$$\mathsf{E}_{\mathsf{b}} = \mathbf{e} \cdot (\mathsf{V}_{\mathsf{p}} - \mathsf{V}_{\mathsf{cathode}}) \tag{3.3.2}$$

One of the main parameters characterising sputtering is the so-called sputter yield (Y), which refers to the average number of atoms ejected from the target's surface for each incident ion. There are many factors that influence Y, such as the energy and mass of the incoming projectile ion (most commonly argon), the ion's η , with respect to the target's surface and crystallographic planes, as well as the target condition (material, crystallographic structure), which in turn are dependent on other characteristics. At this time, we will focus on parameters related to how the surface binding energy and energy transfer during bombardment or collisions influences Y.



Figure 10 Schematic overview of target sputtering events: (*i*) ion acceleration across the sheath, (*ii*) atomic collisions within the target and (*iii*) target particle ejection, adapted from [43];

When an ion strikes the target, some of the target atoms may gain a certain portion of energy through collisions, i.e. through momentum transfer, either directly with the bombarding ion or with its neighbours. To move an atom from its initial surface site on the target, it needs to overcome a potential energy barrier, namely its surface binding energy (E_{sb}) , which is specific for each material (see [43] for example list). Furthermore, the atom must possess a greater energy than that of the threshold energy $(E_{th}, \text{Eq. } 3.3.3)$, which is the minimum energy required for sputtering to occur. The method for calculating E_{th} will depend on the difference in mass between the bombarding ion (m_b) and the target atom (m_t) [51]. The final relationship, under which sputtering can occur is given in Eq. 3.3.4:

$$E_{th} = \begin{cases} \frac{E_{sb} \cdot \left(1 + 5.7 \frac{m_b}{m_t}\right)}{\Lambda} & \text{if } m_b \leqslant m_t \\ E_{sb} \cdot \frac{6.7}{\Lambda} & \text{if } m_b \geqslant m_t \end{cases}$$
(3.3.3)

$$E_{th} + E_{sp} > \frac{E_{sb}}{\Lambda}$$
, where $\Lambda = \frac{4 \cdot m_b \cdot m_t}{(m_b + m_t)^2}$ (3.3.4)

where: Λ – energy transfer factor for binary collisions, E_{sp} – binding energy of a projectile to the target's surface (0 for noble gas ions). To depict how influential these factors are, the E_{th} for example elements under Ar^+ bombardment and self-sputtering (sputtering by the ion of the same element) are listed in Table 1, while the sputtering yield for those elements for different bombarding energies is presented in Figure 11.

element	Zr	Sn	С	Nb	Si	Cu	Al	Ag	Zn
<i>E_{th}</i> / eV, Ar+ sputtering	24.61	11.61	107.38	29.64	34.22	15.8	25.79	11.11	6.03
<i>E_{th}</i> / eV, self-sputtering	36.46	18.32	43	44.16	27.01	20.36	19.78	17.21	7.88

Table 1 The E_{th} for selected alloys under Ar⁺ bombardment and self-sputtering conditions;



Figure 11 Sputtering yield as a function of bombardment energy for C, Si, Zr, Nb, Sn, Al, Cu, Ag and Zn under (A) Ar⁺ and (B) self-sputtering conditions;

Based on the above, we can expect that the situation will get more complex when using alloyed or compound targets, or under mixed gas conditions. For example, during the experimental work of this thesis, metal target sputtering was coupled with a reactive gas mixture, therefore, we have the situation of various masses of the bombarding species, as well as target surface changes form a metal to a compound material.

3.4 HIGH POWER IMPULSE MAGNETRON SPUTTERING

High power impulse magnetron sputtering (HiPIMS) is a variation of magnetron sputtering, where high power densities are applied in short pulses, facilitating the

generation of a high number of ions in the dense plasma at the target $(10^{18}-10^{19} \text{ m}^{-3})$ [52]. This MS method was developed and first reported by Kouznetsov et al. in 1999 as a way to both stay below the power limit for target/magnetron damage, while simultaneously ensuring high ionic flux densities [53]. Currently, this technology is widely used for both academic and industrial applications, with numeral published studies describing the associated physics (nicely assembled and described in the book of Lundin et al. [46]. Figure 12A depicts a comparison between DCMS, pulsed DCMS (pDCMS), modulated pulse power magnetron sputtering (MPPMS) and HiPIMS, as functions of duty cycle (time percentage of when the discharge is on) and peak power density. Although the HiPIMS process's duty cycle is severely restricted (typically <5 %) compared to DCMS (continuous, 100 %), considerably higher peak power densities of up to three orders of magnitude can be reached, which enables reaching the previously mentioned high plasma densities. Besides obtaining increased plasma densities, HiPIMS facilitates the sputtering of low melting temperature materials, such as those used in this work, i.e. indium (156.6 °C), tin (231.9 °C) or zinc (419.5 °C). Low duty cycles of <5 % mean that for most of the sputtering time the discharge is off, which provides enough time for the heat to be taken away from the target even when high powers are applied. In the case of continuous sputtering, often the magnetron's cooling system is not efficient enough to dissipate the heat, resulting in target damaging or even melting (Figure 12B).



Figure 12 (A) Comparison between continuous DCMS, pulsed DCMS, MPPMS and HiPIMS, based on their peak power densities and duty cycles (adapted from [54]), and (B) photograph of In target melted by applying too high powers during DCMS;

A further advantage of HiPIMS is its tremendous flexibility, as it is characterised a much wider parameter range than its DC counterpart, such as providing independent control over the sputtering frequency (duty cycle) and pulse width. The decoupling of these parameters enables modifying sputtering rates without changing the plasma properties, which is beneficial when wanting to adjust deposition rates. Moreover, by changing the

pulse width it is possible to influence the type of generated species, their flux, energy and mobility when reaching the substrate, with the behaviour of the sputtering process at different pulse widths being target material dependent [55]. Therefore, understanding the effects that these various HiPIMS parameters can bring about enables gaining more control over the thermodynamic and kinetic conditions at the substrate, which we saw in the previous subsection allows to steer the characteristics of the growing film, e.g. chemical composition and structure, as well as applicational properties, such as optical, electrical, mechanical etc. [53].

3.4.1 Reactive High Power Impulse Magnetron Sputtering

HiPIMS is not only used for the deposition of metals, but also compounds. There are different approaches to producing compound thin films, i.e. by sputtering directly from compound targets using inert and/or reactive gasses or from non-compound (metallic) targets, where a reactive or inert/reactive gas mixture is necessary. Although both methods have their challenges, sputtering from compound targets can be particularly difficult, as often producing them with the desired stoichiometry and purity is challenging, resulting in non-stoichiometric films. Furthermore, they are usually non-conductive and limited to RF sputtering. Therefore, to overcome these limitations and provide greater process control, combining aspects of both physical and chemical vapour deposition through metallic target sputtering under reactive gas conditions (often mixed with Ar) can be employed. The next paragraphs will serve to explain the main phenomena behind reactive sputtering, however, more information can be found in the tutorial prepared by Anders [56] or in the book of Depla and Mahieu [57].

When a reactive gas is introduced into a chamber, it will react not only with the deposited material, but with all chamber components, including the sputter target. A general overview of ongoing interactions during the reactive sputtering of a compound and non-compound target are shown in Figure 13A. In the case of compound targets, mainly Ar is responsible for sputtering, with the target already consisting of the desired material. For non-compound targets, the reactive gas will react with the target's exposed surface and form a thin compound layer, often referred to as target poisoning. There are several mechanisms responsible for this phenomenon, including low-energy reactive gas molecular and\or atomic species being chemosorbed at the target's surface, implantation of reactive gas atoms via inert gas bombardment and/or direct reactive gas ion implantation, as well as diffusion of the reactive gas into the hot target's surface layer (the back of the target is commonly cooled) [56]. Although the thickness of the compound layer is generally greater than a monolayer, the thickness will not be homogenous across the entire target's surface, especially within the race-track. This results from competing mechanisms of surface metal-reactive gas reactions and sputtering. With the poisoning of the target and, essentially, the changing of the sputtered material, we can expect considerable differences in sputtering yields due to changes in E_{sp} and E_{th} . However, an additional and very

important parameter in the context of magnetron sputtering is affected, namely the SE *emission yield* or *coefficient* (γ_{see}). This parameter is responsible for sustaining magnetron discharges (compensating the loss of bulk plasma electrons to chamber surfaces) through ionising the working gas and/or supplying energy to other electrons. During reactive sputtering, its value can change significantly, depending on the metal-reactive gas pairing, a phenomenon extensively studied by Depla et al. [58]. For example, indium is characterised by a notable decrease in γ_{see} upon nitriding (the effects of which will be discussed later in the experimental section of this thesis), whereas for aluminium it increases. One way, through which it can be possible to track the ongoing reactive sputtering phenomena at the target, is by following the so-called hysteresis effect (Figure 13B), which reflects process instabilities originating from the constantly evolving target conditions. Firstly, sputtering is in the *metallic regime*, where all the reactive gas is incorporated into the metal deposited on all chamber surfaces and installed components, without the formation of a compound layer on the target. Therefore, we can already note that the size of the vacuum chamber will affect hysteresis development, i.e. if we run the same process but in two differently sized chambers, the effect probably will not be the same (this is also an example of how vapour process reproducibility from system to system can be difficult or even impossible). With increasing reactive gas flows, all of the sputtered material binds to form a compound, while excess gas is free to react with the target. The sputtering process enters the *compound regime* $(I \rightarrow II)$. Here, the sputtering yield generally decreases, as the chemical bond strength of compounds is much higher than of pure metallic bonds. With that, there are fewer metallic species available to bind with, therefore there will be an "increase" in available reactive gas particles. Next, if the reactive gas supply is reduced beyond the initial transition point $(I \rightarrow II)$, the target's compound layer can no longer be maintained $(II \rightarrow III)$ and the system returns to the metallic regime (III \rightarrow IV).



reactive gas flow, Qo

Figure 13 (A) Overview of interactions from the viewpoint of film deposition and ion-solid behaviour when sputtering from compound and non-compound targets in the presence of an inert/reactive working gas mixture, and (B) theoretical evolution of target condition during reactive sputtering as a function of reactive gas partial pressure (p_o) and reactive gas flow (Q_o), dashed black line indicates lack of sputtering (direct proportionality between p_o and Q_o);

Although the partial pressure of the reactive gas enables determining the reactive gas flux to all surfaces, it is possible to follow the development of the hysteresis effect by tracking other process parameters as a function of gas flow [46]. For example, the deposition rate can be used, as within the compound regime, the sputtering yield generally decreases, as the chemical bond strength of compounds is much higher than pure metallic bonds. Otherwise, the discharge voltage can also be used, as the γ_{see} usually changes upon target poisoning, affecting the discharge voltage. It should be noted, however, that the hysteresis effect is not always present/visible. Once again, the extent of the effect is dependent on the metal-reactive gas pairing, but also on the sputtering technique. This is evidenced by studies performed by Seo et al. [59] (NbO_x) and Mareš et al. [60] (including AlO_x, CrO_x, ZrO_x , HfO_x), where different hysteresis loops, or indeed their absence, were noted (Figure 14). Exact reasons behind hysteresis reduction or elimination are still not fully understood, however, various theories have been proposed. These include efficient cleaning of the target's surface through high power density pulses, reactive gas rarefaction (the hot target's surface heats the gas, causing a decrease in its density in that area), or back-attraction of ionised metal atoms to the target. The study performed by Mareš et al. [60] supports the latter, where the experimental findings were additionally backed up by Monte-Carlo simulations.



Figure 14 (A) Average discharge power and deposition rate vs oxygen flow for Nb sputtering in a O_2/Ar mixture (f = 50 Hz, O_2 flow varied) via DCMS, HiPIMS and MPPMS, the solid and dashed lines stand for experiments with increasing and decreasing oxygen flows, respectively (adapted from ref. [59]), and (B) O_2 partial pressure vs oxygen flow during Al, Cr, Zr and Hf sputtering via Mf-PDCMS and HiPIMS (adapted from ref. [60]);

HiPIMS provides plenty of parameters to steer the sputtering process, as well as to reduce or overcome certain detrimental effects of target poisoning. However, this is not always enough to obtain films of the desired chemical composition, as the reactivity of the gas itself also needs to be considered. For example, although oxygen is already reactive in molecular form, molecular nitrogen is neutral and requires further activation or dissociation. As will later be shown in the experimental work, the plasma generated through HiPIMS is not always able to provide sufficient amounts of reactive nitrogen to the substrate to form stoichiometric nitride films.

3.5 SURFACE PROCESSES DURING DEPOSITION

Over the years of film fabrication, there have been many attempts to link the deposition conditions with the characteristics of deposited films to facilitate process parameter selection for attaining the desired material. In 1969, while working on film fabrication through evaporation, Movchan and Demchishin put forward the idea for a so-called structure zone diagram (SZD) [61]. Three zones were classified by relating the film's structure with the homologous temperature $(T_h, \text{Eq. 3.5.1})$, i.e. the ratio of the temperature of the growing film (T_f , often the substrate temperature) and the deposited material's melting temperature (T_m) . Within the following years, magnetron sputtering had become widespread and in 1974 Thornton modified the SZD to account for the influence of working pressure [62]. Since then, magnetron sputtering has expanded into the realm of high energy depositions, such as through the development of the previously mentions HiPIMS technique. To this end, in 2010 Anders proposed an extended version of the SZD (Figure 15) to accommodate plasma-related phenomena [63]. Anders's extension replaces T_h by a generalised temperature $(T^*, \text{ Eq. } 3.5.2)$, to account for heat supplied by the incoming particles' potential energy, the working pressure by a normalised energy $(E^*, \text{ Eq. } 3.5.3)$, which considers the incoming particles' kinetic energy and its role in displacement and heating effects, as well as introduces the net thickness of the film (t^*) :

$$T_{\rm h} = \frac{T_{\rm f}}{T_{\rm m}} \tag{3.5.1}$$

$$T^* = \frac{T_h + \frac{1}{k} \cdot \sum_{\alpha} \frac{E_{\text{pot}, \alpha} \cdot J_{\alpha}}{N_{\text{moved}, \alpha}}}{\sum_{\alpha} J_{\alpha}}, \text{ where } E_{\text{pot}} = E_c + (E_i - \phi)$$
(3.5.2)

$$E^* = \frac{\sum_{\alpha} \frac{E_{kin, \alpha} \cdot m_{\alpha} \cdot J_{\alpha}}{E_c \cdot m_s}}{\sum_{\alpha} J_{\alpha}}, \text{ where } E_{kin} = E_0 + z \cdot e \cdot V_{sh}$$
(3.5.3)

where: α – arriving species, J_{α} – flux of arriving species, N_{moved} – number of displaced atoms, φ – electron work function, m_{α} – mass of arriving species, m_s – sputtered atom mass, and E_{pot} , E_c , E_i and E_{kin} – potential, cohesive, ionisation and kinetic energy, respectively. The SZD provides an overview of general trends of plasma-related deposition parameters, however, many aspects remain left out. As Anders himself strongly highlights "any such presentation can only serve for rough orientation and each combination of substrate, film material, and deposition conditions represent a unique system that is not adequately described by an SZD". For instance, time variations are not factored in, where, in the context of HiPIMS or other pulsed processes, they can dramatically influence the characteristics of the deposited film. The extent of this influence was demonstrated by Lapeyre *et al.* [55], who studied the effect of pulse width variation on the nature of the discharge and type of generated species during Cu, Ag and Zr sputtering, as well as the structure and morphology of the resulting fabricated films, which for a similar chemical composition ranged from crystalline to amorphous. Therefore, despite there being certain guidelines to refer to when designing a new deposition process, each process parameter should be carefully considered when wanting to achieve specific film properties. However, there is another way besides trial and error to gain an understanding on the deposition environment and screen for the optimal conditions. *In situ* diagnostic tools enable to establish trends between the plasma environment and process parameter in a relatively efficient manner. Such techniques were used throughout the experimental studies included in this thesis to determine the type of arriving species, their energy and temporal distribution.



Figure 15 SZD proposed by Anders depicting the dependence of film structural features as a function of generalised temperature T^* , normalised energy flux E^* and net film thickness t^* , with the zone boundaries being gradual and for illustration only (taken from [63]);

Compared to some other technical fields, results in plasma physics can be less precise.

- H. R. Kaufman and R. S. Robinson

The objective of the experimental work performed within the scope of this thesis was to investigate the validity of a hybrid vapour deposition approach, mainly that of combining magnetron sputtering-based techniques with a volume microwave plasma, for enhanced process control. To this end, three material systems were selected as case studies for the proposed microwave plasma-assisted sputtering (MARS) combination, namely diamond-like carbon (DLC) [64], indium nitride (InN) [65] and zinc tin nitride (ZTN). The investigations entailed the *in situ* analysis of the created deposition environment, as well as *ex situ* characterisation of the fabricated thin films. The main concepts of MARS are summarised in Figure 16. The advantage of the used system is its ease of adaptability for both diagnostics and depositions. This enables a high level of processing flexibility for studying multiple deposition environments in a relatively simple and efficient manner for thin film property tailoring.



Figure 16 Overview of possible process variations and parameter manipulation via the hybrid modular approach;

4.1 MA-HIPIMS CASE STUDY: DIAMOND-LIKE CARBON

The information presented in this chapter has been published in the work "From pulsed-DCMS and HiPIMS to microwave plasma-assisted sputtering: Their influence on the properties of diamond-like carbon films", prepared by C. Hain, D. Brown, A. Welsh, K. Wieczerzak, R. Weiss, J. Michler, A. Hessler-Wyser and T. Nelis [64].

4.1.1 Introduction

Diamond-like carbon (DLC) is an amorphous carbon material, where its chemical and mechanical properties have made it an attractive choice for films in applications related to automotive and aerospace industries, biomedicine, magnetic storage media and many others [66–71]. The mechanical and optical properties of DLC primarily stem from sp³ and sp² carbon atom hybridisations, where diamond, composed of 100 % sp³, is extremely hard (approx. 100 GPa) and transparent, whereas graphite, composed of 100 % sp², is rather soft (< 5 GPa) and opaque [69]. Therefore, acquiring the ability to control sp^2 and sp^3 formation within the DLC films would allow to tune the material's properties for specific applications. There exist different techniques for DLC film fabrication, with chemical (CVD) and physical vapour deposition (PVD) and their variations [72, 73] being among the most popular. CVD uses gaseous hydrocarbon precursors as the source of carbon, therefore hydrogenated DLC films are obtained. During PVD, the carbon source can be a pure carbon target, enabling the production of non-hydrogenated amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C) films. Such films exhibit higher hardness, greater stability with temperature [74–76] and under humid conditions [77–79] than their hydrogenated counterparts. The mechanism behind sp² and sp³ formation, i.e. subplantation, occurring during PVD-based fabrication is schematically shown in Figure 17. Subplantation occurs through direct C⁺ penetration into the film's surface and/or indirectly through the displacement of surface atoms into interstitial sites. This entails the penetration of impinging hyperthermal species, ranging from 1 to 1000 eV, into the top layers of the growing film, inducing sp² to sp³ transformations. As graphitic structures exhibit a lower displacement energy than diamond ones (25 eV vs 80 eV), they will be preferentially displaced upon ion bombardment [80].



Figure 17 sp² and sp³ formation mechanisms through direct (C^+ film penetration) and indirect (displacement of surface C atoms through Ar^+ bombardment) subplantation, adapted from [69, 81];

Carbon is characterised by a low ionisation rate [82], and high ionisation potential (11.26 eV) [54], therefore high plasma densities are beneficial for creating carbon ions. With increased plasma densities, more argon atoms can be ionised, additionally leading to more electrons being present in the plasma. The presence of both can facilitate carbon ionisation either through argon ion-carbon collisions and energy transfer or electron-carbon collisions. Direct-current magnetron sputtering (DCMS) is characterised by low plasma densities (10¹⁴-10¹⁶ m⁻³) and low degrees of ionisation [83]. At the other end of the PVD spectrum is cathodic arc deposition (Arc-PVD), where an arc is generated to vaporise the cathode target. Here, it is possible to reach high plasma densities, (10¹⁸-10²⁶ m⁻³) [52], however, this method often results in the formation of droplets or macroparticles of various quantities on the film's surface [84, 85]. Therefore, a compromise needs to be found between these two extremes. One way of overcoming these issues is moving towards pulsed-DCMS (pDCMS) [86, 87], and its further extension high power impulse magnetron sputtering (HiPIMS) technique. In this case, high power densities are applied in short pulses, facilitating the generation of highly ionised species of the sputtered material, through the generation of high plasma densities at the target (10¹⁸-10¹⁹ m⁻³) [52, 88], and producing high-density films [14, 42, 54, 89]. For DLC, it has been proven that HiPIMS enhances the deposition rate [90] and through sputtering in short, but highly energetic pulses, it facilitates the production of hard and dense DLC films [88, 91-97]. An alternative method for increasing the ionisation of carbon species is the introduction of additional plasma sources. Some work has been performed in this direction for DLC films, where cylindrical microwave (MW) plasma, using the electron cyclotron effect (ECR), was combined with a DC sputter source, equipped with a cylindrical target in the down-stream configuration, however, without the presence of additional magnetic fields [98, 99]. Recent developments in solid-state-based microwave generator sources [38] and associated impedance-matched applicators has allowed for the design of new reactor configurations using microwave plasma to further facilitate hybrid plasma processes.

Despite many options for producing DLC films, linking the influence of deposition parameters on the properties of DLC films or, indeed, characterising DLC properties, is not trivial. The main issues hindering DLC analysis are: (1) the problem of consistent characterisation of the influence of multiple process parameters on the produced films and their reproducibility from system to system, and (2) only a few analytical techniques provide direct answers concerning carbon structuring (sp² and sp³ contents), meaning that result interpretation is required. Therefore, it is important to look not only at the properties of the film but also the deposition setup, and in turn, the deposition environment.

In this work, DLC films were deposited using two systems, via pDCMS and microwave plasma-assisted pDCMS (MA-pDCMS), as well as HiPIMS and MA-HiPIMS, respectively. The progression through these techniques, especially in the direction of including microwave plasma, and linking their characteristics to the properties of the fabricated DLC films show the different ways of producing DLC films with comparable properties, while highlighting the limitation of sputtering techniques for attaining high-hardness films.

4.1.2 Experimental section

Deposition setup

System 1, a customised high-vacuum "sputter-down" setup (Malachite Technologies, USA) used to produce DLC films via pDCMS and MA-pDCMS, is shown in Figure 18A. The reactor is arranged in a configuration, where a ϕ 50 mm sputtering cathode (Angstrom Sciences, USA) and four Aura-Wave ECR [38] coaxial plasma sources (SAIREM, France) are installed in the reactor's lid. The microwave plasma sources are evenly spaced around the sputter cathode, 75 mm from centre and positioned nearly planar with the sputtering target's surface. The sputter cathode power supply (Advanced Energy, USA) is configured to operate in unipolar negative pulsed-DC power control mode. Each Aura-Wave plasma source is connected by a LMR400 type coaxial cable to discrete variable power output 200 W, 2.45 GHz solid state microwave generators (SAIREM, France). The solid-state generators have built-in frequency tuning functions to allow for minimizing reflected power and efficient coupling of the microwave power into the plasma load. The system is evacuated via a TPH 2301 turbomolecular pump (Pfeiffer Vacuum, Germany), backed up by an XDS35i dry scroll pump (Edwards Vacuum, UK), to reach a minimum base pressure of approx. 6×10⁻⁵ Pa. The plasma gas supply is controlled via a 200 sccm mass-flow controller (MKS Instruments, USA), and enters the chamber through a connection in the chamber's wall. Substrates are introduced into the process chamber by means of a load-lock sample transfer chamber and are placed on a ϕ 150 mm substrate stage and positioned 75 mm below the sputtering target. The substrate stage is electrically isolated and connected to a MDX series DC power supply (Advanced Energy, USA) configured to operate at constant voltage and provides the means to bias the substrate to a negative potential during film deposition.

System 2 (Figure 18B) is a HEXL Modular Deposition System, equipped with 3 magnetrons in unbalanced configuration (Korvus Technology, UK). The chamber is evacuated via a TC 400 turbomolecular pump (Pfeiffer Vacuum, Germany), backed up by an SH-110 dry scroll vacuum pump (Agilent Technologies, USA). The interspace of the double O-ring system is evacuated by an IDP-3 dry scroll vacuum pump (Agilent Technologies, USA). In this configuration, the maximum flow rate allowing for stable operation is 120 sccm of argon, where the flow rate is controlled via a 200 sccm mass-flow controller (Teledyne Hastings Instruments, USA). The gas enters the chamber through the three installed magnetrons. The system allows for reaching a minimum base pressure of approx. 2×10^{-5} Pa. A full range compact gauge (Pfeiffer Vacuum, Germany) is used to determine the pressure inside the reactor. Further details can be found in *appendix A1*. For inducing pulsed sputtering, HiPIMS HiPSTER type 1 generators (Ionautics, Sweden) were used, whereas the previously described Aura-Waves and solid-state microwave generators (SAIREM, France) were used for creating the microwave volume plasma. The magnetrons and microwave generators were placed alternately on each chamber wall. A rotary sample holder was attached to

the lid of the chamber and the distance between the magnetrons and the substrates was approx. 120 mm. A GEN 1U 750 W power supply (TDK-Lambda, Japan) was connected to the rotary substrate holder using a coaxial cable via a sliding contact installed between the inner and outer part of the holder's rotation axis. The grounding was attached to the chamber's body. This enabled supplying a bias voltage, variable between 0 and -600 V, to the substrate to manipulate ion behaviour in its vicinity. The bias voltage stability at the substrate holder during HiPIMS operation was measured to be better than 1 %.



Figure 18 Configuration of (A) *system 1* for pDCMS-based processes, (B) *system 2* for HiPIMS-based processes, left: front view, right: top view, 1 – magnetrons, 2 – MW plasma sources, 3 – rotary substrate holder, 4 – butterfly valve;

DLC film fabrication

Series of DLC films were fabricated using the previously described equipment, by means of DC-bias pDCMS, MA-pDCMS, HiPIMS, MA-HiPIMS and pulsed-bias MA-HiPIMS. Both systems used ϕ 50 mm 99.999 % purity graphite disc (Kurt J. Lesker Company, USA) as the sputtering targets, 6 mm and 3 mm thick for *system 1* and 2, respectively. In both cases, the substrates were ϕ 50 mm <100>-oriented silicon wafers (*system 1* UniversityWafer, Inc., USA, *system 2* MicroChemicals, Germany). Once the substrates were cleaned *ex situ*, they were placed inside the deposition chamber, where they were subjected to a pre-treatment procedure. The aim of this process is to remove organic pollutants and native oxides from the substrates' surfaces by being exposed to microwave plasma, inducing so-called sputter cleaning. Ultra-high purity argon was used as the plasma-forming gas (*system 1*: County Specialty Gases, USA, *system 2*: Carbagas, Switzerland). This step additionally aims at improving the adhesion between the substrate and deposited film. A summary of substrate cleaning and pre-treating is presented in Table A.1.

The deposition process is initiated directly after the pre-treatment process without breaking vacuum. The magnetrons are switched on while the microwave-generated plasma is on to avoid the redeposition of contaminants and/or reoxidation. For non-MW processes, the microwave generators were turned off once the plasma surrounding the magnetrons was stable. Otherwise, the microwave generators remained on for the duration of the

process. A total of five DLC film series were deposited. *System 1* was used for pDCMS and MA-pDCMS, where for all depositions the pulse-off settings were fixed at 0.4 μ s with a repetition rate of 100 kHz and constant sputtering power of 300 W. *System 2* was used to for HiPIMS and MA-HiPIMS, where the HiPSTER units were operated in a peak current limiting mode, i.e. the voltage regulation was set to assure a constant peak current of 30 A. The HiPIMS pulse length was set to 30 μ s with a repetition rate of 600 Hz. A summary of the used deposition parameters is presented in Table 2.

system	process type	pressure / Pa	Ar flow / sccm	microwave power / W	substrate bias / V*	
	nulsed direct-current				0	
	magnetron sputtering (pDCMS)			/	-100	
1 mic pL			100	3×45		
	microwave plasma-assisted pDCMS (MA-pDCMS)	0.5		3×100	-100	
				3×200		
			110			
2	high power impulse magnetron sputtering (HiPIMS)	0.6	60	/	0 ÷ -350	
		0.4	60			
	microwave plasma-assisted			3×50	0 ÷ -300	
	' HiPIMS (MA-HiPIMS)	0.4	60		-250 pulsed**	

Table 2 Selected process parameters for DLC film deposition;

*direct-current substrate bias, unless noted otherwise; **pulsing frequency 600 Hz;

Deposition environment analysis

Detailed deposition environment analyses were conducted for HiPIMS-based processes. The voltage and current outputs signals supplied by the HiPSTER units were monitored using a mixed signal oscilloscope (Tektronix, USA). Data were acquired using the averaging mode, based on 128 pulses.

Plasma properties in the vicinity of the substrate were obtained by means of Langmuir single probe (Impedans, Ireland) measurements under microwave plasma, HiPIMS and combined MA-HiPIMS conditions. The chamber properties selected for these tests were 0.4 Pa with 60 sccm of Ar. The Langmuir probe consisted of a ϕ 0.4 mm, 10 mm tip and a DC reference. A voltage sweep from -20 to 30 V, with a step of 0.5 V, was performed and the resulting current was tracked. The probe was positioned at the height where the substrate would be. Microwave plasma characterisation was completed in time-averaged

mode, whereas HiPIMS and MA-HiPIMS conditions were investigated in time-resolved mode using a HiPSTER Sync Unit (Ionautics, Sweden) as the external trigger. The HiPIMS pulse was set to start after 20 µs of delay in respect to the Langmuir probe measurement in all cases.

Temperature measurements, using a ϕ 1 mm, 50 mm custom-made microwave plasma-resistant temperature probe (Mesurex, France), were performed at substrate height to evaluate sample heating during sputtering and under microwave plasma conditions.

Film analysis

Raman spectroscopy via an inVia dispersive Raman System H45383 equipped with a green 514 nm laser (Renishaw, UK) was used to determine the type of bonds present in the DLC films and evaluate the sp² and sp³ hybridisation contents. The gathered spectra were processed through background removal and double Gaussian D and G peak fitting to extract G peak position, D to G peak intensity ratios (I_D/I_G), and G peak full width at half maximum (FWHM).

DLC film densities were obtained via X-ray reflectivity (XRR) using a D8 Discover X-Ray Diffractometer (Bruker, USA). The incident beam (Cu K α) was conditioned using a Göbel mirror. The measurements were done in θ –2 θ geometry and the reflectivity patterns were analysed by fitting the data to a physical model, created by selecting a silicon base with an SiO₂ layer and a carbon layer on top, using the DIFFRAC LEPTOS 7 software (Bruker, USA). Measurement uncertainty was determined to be in the range of 5 %.

The thickness and stress of the films produced via *system 1* were measured using a Dektak IIA stylus profilometer (Bruker, USA). Film stress measurements were performed to correlate the obtained results against film hardness and provide initial process feedback. The profilometer was set to a scan length of 40 mm, after which the Dektak IIA software calculated the radius of curvature of the wafer surface and compared it against a similar scan taken on the wafer prior to depositing. From the resulting change in curvature, the software used the Stoney equation [100] to calculate the film stress based on known material properties and film thickness.

Samples produced by both systems were cleaved and their fracture cross-sections, as well as their surface morphology, were imaged using a Hitachi S-4800 high-resolution cold field emission (CFE) scanning electron microscope (SEM) (Hitachi High-Tech Corporation, Japan).

The hardness and elastic modulus of all DLC films were determined by means of nanoindentation using a Hysitron Ubi Nanoindenter (Bruker, USA). Different indenter tips were used, depending on film series thickness, to prevent exceeding penetration depths greater than 10 % of the films' thickness [101], while obtaining plastic deformation for reliable hardness measurements. Films deposited via *system 1* were measured using a diamond cube corner tip (for shallow indents and low loads), whereas films fabricated

via *system 2* using a diamond Berkovich indenter tip. Machine compliance was adjusted accordingly for a given tip. The tip area function was calibrated on fused silica for each tip separately in the relevant measurement range. For obtaining a representative average, 16 indents were performed on each film. The maximum load value was held constant for 2 s, whereas loading and unloading each lasted 5 s. Load-displacement curves were analysed by applying the Oliver and Pharr approach [102], using 0.2 for the Poisson's ratio of DLC [103, 104].

4.1.3 Results

The pDCMS- and HiPIMS-based processes, although closely resembling one another, differ in terms of their sputtering characteristics. The comparison of these techniques aims to provide an improved understanding on the correlation between the generated deposition environment, especially plasma conditions, and the properties of the fabricated DLC films.

pDCMS-based DLC films

XRR was performed on the pDCMS and MA-pDCMS films to determine their thickness and density. To facilitate the fitting procedure, the thickness of the films was first evaluated using profilometry. The results from the profilometer and XRR are similar, as can be seen in Table 3. Film densities differed depending on the used fabrication method. The grounded pDCMS sample has the lowest density, which is increased by applying a negative bias of -100 V. Further film densification was obtained by introducing the microwave plasma in the vicinity of the sputter target. The obtained densities are on the higher end of those reported previously [88, 105].

series	thickness profilometer / nm	thickness XRR / nm	density / g/cm ³
pDCMS, grounded	91	91	2.55
pDCMS, -100 V bias	81	82	2.65
MA-pDCMS, 3×45 W	74	76	2.75
MA-pDCMS, 3×100 W	71	76	2.86
MA-pDCMS, 3×200 W	72	74	2.88

Table 3 Fitted XRR results of pDCMS and MA-DCMS DLC films;

Next, the samples' surface morphology and cleavage were imaged via SEM, with the extremes, pDCMS grounded sample and MA-pDCMS 3×200 W sample, selected as examples (Figure 19). Clear differences can be observed between the two films. The pDCMS sample's fracture cross-section has a granular morphology, which continues to its

surface. The MA-pDCMS sample exhibits faint columnar-like structuring, with a smooth surface without any distinguishable features.



Figure 19 SEM imaging of fracture surface and surface morphology of DLC films: (A,B) pDCMS with grounded DC substrate bias, (C,D) MA-pDCMS using 3×200 W MW power, with a DC substrate bias of -100 V;

Afterwards, the films were characterised by means of Raman spectroscopy, stress measurements and nanoindentation (Figure 20). The shape of the Raman spectra obtained from each sample closely resemble one another, especially between the MA-pDCMS samples. This is reflected by the results from nanoindentation, where the mechanical properties do not vary greatly. The elastic modulus remains relatively stable for all samples, independent of the applied fabrication method. In terms of hardness, the only substantial change is observed between the grounded and biased sample, from approx. 24±1 to 30±1 GPa. The addition of microwave plasma had no significant effect on the hardness, with respect to the non-MW biased sample. However, a clear increase in compressive film stress when applying a substrate bias during the growth was observed. The film stress continues to increase with the addition of microwave plasma until it eventually plateaus with increasing microwave power.



Figure 20 Results from (A) Raman spectroscopy, with marked D and G peak double gaussian fitting of grounded pDCMS sample, (B) nanoindentation and film stress measurements of two pDCMS samples, grounded and -100 V substrate bias, and of three MA-pDCMS samples with -100 V substrate bias, 3×45 W, 3×100 W and 3×200 W;

HiPIMS-based DLC films

— HiPIMS plasma environment

The HiPSTER units are operated in a peak-current limiting mode, with a 30 μ s pulse length and 600 Hz repetition frequency, translating to a duty cycle of 1.8 %. Feedback parameters for the 30 A limited setup were: voltage -925 V, current 125 mA, average power 90 W. The temporal evolution of voltage and current is shown in Figure 21, where the supplied voltage rises to its max. value of approx. -925 V within 150 ns and gradually reduces to -900 V towards the end of the pulse. It is further reduced to -150 V within 10 ns, after which it is variated to ensure rapid decrease in pulse current. The discharge current increases exponentially from 0 to 30 A over the 30 μ s pulse.



Figure 21 Temporal evolution of the HiPIMS pulse shape during 30 µs;

Langmuir probe measurements at the position of the substrate allowed to determine the properties of the HiPIMS plasma and the effect of microwave plasma during sputtering. The considered parameters were: plasma potential (V_p) , electron temperature (kT_e) , ion density (n_i) and electron density (n_e) . Firstly, the microwave plasma was analysed on its own to serve as a reference point for the MA-HiPIMS conditions. The power on each source was set at 50 W. As the microwave plasma was constant, measurements were conducted in time-averaged mode. The average plasma properties obtained from a single source and their joint effect are shown in Table 4.

no. of sources	V _p / V	kT _e / eV	n_i / m^{-3}	n _e / m ⁻³
1	12.14 ± 0.07	2.47 ± 0.02	$1.68 \times 10^{16} \pm 4.54 \times 10^{13}$	$9.57 \times 10^{15} \pm 1.28 \times 10^{14}$
3	14.83 ± 0.11	2.78 ± 0.01	$5.32 \times 10^{16} \pm 2.96 \times 10^{14}$	$3.10 \times 10^{16} \pm 5.41 \times 10^{14}$

Table 4 Ar microwave plasma properties generated by one (averaged) and three sources;

The Langmuir probe results from HiPIMS and MA-HiPIMS are shown in Figure 22. For the HiPIMS measurements, the probe was not able to obtain results for the first 5 µs, due to the large displacement currents induced by the HiPIMS voltage rise. The maximum plasma potential and electron temperature values are registered at the end of the pulse, with the maximum values for ion and electron density slightly after that. During the afterglow, the charged particles are released from the magnetron trap, enabling them to travel towards the substrate region. Following the afterglow, all values drop, which corresponds to the fact that the plasma is no longer ignited. Under MA-HiPIMS conditions, the first 20 µs show the properties of the microwave plasma (listed in Table 4). When the HiPIMS pulse starts at 20 µs, the Langmuir probe continues to operate normally, as the plasma generated by the microwave source shields the probe from the rapidly varying electric field generated by the target potential surge and no significant displacement currents are generated in the probe. Once the magnetron plasma ignites, the measured plasma properties decrease to values similar to those obtained during non-MW HiPIMS analysis. The plasma potential, electron temperature and ion density reach their minimum value just before the end of the pulse, whereas the electron density drops just after the end of the pulse. After the HiPIMS pulse has ended, the V_p and kT_e gradually rise until reaching the steady-state values of the microwave plasma. The same, however, cannot be said for the behaviour of the ion and electron densities. After the end of the pulse, the n_i and n_e values considerably exceed the original measured values, with their maximum measured 70 µs after the end of the pulse. After reaching the maximum values, they gradually decrease until reaching the values of the originally measured MW plasma.



Figure 22 Langmuir probe results of selected plasma properties, i.e. V_p , kT_e , n_i and n_e , at the location where the substrate would be, under: (A-D) HiPIMS and (E-H) MA-HiPIMS DLC sputtering conditions, grey areas mark measurement uncertainties, green areas mark pulse duration (30 µs), light green areas mark the period when only the MW plasma is on, scales adapted to the data range;

The temperature near the substrate was measured under pure HiPIMS and MA-HiPIMS to evaluate the possibility of material graphitisation (Figure 23), which occurs at temperatures exceeding 300 °C [74–76]. During sputtering, the temperature reaches a maximum temperature around 35 °C, whereas when turning on the microwave plasma, the temperature rises quickly and stabilises at approx. 130 °C.



Figure 23 Results from temperature probe measurements during HiPIMS and MA-HiPIMS (three magnetrons and three MW plasma sources);

DLC film characterisation

The DC-bias HiPIMS and MA-HiPIMS, as well as pulsed-bias MA-HiPIMS fabricated DLC films were cleaved and analysed via SEM to determine their thickness, as well as surface morphology and fracture surface. Representative SEM images of samples produced at a substrate bias of -250 V are shown in Figure 24. The thickness of all HiPIMS-based films was homogeneous and in the range of 500 nm. The interface with the substrate can be clearly distinguished, with the films being free of cracks, pores, and signs of delamination, indicating that good quality films are attained. For the HiPIMS sample, faint columnar features can be seen on the fracture surface image, and the tops of those columns can be seen on the surface of the film. The MA-HiPIMS film appears to be much rougher, where both the cleavage and surface possess a randomly-orientated grainy morphology. In contrast, the MA-HiPIMS pulsed-bias sample's fracture surface has a clear columnar structure, while its surface has fewer features than the two previous samples, with only small grains being detected.

Next, Raman spectroscopy and nanoindentation were performed (Figure 25), as well as XRR. Starting with the three HiPIMS series, a change in spectrum shape is observed with the change in bias voltage for all series, as well as small differences between each series (Figure 25A, C, E). In all cases, peak broadening occurs with the increase in applied bias voltage. Additionally, films deposited at 0.4 Pa exhibit wider peaks than those deposited at 0.6 Pa. The hardness increased with increasing bias, with changes in Young's modulus resembling that of hardness. The maximum hardness value for each series is in the range of 25 GPa, whereas the minimum values differ between series deposited at different pressures, for 0.6 Pa approx. 5 GPa and 0.4 Pa, 10 GPa. Similar hardness trends as a function of substrate bias and working pressure have been reported in [94, 106]. The density values obtained from XRR measurements correspond with the trend from nanoindentation,

meaning that with an increasingly negative substrate bias, the density of the films increases, from approx. 2.6 g/cm³ for the softest films up to approx. 2.9 g/cm³ for the hardest ones. The obtained film densities are on the higher end of what has been reported for HiPIMS films [88, 107, 108], going into the density range of DLC films produced via pulsed laser deposition (PLD) [109] and filtered ion-beam deposition [110].



Figure 24 SEM imaging of DLC film fracture surface and surface morphology of films produced via HiPIMS, DC-bias (A, B), MA-HiPIMS, DC-bias (C, D) and MA-HiPIMS, pulsed-bias (E, F), applied substrate bias -250 V;

The results from the MA-HiPIMS series were set against the 0.4 Pa, 60 sccm Ar, HiPIMS series (Figure 25E), as the only difference in deposition parameters is the presence of 3×50 W microwave plasma in the former. When comparing the Raman spectra it can be seen that they greatly resemble one another. Therefore, it was expected that the films' sp² and sp³ hybridisation ratio would be similar, resulting in similar mechanical properties.

However, when comparing the hardness and elastic modulus of these films, there are significant differences. On the example of the films produced at -250 V, the HiPIMS film had a hardness and elastic modulus of approx. 25±1 GPa and 305±16 GPa, respectively, whereas for the MA-HiPIMS film the obtained values were approx. 8±1 GPa and 93±7 GPa. Additionally, although MA-HiPIMS Raman spectra exhibit the same broadening effect with increasing bias voltage, a significant increase in mechanical properties only occurred at -300 V, rather a gradual increase like for the HiPIMS films. The density of the DC-bias MA-HiPIMS samples was approx. 2.3 g/cm³. The Raman spectrum of the -250 V pulsed-bias MA-HiPIMS sample closely resembled the DC-biased HiPIMS and MA-HiPIMS samples. The obtained hardness and elastic modulus were measured to be approx. 23±2 GPa and 234±15 GPa, respectively. Substituting DC-bias for pulsed-biasing allowed reaching a higher density of approx. 2.6 g/cm³.



Figure 25 Raman spectra and nanoindentation results of HiPIMS-based DLC films: (A, B) HiPIMS, o.6 Pa and 110 sccm Ar flow, (C, D) HiPIMS, o.6 Pa and 60 sccm Ar flow, and (E, F) HiPIMS, o.4 Pa and 60 sccm Ar flow, MA-HiPIMS and pulsed-bias MA-HiPIMS; Raman spectra: HiPIMS (full line), MA-HiPIMS (dashed line), pulsed-bias MA-HiPIMS (dotted line); nanoindentation: HiPIMS (square), MA-HiPIMS (circle), pulsed-bias MA-HiPIMS (triangle);

4.1.4 Discussion

Plasma conditions vs DLC film properties

The selected pDCMS parameters for *system* 1, with a pulse-off setting of 0.4 ms, repetition rate of 100 kHz and constant sputtering power of 300 W, translate to a duty cycle of 96 %, an average pulse power of approx. 312.5 W and pulse energy of 0.003 J. With the distance between the target and the substrate set at 75 mm, and an applied pressure of 0.5 Pa, the mean free path is approx. 13 mm (assuming room temperature). This means that the sputtered and argon species will experience on average 6 collisions on their way to the substrate. In the case of the applied HiPIMS parameters used in *system* 2, with a duty cycle of 1.8 %, the instantaneous power reaches 20 kW at the end of the pulse, with the pulse energy measured at 0.15 J, or an average pulse power of 5 kW for an average power of 90 W. The distance set between the target and the substrate was 120 mm. For pressures of 0.6 Pa and 0.4 Pa, the mean free paths were calculated to be approx. 10 and 16 mm, meaning an average collision rate of 12 and 8, respectively.

Within a single HiPIMS pulse, considerably higher plasma densities are assumed to be reached at the magnetron than during a pDCMS pulse, with average pulse power being 16-times greater for HiPIMS. This promotes the generation of ionised species. However, compared to *system 1 (with 6 collisions on average)*, there is a higher chance of the generated species to collide. These collisions will decrease the portion of ionised species impinging the substrate/growing film surface with an energy below the optimal value of 100 eV [69, 81] for sp² to sp³ transformation through both direct (carbon-induced) and indirect (argon-induced) subplantation (Figure 17). This is supported by the comparison between nanoindentation results obtained for DLC films produced via HiPIMS (Figure 25B, D, F) at different pressures (0.4 Pa and 0.6 Pa). At 0.4 Pa (avg. collision rate 8), a film hardness of approx. 20 GPa is attained using a substrate bias of -50 V, whereas to reach similar hardness values at 0.6 Pa (avg. collision rate 12), a substrate bias of -150 V is required.

Time-resolved Langmuir probe measurements under HiPIMS conditions enabled tracking the plasma properties of the magnetron during sputtering, as well as in the presence of microwave plasma. As was mentioned in the *Results* section, the maximum plasma potential and electron temperature in the substrate region are reached towards the end of the HiPIMS pulse, with the maximum values for ion and electron density reached slightly later, after the species have been released from the magnetron trap (Figure 22A-D). Igniting the pulsed magnetron sources in the presence of continuous microwave plasma caused significant perturbations to its otherwise stable properties. During the HiPIMS pulse-on time, the plasma properties change from the values observed for the continuous microwave plasma to values typical for the HiPIMS mode. This behaviour can be attributed to the electric field generated by the high voltage supplied to the target, which is not yet shielded by the just-developing high density plasma in the vicinity of the target. Similar effects have been observed in pulsed RF discharges [111], with the interpretation being further supported by the registered strong perturbation of the Langmuir probe operation during HiPIMS pulse onset in the absence of the volume MW plasma. The generated negative electric field draws the argon ions of the MW plasma towards the magnetrons causing the observed decrease in all analysed plasma properties in the vicinity of the probe (substrate height). The highest ion and electron densities at the substrate area are observed after the end of the HiPIMS pulse, in the presence of the MW plasma. Here, the microwave plasma enhances the transfer of charged particles from the dense plasma generated at the target towards the substrate.

Neither the use of microwave plasma nor the change in substrate biasing affected the deposition rates of pDCMS- and HiPIMS-processes, which were approx. 8.6 nm/min and 1.6 nm/min, respectively. The former is much greater than the latter, due to its much higher duty cycle. The deposited DLC films from both pDCMS and HiPIMS processes without microwave plasma were characterised by a mostly granular-like fracture surface, which was additionally reflected by a granular surface morphology (Figure 19A, B and Figure 24A, B, respectively). With the addition of microwave plasma for MA-pDCMS processes, the DLC film's cleaved surface became columnar-like, without any characteristic features on its surface (Figure 19C, D). Furthermore, the film's density increased from 2.55 g/cm³ for the grounded pDCMS film to 2.88 g/cm³ for the -100 V, 3×200 W MA-pDCMS sample (Table 3). DLC film densification can be explained by following the evolution in substrate current with changing processing conditions, depicted in Figure 26.



Figure 26 Substrate currents as a function of substrate bias registered during pDCMS, MA-pDCMS (with marked applied microwave plasma power), HiPIMS with DC substrate biasing and MA-HiPIMS with pulsed substrate biasing (see legend for details);

The substrate current rises from 0 mA for the former to a maximum of 175 mA for the latter, which is linked with the generation of high plasma densities (and high current densities) by the microwave plasma sources (for estimations on plasma properties

generated within system 1, see appendix A1, Table A.2). In turn, densification through indirect subplantation (Figure 17) most probably occurred, as an increase in internal film stress was also registered (Figure 20B). In the case of DLC films produced via MA-HiPIMS with DC substrate biasing, a different effect was observed. The films exhibited increased granularity of both the fracture cross-section and surface morphology in comparison to the HiPIMS-deposited films, with the DLC film density and mechanical properties also decreasing to approx. 2.3 g/cm³ and $H=8\pm1$ GPa, $E=93\pm7$ GPa (for -250 V substrate bias), respectively. Comparing MA-pDCMS and MA-HiPIMS substrate currents for the same substrate bias (-100 V) and similar microwave powers (3×45 W vs 3×50 W), similar values were measured. The main difference lies in the positioning of the microwave sources, where for MA-pDCMS the sources placed at the sputtering target, and for MA-HiPIMS, are at the height of the substrate. It is at those positions that the argon plasma density will be the greatest. Therefore, the MA-HiPIMS-produced films will more likely be subjected to high-energy Ar ion bombardment [112]. Rather than generating sp^3 bonds due to indirect subplantation (Figure 17) the authors believe that the bombardment could have caused local temperature spikes that were not registered by the temperature probe and resulting in film graphitisation. Based on the previously performed Langmuir probe measurements (Figure 22), a substrate bias pulsing strategy was developed for the MA-HiPIMS process so that the bias was only applied once the generated carbon species were released from the magnetron trap, decreasing the effect of Ar-ion bombardment. The measured substrate currents resembled those registered for HiPIMS processes without microwave plasma, which corresponds to the similar plasma properties obtained from Langmuir probe measurements. The films fracture cross-section and surface morphology resemble that of the MA-pDCMS sample, exhibiting columnar structuring and a surface with few characteristic features (Figure 19E, F). The pulsed-bias DLC film had a higher density of 2.6 g/cm^3 than its DC-biased counterpart. The measured mechanical properties were also higher, i.e. $H=23\pm2$ GPa and $E=234\pm15$ GPa. These results highlight the importance of microwave plasma source positioning in respect to the substrate, as it can have a detrimental effect on the quality of the produced films.

DLC film structuring

Raman spectroscopy exhibits sensitivity to changes in the carbon structure, e.g. crystallinity, carbon bonds and clustering. There are two main peaks in the Raman spectra of amorphous carbon, i.e. the D band appearing at approx. 1355 cm⁻¹ and the G band at approx. 1581 cm⁻¹. The D band appears due to the A1g breathing mode and requires a defect for its activation. The G band originates from the E2g stretching mode and occurs at all available sp² sites, rings, or chains. Explanations behind the interpretation of the obtained spectra are provided by Ferrari *et al.* [113–115], where the transition mechanism and Raman spectroscopy response from graphite to tetrahedral amorphous carbon (ta-C) DLC is proposed, by correlating the evolution of D and G peak intensity ratios (I_D/I_G) with the

migration of the G peak shift. This transition is referred to as the *amorphisation trajectory*. Three transition stages are distinguished: (1) from graphite to nanocrystalline (nc) graphite, where only sp²-type hybridisations are present, (2) from nc-graphite to amorphous carbon, and (3) from a-C to ta-C. The Raman spectra obtained from pDCMS-based methods did not show any distinct trends, with the spectra closely resembling one another (Figure 20). The spectra obtained from HiPIMS-based DLC samples (Figure 25) showed a broadening effect with increasing substrate bias. The broadening effect results from a higher level of disorder within the amorphous structure [116] of the fabricated DLC films. When considering the amorphisation trajectory from graphite to tetrahedral amorphous carbon, there are many possible intermediate configurations of carbon atoms (rings, partial rings, chains) [117] that may occur and cannot be determined with certainty. However, each configuration will have its own vibrational frequency, which will be detected by Raman spectroscopy. With the increase in various carbon configurations randomly distributed throughout the amorphous structure of the DLC film, more vibrational modes will be registered, and the corresponding peaks will overlap over one another, causing overall peak widening. When comparing the measured hardness with the previously analysed Raman spectra, it can be noticed that peak broadening coincides with hardness increase. This may suggest that a higher level of disorder of carbon configurations (also film densification and the presence of residual stress) within the films' amorphous structures induces a certain strengthening effect, resulting in higher hardness. The Raman spectra of all produced DLC films were deconvoluted to determine if any further trends could be observed (Figure 27) by tracking the evolution of I_D/I_G ratio as a function of G peak position, and G peak FWHM as a function of measured film hardness.

Following the obtained I_D/I_G ratios and G peak positions, it was determined that the produced DLC films lie within the 2nd amorphisation stage (Figure 27A), however, no trends could be distinguished, with most of the films falling within the same value range (Figure 27B). The provided example hardness values further highlight the lack of trends, as based on the amorphisation trajectory, films with similar I_D/I_G ratios and G peak positions should have similar sp^2/sp^3 contents and, in turn, similar mechanical properties would be expected. Indeed, deviations from the ideal three-stage amorphisation trajectory model of non-hydrogenated films have been previously reported [118]. This is especially true when comparing the previously shown HiPIMS and MA-HiPIMS (0.4 Pa, 60 sccm Ar) results, where the Raman spectra and G peak FWHM closely resemble one another, however, the HiPIMS film had a hardness of approx. 25±1 GPa and the MA-HiPIMS had a hardness of approx. 8±1 GPa (for a substrate bias of -250 V). When tracking G peak FWHM changes as a function of DLC film hardness (Figure 27C), for almost all produced DLC films the FWHM increases with increasing hardness. The exception is the MA-HiPIMS DC-bias series, where similar FWHM values were obtained as for the HiPIMS series, however, the hardness values are significantly lower. This in in agreement with the Raman spectra broadening trends observed in Figure 25. For a FWHM value of around 125, the MA-HiPIMS sample has a hardness of 8±1 GPa, whereas the HiPIMS sample possesses a hardness of 26±2 GPa. The

main characteristic differentiating the MA-HiPIMS DC-bias series from all other deposited films is its highly granular structure, as observed via SEM (Figure 19 and Figure 24), and has been determined to be the contributing factor. Based on these results, using the G peak FWHM provides a more solid basis for DLC results interpretation, however, it should be highlighted that Raman spectroscopy, although a useful technique, is unable to "see" all the factors contributing to DLC material structuring.



Figure 27 Raman spectra interpretation of all fabricated DLC films (see legend for deposition method symbols), where: (A) I_D/I_G ratio as a function of G peak position within the full amorphization trajectory range from graphite to ta-C [113, 114] with the 2nd stage range (nc-graphite to a-C, 0-20 % sp³) marked with a red arrow, (B) experimental result range of I_D/I_G ratio vs G peak position with hardness values included for selected samples, and (C) G peak FWHM as a function of measured DLC film hardness;

4.1.5 Conclusions

In this work, DLC films were produced by means of pDCMS, MA-pDCMS, HiPIMS, MA-HiPIMS with DC substrate biasing and MA-HiPIMS with pulsed substrate biasing. The aim of comparing these techniques was to provide an improved understanding on the

correlation between the generated deposition environment, especially plasma conditions, and the properties of the fabricated DLC films. For both cases, it was demonstrated that standard sputtering cathodes can be arranged close to microwave plasma sources. The inclusion of high-density microwave plasmas can be used to increase the ion current present at the substrate during film growth, enabling a modification of the physical properties of the fabricated layer. An intriguing point that can be noted by comparing the results obtained from all studied deposition methods, is that despite using various microwave source configurations and sputtering conditions, the upper hardness limit for DLC films fluctuated around 30 GPa. This shows the limitation of sputtering and the challenge of increasing the ionisation of carbon. The initial idea of post-ionisation via microwave plasma did not have a significant effect in reaching higher hardness values, however, it did contribute to attaining smoother surfaces in both pDCMS- and HiPIMS-based methods, which could prove to be beneficial for DLC films working under wear conditions.

4.2 MAR-HIPIMS CASE STUDY 1: INDIUM NITRIDE

The information presented in this chapter has been published in the work "Microwave plasma-assisted reactive HiPIMS of InN films: Plasma environment and material characterisation", prepared by C. Hain, P. Schweizer, P. Sturm, A. Borzì, J.E. Thomet, J. Michler, A. Hessler-Wyser and T. Nelis [65].

4.2.1 Introduction

Reactive magnetron sputtering is a deposition technique combining aspects of both physical and chemical vapour deposition, through which compound films are produced by sputtering from a non-compound target in the presence of reactive gases, e.g. oxygen or nitrogen [56, 57]. This process is advantageous over compound target sputtering, as compound targets of the desired stoichiometry and purity are often difficult to produce, resulting in non-stoichiometric films. Furthermore, they are usually non-conductive and limited to radiofrequency (RF) sputtering. However, when adding a reactive gas to the inert working gas, chemical reactions can occur on the target's surface to induce so-called target poisoning, where a compound layer forms [119]. With this, the discharge behaviour of the target can change significantly, most notably due to differences in the secondary electron emission coefficient (γ_{see}). The extent of the change depends on both the target material and type of reactive gas, as studied by Depla et. al. [58]. In some cases, e.g. indium upon nitriding, the γ_{see} considerably decreases. With the electron population being a key parameter in igniting and sustaining magnetron discharges, a drop in γ_{see} can disrupt the sputtering process. In the case of reactive high power impulse magnetron sputtering (R-HiPIMS), this can result in the generation of time lags, i.e. delays in current onset [120], despite the use of high voltages during discharge ignition. Such difficulties will, in turn, cause problems in film fabrication process control and reproducibility.

Another aspect of reactive sputtering is ensuring compound material deposition of the desired stoichiometry, structure and applicational properties. This can be greatly influenced by reactions occurring between the sputtered material and reactive gas. Nitrogen is rather inert, therefore, to ensure its dissociation and reactive species generation, different strategies have been tested, ranging from applying direct-current (DC) and RF, to the incorporation of additional ionisation sources [121–124]. In particular, electron cyclotron resonance (ECR) [125–128] has been reported to improve reactive gas dissociation and film property optimisation for both oxides and nitrides.

Despite various reported studies on reactive sputtering, there are still aspects that have not been investigated in detail. These include studying the influence of reactive gas on the deposition environment an determining the means to provide enough reactive species to obtain stoichiometric compound materials. Therefore, in this work, the plasma conditions during indium nitride (InN) thin film fabrication via microwave plasma-assisted reactive HiPIMS (MAR-HiPIMS) were studied.

InN is a III-V semiconductor with a variable bandgap [129-132], and high electron mobility [133], due to which it is used for various applications in optoelectronics. It is among the more difficult nitrides to produce, owing to its low dissociation temperature (500 $^{\circ}$ C), causing InN decomposition into metallic In and N_2 gas [134–136]. Reactive sputtering enables depositing materials usually at much lower temperatures than its chemical-based counterparts, however, stoichiometric InN fabrication can still be challenging. Natarajan et. al. stated that only atomic nitrogen chemisorbs on pure indium [121], however, in view of the complexity of interactions between activated nitrogen, i.e. metastable and ionic N₂, and metallic surfaces [137], it is unlikely that only atomic nitrogen participates in the formation of InN. Nevertheless, as ground state N₂ does not react with indium, efficient nitrogen activation is beneficial for InN growth. Therefore, combining low temperature reactive sputtering with additional means to create reactive nitrogen species within a volume microwave plasma could prove beneficial for InN film fabrication. This is particularly true in view of competing oxidation reactions with residual oxygen present in the discharge chamber, as it can deteriorate InN's applicational properties [138]. With that in mind, besides in situ deposition environment analyses, the structure and optoelectronic properties of the obtained InN thin films were studied.

4.2.2 Experimental section

Deposition setup

The used deposition chamber was a HEXL Modular Deposition System, equipped with one magnetron in unbalanced configuration (Korvus Technology). The chamber was evacuated using HiPace 700 molecular (Pfeiffer Vacuum) and nXDS 10i dry scroll vacuum (Edwards Vacuum) pumps. A full range compact gauge (Pfeiffer Vacuum) was used to determine the pressure. Ar and N_2 flows were controlled via mass-flow controllers (Teledyne Hastings

Instruments). A HiPSTER 1 power supply unit (Ionautics) was used for initiating pulsed sputtering, and Aura-Wave ECR coaxial plasma sources (SAIREM) enabled generating the volume microwave plasma [37, 38]. A rotary sample holder was attached to the chamber's lid, with the magnetron-substrate distance set to 12 cm. A GEN 1U 750 W power supply (TDK-Lambda) was connected to the substrate holder and the grounding was attached to the chamber's body. Further details can be found in *subchapter 4.1*.

Film fabrication

Thin films were fabricated via R-HiPIMS and MAR-HiPIMS. The sputtering target was a ϕ 50 mm, 3 mm thick, 99.999 % purity In disc (Kurt J. Lesker Company). The substrates were ϕ 50 mm, 279×20 μ m thick, n-type <100>-oriented Si wafers (MicroChemicals) and $76 \times 26 \times 1$ mm glass slides (Carl Roth GmbH + Co. KG). The system was evacuated until reaching a minimum base pressure of 5×10⁻⁴ Pa. A pre-treatment step was applied for 5 min to remove organic pollutants and native oxides from the substrate's surface by exposing it to a microwave Ar (UHP grade) plasma to induce so-called sputter cleaning. The parameters were as followed: 3×50 W MW power, 10 sccm of Ar, pressure of 0.2 Pa, and a DC substrate bias of -150 V. The deposition process was initiated directly after pre-treatment without breaking vacuum. With the MWs kept on to prevent contaminant redeposition onto the substrate, the In target was pre-sputtered underneath a shutter to remove any contaminants or oxides from its surface. The DC substrate bias was reduced to -20 V. Afterwards, the shutter was lifted and for R-HiPIMS the MW plasma was turned off. For MAR-HiPIMS, the microwave generators remained on for the duration of the process. Each process lasted 90 min to reach a film thickness of 100 nm, with the wafer fully rotating at 15 rpm to facilitate uniform deposition. The temperatures near the substrate, measured using a ϕ 1 mm, 50 mm microwave plasma-resistant temperature probe (Mesurex), were approx. 30 °C and 100 °C for the R- and MAR-HiPIMS processes, respectively.

Deposition environment analysis

The voltage-current outputs and Langmuir probe measurements were performed in the same way using the same equipment as described in *subchapter 4.1*.

Optical emission spectroscopy (OES) was performed using wavelength calibrated HR2000+ and HR2000CG-UV-NIR spectrometers (Ocean Optics), with spectral ranges of 200-480 nm and 200-1100 nm, respectively. The emitted light was transmitted from a 25 mm focal length f/2.8 quartz lens (Pentax) to the spectrometer using a QP400-2-SR-BX 200-1100 nm wavelength-ranged optical fibre (Ocean Optics).

The plasma's chemistry was determined using a prototype time-of-flight mass spectrometer (TOFWERK), providing mass spectra of all mass-to-charge ratios up to 500 Th with mass resolution (full width at half maximum, FWHM) of 500 for low mass-to-charge ratios

 (Ar^{2+}) and 1000 for heavier ions (¹⁸⁰Hf⁺). The instrument includes an electrostatic energy analyser to measure plasma ion energies. A 20 µm orifice positioned at the substrate height was used to sample ions from the plasma into the mass spectrometer (via differentially pumped transfer optics). During measurements, the orifice plate was grounded and the residual pressure in the sampling ion optics was below 5×10^{-3} Pa. It was therefore assumed that collisions after the sampling orifice, potentially leading to charge transfer or recombination reactions, could be neglected.

Film analysis

X-ray diffraction (XRD) was performed using a PanAlytical Empyrean diffractometer (Malvern Panalytical), equipped with optics for primary and diffracted beam conditioning, and a 5-axis cradle as a sample holder. The exploited wavelength was Cu K α = 1.5418 Å. Radial ($\theta/2\theta$) measurements were collected in the 2 θ angular range from 20° to 90° in grazing incidence (GIXRD), with the incident angle fixed at 0.5°. The angular acceptance to the samples and detector were reduced via divergence and soller slits, as well as a parallel plate collimator for the detector. The angular resolution of the exploited setup was experimentally determined by measuring the FWHM of the rocking curve of the c-Si 004 reflection, which was ±0.03°. Consequently, the presented measurements are considered to be within an accuracy interval of $\pm 0.03^{\circ}$. The texture was analysed by performing a pole figure of the reflection of interest. The footprint of the X-ray beam on the sample's surface was minimised to avoid drastic changes of irradiated volume during pole figure recording. Background modelling and subtraction, peak identification and fitting and phases identification were performed via the HighScore Plus software (Malvern Panalytical) [139]. All measured diffractograms resulted in a reliable fitting against pseudo-Voigt functions. Texture analyses was completed using the X'Pert Texture software (Malvern Panalytical).

X-ray reflectometry (XRR) was performed using a D8 Discover X-Ray Diffractometer (Bruker) to estimate the films' density. The incident beam (Cu K α = 1.5418 Å) was conditioned using a Göbel mirror. The measurements were done in $\theta/2\theta$ geometry, and the XRR diffractograms were analysed by fitting the data to a physical model created using the DIFFRAC LEPTOS 7 software (Bruker), by selecting a silicon base and a SiO₂ interlayer, with either In or InN as the top layer (density uncertainty determined to be approx. 5 %). Film fracture cross-sections and surface morphologies were imaged using a Hitachi S-4800 high-resolution cold field emission scanning electron microscope (SEM) (Hitachi High-Tech Corporation). Transmission electron microscopy (TEM) was performed using a FEI Titan Themis 200 G₃ (ThermoFisher) at 200 keV to characterise the structure and grain size of a 30 nm InN film deposited onto a TEM grid (copper grid + carbon membrane, Ted Pella). The integrated SuperX detector was used for energy-dispersive X-ray spectroscopy (EDX). The films' optical bandgap (E₀₄) was characterised using an UVISEL spectroscopic ellipsometer (Horiba), with Drude and Tauc-Lorentz single oscillators to model the layers,

and via a Lambda 950 UV/Vis/NIR spectrometer (PerkinElmer). Multi-model analysis was performed by combining the ellipsometry measurements with the total reflectance and transmittance of the spectrometer. The material's electron mobility was measured via an Ecopia HMS-3000 Hall Measurement System (Bridge Technology).

4.2.3 Results

HiPIMS pulse and plasma property analysis

During all experiments and depositions, the following parameters were used: $25 \ \mu s$ pulse width and 100 Hz repetition rate, with the HiPSTER operated in voltage-limited mode at -950 V, 0.6 Pa pressure and 60 sccm Ar flow. The N₂ flow was varied from 0 to 40 sccm, as was the microwave power from 0 to 200 W on each of the three sources.

Firstly, the evolution of the HiPIMS discharge current as a function of N_2 flow and MW power was investigated, with selected results shown in Figure 28. For a pure Ar discharge, a peak current of 7 A is reached by the end of the 25 µs pulse. No significant influence of MW power on the current was observed. When adding 20 sccm of N_2 , a discharge time lag appears, meaning that a current is not detected for the first few microseconds. A delay in current onset is also present for 40 sccm N_2 , with an additional change in discharge nature visible by the slower current rise. Upon turning on the MW plasma at 3×5 W, the time lag slightly increases. With continued sputtering, with or without the low MW power, the current onset delay is susceptible to variations. However, by increasing the MW power to 3×10 W, the time lag disappeared. Further increases in MW power do not seem to change the nature of the discharge for 20 sccm N_2 . For the highest N_2 flow of 40 sccm, the increase in MW power induces the discharge current to rise at a significantly higher rate to reach a peak value just below 8 A. Therefore, the addition of MW plasma enables decoupling the reactivity of N_2 from the undesired effects of target poisoning.



Figure 28 Current evolution during In HiPIMS under varying MW plasma powers 3×0 ÷200 W (three MW sources) and Ar/N₂ flows: pure Ar flow, 60/20, and 60/40, sputtering conditions: 25 µs pulse width, 100 Hz sputtering frequency, -950 V discharge voltage, 0.6 Pa pressure;

Simultaneously, OES was performed facing the magnetron discharge to identify the type of generated species and track changes influenced by the N_2 flow and MW power. Example spectra (Figure 29A,B) obtained under MAR-HiPIMS conditions show the emission of atomic In(I) and ionic In(II) [140], nitrogen's first positive system (FPS), second positive system (SPS), and first negative system (FNS), as well as the presence of atomic N [141, 142] (selected emission lines listed in *appendix A2*, Table A.3). Figure 29C shows the changes in the In(I)/In(II) and atomic nitrogen/nitrogen species sum ratios as a function of N₂ flow and MW power. The MW plasma did not significantly influence In species generation, however, with increasing N₂ flow, the emission of In(II) dropped by around 10 % at 10, 20 and 30 sccm N₂, and 35 % at 40 sccm N₂. In contrast, the presence of MW plasma considerably affected the generation of various nitrogen species, most notably doubling the atomic N contribution at 3×200 W, with respect to the value obtained without MW plasma.



Figure 29 (A, B) Example OES spectra obtained during MAR-HiPIMS (In HiPIMS: 25 μ s, 100 Hz; MW: 60/40 sccm Ar/N₂, 3×200 W, 0.6 Pa), (C) changes in In(I)/In(II) ratios (full bars) and atomic N/N species sum ratio (lined), as a function of N₂ flow and MW power;

Langmuir probe measurements were performed under microwave plasma conditions for different N₂ flows and MW powers (Figure 30A-C) to monitor their effect on the: plasma potential (V_p), electron temperature (kT_e), electron (n_e) and ion (n_i) densities. The V_p differed for pure Ar plasma and all Ar/N₂ plasmas, independently of the N₂ flow. The V_p for pure Ar plasma increases sharply with increasing MW power until reaching 15 V at 3×50 W, after which it does not greatly increase and stabilises at 18 V in the MW power range 3×100,200 W. The addition of N₂ causes a decrease in V_p , where at 3×50 W it is 12 V. However, for nitrogen-containing plasma, with increasing MW power, the V_p increases rapidly, until stabilising in the range of 3×100,200 W at 22 V. The kT_e is strongly influenced by the addition of N₂ to the discharge gas. The highest values were recorded for pure Ar plasma, where it reached a maximum value of 2.4 eV at 3×50 W. The kT_e significantly drops with the addition of N₂, with the maxima of approx. 1.7, 1.3, 1.1 and 1.0 eV for 10, 20, 30 and 40 sccm, respectively, reached at 3×75 W and stabilised around these values with increasing powers. The n_e and n_i did not differ significantly with the addition of N₂ and followed a similar trajectory with increasing MW power as the pure Ar plasma.

Next, time-resolved Langmuir probe measurements under MAR-HiPIMS conditions in the substrate region were performed to determine the effects of the HiPIMS and MW plasmas on one another (Figure 30D-F). The HiPIMS pulse was initiated 20 μ s after the Langmuir probe, at which point the initially measured plasma properties of the MW plasma change, resembling those of the HiPIMS plasma, with the V_p decreasing from 13 V to 5 V and the kT_e increasing from 1 eV to 3.5 eV. The drops in ion and electron density at the substrate height during the HiPIMS pulse and subsequent increase after the pulse are due to the charged species being drawn towards the magnetron via the high generated electric field.



Figure 30 Langmuir probe measurements of V_p , kT_e , n_e and n_i at the substrate region (A-C) under MW plasma conditions for different N₂ flows and MW powers, (D-F) under MAR-HiPIMS sputtering conditions (In HiPIMS: 25 µs, 100 Hz; MW: 60/40 sccm Ar/N₂, 3×50 W, 0.6 Pa), grey areas mark measurement uncertainties, dark green areas mark pulse duration, pale green areas mark the period when only the MW plasma is on, scales adapted to the data range;

Time-resolved ToF-MS (Figure 31) allowed to simultaneously identify Ar^+ , Ar^{2+} , N_2^+ , N^+ and In^+ species in the substrate region. More importantly, however, the measurements enabled determining the energies of the incoming ions, which could be grouped into three energy/charge (E/Q) categories: *low* (0,6 V), *mid* (6,12 V), and *high* (12,20 V). The *low* and *high* E/Q groups were determined to originate from HiPIMS, with the increase in the number of ions detected within the timescale of the HiPIMS 25 μ s pulse, after which their population decreased. The *mid* E/Q ion group was associated with the MW plasma. During the HiPIMS pulse, the population of argon and nitrogen ions drops significantly, after which it quickly increases to its initial value. The upper E/Q of 12 V resembles the MW plasma's V_p (13 V). Furthermore, an increase in In⁺ population is observed over the course of 75 μ s after the HiPIMS pulse. Afterwards, the number of In⁺ slowly decays at an exponential decay time of $\tau \approx 1.3$ ms. With this it is again possible to highlight phenomenon decoupling through MW plasma incorporation, i.e. the dissociation of ion production and their energy (with a majority of ion energies determined by the MW plasma), as well as nitrogen ion generation from the magnetron plasma.



Figure 31 ToF-MS measurements performed at the substrate region under MAR-HiPIMS sputtering conditions (In HiPIMS: 25 μ s, 100 Hz; MW: 60/40 sccm Ar/N₂, 3×50 W, 0.6 Pa), (A) averaged ion E/Q distribution over entire measurement period, temporal evolution of *low* and *high* E/Q groups (top), *mid* E/Q group (bottom);

InN film characterisation

Firstly, GIXRD was performed on films fabricated via R-HiPIMS and MAR-HiPIMS (Figure 32A). For the R-HiPIMS samples, multiple peaks were registered, all assigned to metallic indium. The diffractogram of the MAR-HiPIMS sample contains only one peak, identified as (0002) oriented indium nitride (the other being from the Si substrate). A pole figure of the MAR-HiPIMS sample was prepared, with the (0002) pole in the centre (Figure 32B), where fibre-texturing was determined with a high degree of mosaicity (intensity of the scattering extending over a Ψ range of approx. 15°). The density of the MAR-HiPIMS film
measured via XRR was approx. 6.9 g/cm³ (InN bulk density 6.9 g/cm³ [143]), whereas the R-HiPIMS film density was greater at 7.1 g/cm³ (In bulk density 7.3 g/cm³).



Figure 32 (A) GIXRD of InN films deposited via R- and MAR-HiPIMS, dotted lines mark In and InN non-stressed positions [144], (B) pole figure of the MAR-HiPIMS sample with the InN (0002) pole in the centre;

SEM and TEM were used for volume film microstructure and morphology characterisation (Figure 33). The R-HiPIMS sample is characterised by high surface roughness and thickness inhomogeneities ranging from around 50 to 80 nm. Cauliflower-shaped grains, along with randomly distributed larger grains, are present on the film's surface. The MAR-HiPIMS film, in contrast, has a homogeneous thickness of 100 nm. The fracture surface revealed columns, the tops of which are reflected in the extremely fine round features on the sample's surface (Ø approx. 5 nm). The bright-field TEM (BF-TEM) images of the two samples show a continuous crystalline film for both cases. Selected area electron diffraction (SAED) confirms that without microwaves there is no nitride formation, with metallic indium being deposited instead. The microwave plasma-assisted process leads to a single phase of indium nitride with a <0001> out of plane texture.

The local chemical composition was analysed using EDX mappings (Figure 34). In the case of R-HiPIMS, only traces of nitrogen were found. Instead, a strong oxygen signal was present, which indicates the presence of a native oxide layer on the metallic indium grains. The MAR-HiPIMS film showed a roughly equal atomic percentages of nitrogen and indium corresponding to a stoichiometric InN phase. Its structure was studied in more detail using high-resolution scanning transmission electron microscopy (HR-STEM), as shown in Figure 35. The grain size of InN lies in the range of 6-10 nm with most grains oriented close to a <0001> zone axis. In high resolution, InN's hexagonal structure is clearly visible (Figure 35B), indicating a high degree of ordering within the grains.



Figure 33 SEM fracture cross-section and surface morphology (~100 nm film on Si substrates), TEM-BF imaging (~30 nm film on TEM grids) and indexed SAED (In : $1 = (011), 2 = (002), 3 = (112), \text{InN} : 4 = (1\overline{1}00), 5 = (1\overline{1}01), 6 = (1\overline{1}02), 7 = (11\overline{2}0)$) of films deposited via (A) R-HiPIMS and (B) MAR-HiPIMS;



Figure 34 STEM HAADF imaging of R- and MAR-HiPIMS samples, with corresponding EDX elemental maps;



Figure 35 HR-STEM images of MAR-HiPIMS InN film: (A) overview, showing the grain size and (B) close-up, showing the atomic structure of (0001) orientated InN;

Ellipsometry and UV/Vis/NIR spectroscopy were used to determine the films' optical properties. The results between the model and the spectroscopic measurements agree within the uncertainty limits. The results of the R-HiPIMS sample resembled those of a metal (in agreement with only In being detected), therefore it was not analysed further. For the MAR-HiPIMS sample, the E_{04} value from UV/Vis and ellipsometry were 1.56 and 1.50 eV, respectively (Figure 36). Hall effect measurements were performed on the MAR-HiPIMS sample to determine its electron concentration and mobility, which were 2.72×10^{20} cm⁻³ and 7.16 cm²V⁻¹s⁻¹, respectively.



Figure 36 Absorption coefficient vs energy obtained from UV-Vis (full line) and ellipsometry (dashed line) for R- and MAR-HiPIMS InN samples, dotted line marks the E_{04} ;

4.2.4 Discussion

Deposition environment

During R-HiPIMS, the nitrogen introduced into the chamber is subjected to partial dissociation within the magnetron plasma during sputtering and reacts with the surface of the indium target to generate a compound layer. The properties of this layer will significantly differ from those of pure In and will, in turn, change the target's discharge dynamics [56, 58, 120, 131, 145]. One of the main aspects affected by indium nitriding is γ_{see} . It has been shown that under DCMS Ar⁺ bombardment, In's γ_{see} upon nitriding and is almost halved [58], meaning that there will be fewer generated secondary electrons (SEs). This causes a discharge time lag, signalling that the initiation of HiPIMS discharges is hindered. Yushkov and Anders explain that this phenomenon is comprised of two components, i.e. a statistical time lag t_s , which is the time required for the initial electrons to appear in the electric field, and a formative time lag t_{f} , the time needed for developing the discharge from the initial electrons [120]. With an insufficient number of generated electrons to compensate the loss of charged particles due to the ion current, the discharge current is limited. Once there are enough electrons, the discharge proceeds as normal. It is possible to overcome this limitation to a certain extent by extending the HiPIMS pulse width, however, this is not a long-term solution. Another solution could be increasing the voltage, possibly allowing to reach greater currents and bypass the time lag (this was not explored in the scope of this work, as the used generators were limited to 1 kV). The negative effect of target poisoning may progress throughout the process's duration, continuously changing the discharge behaviour, in turn affecting the microstructure and

properties of the fabricated film. With continued target poisoning, the time lag can increase, compromising discharge ignition.

Filling the chamber with a volume MW plasma in a pure Ar discharge does not induce significant changes (Figure 28A). However, a notable effect is observed once nitrogen is added (Figure 28B,C, Figure 29). For low MW powers (here, below 3×10 W), a greater quantity of reactive nitrogen is created, causing more reactions on the In target's surface, increasing the time lag. Further MW power increases, however, not only activate more reactive nitrogen species, but additionally increase ion an electron densities within the chamber, providing electrons to the magnetron discharge. Now there are enough seed electrons to overcome the negative effect of γ_{see} decrease, causing the time lag to disappear. Therefore, it can be summarised that the advantage of including microwave plasma during R-HiPIMS is twofold, (1) activating the otherwise inert nitrogen molecules to ensure attaining stoichiometric InN films, and (2) supplying seed electrons near the magnetron to compensate for the decrease in SEs caused by compound layer formation (Figure 37).



Figure 37 Schematic representation of nitrogen reactivity vs electron generation during In sputtering via HiPIMS, R-HiPIMS, low and higher MW power MAR-HiPIMS;

Gas discharge plasma in Ar/N_2 mixtures is rather well understood [146–148]. However, which of the possible reactions and reaction pathways, including electron impact ionisation, dissociative ionisation, vibrational excitation, and vibrational pumping, to name only few, are dominant depends strongly on the total gas pressure, mixture and excitation mechanisms. Langmuir probe measurements (Figure 30) show a decrease in kT_e upon N_2 addition, which is caused by the vibrational excitation of N_2 via collisions with plasma electrons. Similar effects were observed by Zhiguo *et. al.* within an Ar/N_2 MW-ECR plasma [125]. Furthermore, the reported MW plasma densities are in the same order of magnitude as those reported by Zoubian *et. al.* using the same MW-ECR sources [36], for the given distance between the MW source and Langmuir probe tip, with the trends following higher densities with greater MW powers. When igniting the HiPIMS discharge under MW plasma conditions, Langmuir probe results depicted similar trends reported and explained by Hain *et al.* [64] and Stranak *et al.* [149]. Considerable perturbations are introduced to the MW plasma, where the negative electric field (-950 V) draws the ions

from the substrate region towards the magnetrons causing the observed plasma property changes to those typical for HiPIMS. Further displacement currents are observed at the end of the HiPIMS discharge, i.e. lack of electric field, reflected by the n_e and n_i values just after the pulse. Moreover, an increase in n_i is observed, which would correspond to ions reaching the substrate once released from the magnetron trap.

The ToF-MS results complement Langmuir probe observations, as well as enable determining which of the detected species are generated by the HiPIMS discharges and which by the MW plasma. As mentioned in the Results section, it was possible to distinguish three E/Q ranges (Figure 31). The low and high ranges were attributed to the HiPIMS discharge, where the time profiles show an increase in In ions near the end and after the end of the pulse. Within the low range, an increase in argon and nitrogen species is observed. As N^+ is detected, it can be stated that a certain amount of nitrogen is dissociated within the magnetron plasma, with the ratio between molecular and atomic species detected during the pulse being approx. 40. The mid E/Q ion group was determined to be generated within the MW plasma, where the number of measured argon and nitrogen ions is stable over the entire measurement period, except in the time frame of the magnetron pulse. During that time, a drop in measured species is observed, which corresponds to the behaviour of the plasma potential measured via the Langmuir probe. Following OES results, where an increase in nitrogen peak intensities were detected in the presence of MW (Figure 29), the ratio between molecular and atomic nitrogen is approx. 12. Therefore, the MW plasma facilitates nitrogen dissociation, and does so much more effectively than the HiPIMS plasma. In terms of In ion behaviour, long decay times were registered during both R-HiPIMS (results not included) and MAR-HiPIMS, which is consistent with long term decay rates of heavy sputtered species in the HiPIMS afterglow [150]. However, in the presence of MW plasma, the amount of detected In⁺ over the entire measurement cycle increased by 185 %. The results indicate that the microwave plasma facilitates the transfer of charged particles from the dense plasma generated during In HiPIMS towards the substrate, while inducing post-sputtering ionisation.

InN film characteristics vs fabrication conditions

To determine the influence of the deposition environment on the structuring and properties of InN films, R-HiPIMS and MAR-HiPIMS samples were prepared. Directly, it could be determined that without MW plasma it was not possible to produce InN. Both X-ray and electron diffraction identified the material deposited using R-HiPIMS to be metallic indium. As the R-HiPIMS sample was mainly metallic, focus was placed on the MAR-HiPIMS film. GIXRD showed that InN was obtained, preferentially growing in the (0002) direction. From the pole figure it was possible to determine a fibre-type texture, with a high level of grain mosaicity. This was confirmed via TEM investigations, where the InN grains were predominantly oriented close to a <0001> zone axis, with visible z-axis rotation of the grains, in respect to one another. The optical band gap of the MAR-HiPIMS film (approx. 1.5 eV) is in range of values reported for polycrystalline InN. The measured electron concentration (2.72×10²⁰ cm⁻³) and mobility (7.16 cm²V⁻¹s⁻¹) are also characteristic for films deposited via sputtering [121, 126]. For reported values of perfect InN films, deposited, e.g. by molecular beam epitaxy (MBE), with electron concentrations in the range of 10¹⁷ cm⁻³, the electron mobility can exceed 3000 cm²V⁻¹s⁻¹ [151, 152]. In the work of Walukiewicz et. al [153], an absorption edge of 1.5 eV (or a Burstein-Moss shift of 0.8 eV) induced by an electron concentration of $n=2\times10^{20}$ cm⁻³ was reported. The strength of this Burstein-Moss shift is due to the Fermi stabilisation energy (E_{FS}) penetrating the conduction band of InN. Intrinsic defects will then tend to be n-type, which will make the fermi level (E_F) rise until reaching E_{FS} . Although imperfect, the InN layer fabricated via MAR-HiPIMS matches the characteristics described in literature for defective InN. A possible reason behind the low electron mobility and high electron concentration may be explained by the high degree of grain mosaicity. In these locations, dangling bonds can remain non-passivated, which would flood the layer with surplus electrons, and function as defects/traps for electron recombination. Further studies into improving the applicational properties of InN should include controlling the energy of incoming species. As MAR-HiPIMS facilitates ion generation, it would be possible to steer their behaviour through the application of electric fields near the substrate, e.g. substrate biasing and/or MW plasma pulsing. This should enable reducing prolonged Ar ion bombardment, potentially leading to structure degradation and amorphisation [64, 128].

4.2.5 Conclusions

This work focused on characterising the deposition environment and fabricated thin films via MAR-HiPIMS, where an In target was sputtered in the presence of a mixed Ar/N_2 MW plasma. The combination of *in situ* diagnostics and material characterisation allowed to conclude the following:

- indium is susceptible to target poisoning through surface reactions with nitrogen, with the formation of a compound layer causing a delay in current onset,
- microwave plasma provides enough electrons to sustain the HiPIMS discharge and facilitates inert molecular nitrogen dissociation into reactive metastable molecular and atomic species,
- coupling time-resolved Langmuir probe and ToF-MS measurements allow to characterise the behaviour of the HiPIMS and MW plasmas, by monitoring the temporal evolution of the plasma properties, determining the plasma chemistry, and identifying the origin of the detected ions based on their energies,
- MAR-HiPIMS is successful in fabricating stoichiometric textured InN films, with a high degree of grain mosaicity, with the material's optoelectronic properties within the range of sputtered InN.

Future studies should focus on controlling the incoming charged species, as this could be key in decreasing grain mosaicity, and modifying the optoelectronic properties of the InN film. Different possibilities present themselves, such as synchronising the HiPIMS pulse and the substrate bias and/or MW plasma pulsing to reduce the number of argon ions bombarding the surface of the growing film.

4.3 MAR-HIPIMS CASE STUDY 2: ZINC TIN NITRIDE

The information presented in this chapter is part of an ongoing study that will be submitted under the title "Influence of Microwave Power and Substrate Biasing on the Structure and Properties of ZTN Films Deposited via Microwave Plasma-Assisted R-HiPIMS", prepared by C. Hain, K. Wieczerzak, D. Casari, A. Sharma, A. Xomalis, P. Sturm, J. Michler, A. Hessler-Wyser and T. Nelis.

4.3.1 Introduction

There is a strong need to improve control over thin film deposition processes for tailoring the structure, properties and overall quality of the deposited material for specific applications. The key to unlocking this potential lies in the concept of phenomenological decoupling, i.e. the separation of otherwise interdependent effects. Significant progress has been made over the years, such as the development of high power impulse magnetron sputtering (HiPIMS) [53], where e.g. average power (heat) is decoupled from the produced plasma density, or electron cyclotron resonance (ECR) microwave (MW) sources [36, 38], where e.g. electron and ion motions are decoupled. These developments are of particular interest for the production of compound materials, where deposition is often hampered by difficulties in the procurement and sputtering of compound targets (stoichiometry, purity, conductivity) or by reactive gas-metal target interactions (target poisoning) [56–58, 119]. In our previous work, we reported the combination of ECR MW plasma and HiPIMS for microwave plasma-assisted reactive HiPIMS (MAR-HiPIMS) of indium nitride (InN) [65]. There, we showed that it is possible to decouple the undesired effects of target poisoning (time lags [120]) from the reactivity of nitrogen species, the generation of nitrogen ions from the magnetron plasma, as well as ion production from their energies. Following this line of thought, the next step is to determine the viability of this approach during the potentially more complex process of co-sputtering from different materials. The increase in complexity arises from the lack of detailed knowledge of the reactions that occur between the sputtered atoms and the reactive gas, making it difficult to control the composition and properties of the deposited film. To gain more knowledge in this respect, zinc (Zn) and tin (Sn) were selected for this study (continuing work with temperature-sensitive materials) with the aim of producing tuneable zinc tin nitride (ZTN) thin films.

In recent decades, zinc tin nitride, a semiconductor of the $Zn-IV-N_2$ family, has gained interest in the field of optoelectronics (including photovoltaics) due to its large optical absorption coefficient and the possibility of varying the band gap within the ultraviolet to infrared range. It is considered as a possible replacement for indium gallium nitride (InGaN) as it contains abundant and inexpensive Zn and Sn, is non-toxic and recyclable, and has reported bandgap values of up to ~ 2.0 eV [154, 155]. The tunability of the bandgap of ZTN is dependent on the degree of cation disorder [156], making it an excellent candidate for enhanced control deposition studies. Since the initial computational evaluation by Paudel and Lambrecht in 2008 [157], several groups have carried out follow-up calculations and have successfully prepared ZTN thin films by direct-current (DC) and radiofrequency (RF) reactive MS, as well as molecular beam epitaxy (MBE) with different chemical compositions and structures [154, 156, 158]. The work of Fioretti et al. is of particular interest as it uses a combinatorial approach to explore growth-temperature-composition relationships by producing chemically graded ZTN films at different substrate temperatures via RF reactive sputtering [159]. This has allowed a wide range of structural and optoelectronic relationships to be examined. Despite the advances in material quality for optoelectronic applications, to the best of the authors' knowledge, there are presently no studies that relate the characteristics of the deposition environment to the structure of ZTN films. Therefore, the aim of this study is to deposit a series of ZTN thin films with the same chemical composition but different structures using MAR-HiPIMS. This will be done by varying the power of the microwave plasma sources and the substrate bias strategy, therefore enabling the decoupling of plasma potential and ion energy, and subsequently tracking these changes through in situ deposition environment diagnostics involving HiPIMS discharge current evolution analysis, time-resolved Langmuir probe measurements and energy-resolved time-of-flight mass spectrometry (ToF-MS). The structure of the fabricated ZTN film series were investigated via X-ray diffraction (XRD) and scanning electron microscopy (SEM).

4.3.2 Experimental section

Deposition setup and film fabrication

The same deposition setup was used as for InN (see *subchapter 4.2*), with the only difference being that two HiPSTER 1 power supply units were used instead of one. The sputtering targets were ϕ 50 mm, 3 mm thick, 99.995 % purity zinc and tin discs (HMW Hauner GmbH & Co. KG). A schematic of setup configuration is shown in Figure 38.

The silicon substrates, base pressure and pre-treatment step were the same as those described in *subchapter 4.2*. All ZTN films were fabricated via MAR-HiPIMS, where the working pressure (0.6 Pa) and gas composition ($60/40 \text{ sccm Ar/N}_2$) were constant. Two MW powers of 3×50 W and 3×150 W were selected, and three substrate bias variations were applied, i.e. floating, grounded and -25 V. The sputtering parameters of each target, summarised in Table 5, were set to reach a ratio of Sn to Zn of approx. 1:1, while the deposition time was set to 30 min to reach film thicknesses of approx. 200 nm.



Figure 38 Schematic of deposition setup for MAR-HiPIMS of ZTN (top view);

target	pulse width / s	frequency / Hz	voltage / V	peak current / A	avg. power / W	
Zn	75	150	680	1	10	
Sn	35	150	980	7	36	

Table 5 Summary of Zn and Sn target sputtering parameters;

Deposition environment and film characterisation

The voltage current output was monitored as described in *subchapter 4.1* and the ToF-MS measurements were performed as those included in *subchapter 4.2*. The gathered data from ToF-MS investigations were processed by means of an in-house developed python script. Film fracture cross-sections and surface morphologies were imaged via scanning electron microscopy (SEM), as reported in *subchapters 4.1* and *4.2*. The films' chemical composition was evaluated using a Mira-3 SEM (Tescan), equipped with an Octane Plus SDD energy-dispersive X-ray spectroscopy (EDX) detector (EDAX). The used accelerating voltage was 5 kV, and the chemical analysis was carried out using ZAF correction. X-ray diffraction (XRD) was performed using a D8 Discover X-Ray Diffractometer

(Bruker). The incident beam (Cu k α = 1.5418 Å) was conditioned using a Göbel mirror. Measurements were collected in the 2 θ angular range from 15° to 80° in grazing incidence (GIXRD) geometry, with the incident angle fixed at 1°.

4.3.3 Results and discussion

Deposition environment analysis

Prior to film deposition, the nature of the Zn and Sn discharges under pure Ar and mixed Ar/N_2 , without and with 3×50 W and 3×150 W MW plasma conditions, was evaluated by studying the HiPIMS *I*(*V*,*t*) curves (Figure 39).Based on the obtained curves, it can be

seen that both Zn and Sn are characterised by a similar behaviour to In. Without N₂, the discharge of both targets is stable with and without MW plasma. However, when N₂ is added, a time lag of approx. 5 and 3 µs develops for Zn and Sn, respectively. This indicates the formation of a poisoned compound layer on the surface of the targets, most probably accompanied by a drop in their γ_{see} . In the presence of MW plasma, the time lag disappears, and the discharges are once again stable.



Figure 39 Current evolution during Zn and Sn HiPIMS under varying working gas mixtures (60 sccm Ar and 60/40 sccm Ar/N₂) and MW plasma powers (no MWs, 3×50 W, 3×150 W);

Time-resolved ToF-MS measurements were performed at the height of the substrate to identify the incoming species, along with their energy per charge (E/Q). Selected results obtained during the sputtering of Sn and Zn under Ar/N₂ gas MW plasma conditions are included in Figures 40 and 41, respectively. Firstly, by comparing the contour plots for Ar⁺, N₂⁺, N⁺ between the Sn and Zn discharges, both the measured E/Q values and the general temporal behaviour are similar. However, during Zn sputtering, less gas ions are detected, especially for N^+ (by a factor of 3). Considering that the volume plasma conditions were the same, the cause behind the lower ionic flux is most probably related to the significantly lower peak currents employed for Zn sputtering (1 A vs 7 A for Sn). Therefore, the contribution of dissociated nitrogen species from the HiPIMS plasma, although not as effective as the MW plasma in the case of the studied material system and conditions, should not be disregarded. Moving to the behaviour of the species generated through sputtering, the registered temporal behaviours differ from one another. This is linked to the different employed pulse widths of 35 and 75 µs for Sn and Zn, respectively. An interesting effect that was observed for both materials is that they form ionic molecular nitrides in the plasma phase and reach the ToF-MS orifice (i.e. where the substrate would be) as such. With already this degree of reactivity observed between the metallic and nitrogen species under MW plasma conditions, it is expected that this will facilitate the fabrication of stoichiometric ZTN films. Comparable trends were registered for the higher

MW power conditions of 3×150 W (see *appendix A*₃), however, for all cases, the general E/Q value distribution increased by approx. 2 eV. For both Sn (Figure A.1) and Zn (Figure A.2) sputtering, increasing the MW power resulted in doubling the amount of generate Ar⁺ and N₂⁺. For N⁺ the effects slightly differed, where for Sn the flux increased by a factor of 1.5, whereas for Zn it tripled. In terms of the post-ionisation of the metallic species, no notable differences were observed for the Sn ionic flux, however, for Zn it doubled. Similar trends were observed for the ionic molecular nitrides, with the exception of ZnN₂⁺, where the change in MW power did not seem to have much effect.



Figure 40 Time-resolved ToF-MS contour plots for Ar^+ , N_2^+ , N^+ , SnN^+ , SnN_2^+ ion fluxes, with their associated E/Q, obtained during MAR-HiPIMS Sn sputtering under Ar/N_2 gas MW plasma conditions (MW power 3×50 W), scales adapted to the data range;



Figure 41 Time-resolved ToF-MS contour plots for Ar⁺, N₂⁺, N⁺, Zn⁺, ZnN⁺, ZnN₂⁺ ion fluxes, with their associated E/Q, obtained during MAR-HiPIMS Zn sputtering under Ar/N₂ gas MW plasma conditions (MW power 3×50 W), scales adapted to the data range;

ZTN film characterisation

A total of six ZTN films were fabricated via MAR-HiPIMS. All films were characterised by a chemical composition of a Sn/Zn ratio of approx. 1.1 (via EDX). Next, XRD was performed to determine the deposited materials' structure (Figure 42). The obtained peaks are all related to those of stoichiometric ZTN, and it is visible that changing the substrate bias and MW power had an effect on the structure of the films, despite their similar chemical composition. Exact peak identification is hindered due to the complexity of ZTN's structure, with multiple peak overlaps. However, the general trend is that the material appears less polycrystalline and more "ordered" with the substrate bias progression floating \rightarrow grounded \rightarrow -25 V. Furthermore, for films deposited at higher MW powers on substrates at floating potential and o V seem to have a more orientated structure. For ZTN deposited with a bias of -25 V, already 3×50 W are enough to reduce the number of attained orientations to two, with the dominant orientation being (002) at approx. 32.6°. Comparably, for 3×150 W only two peaks are also detected, however, their intensities are more similar, therefore, a more equal contribution of the two orientations is expected.



Figure 42 X-ray diffractograms of ZTN films deposited under varying microwave power and substrate bias, dashed grey lines mark the ZnSnN₂ (orthorhombic/Pna₂₁) non-stressed positions [144];

The imaged fracture cross-sections of the ZTN films (Figure 43) show a homogeneous thickness of approx. 200 nm. In general, the observed morphologies are in line with the XRD results. Although all films exhibit columnar growth, those deposited at floating and grounded potentials are characterised by discontinuous, slightly triangular columns. This is additionally reflected by the films' surface morphology (mudcrack-like for floating films and rise grain-like for grounded) containing pores. The SEM images also confirm that the use of higher microwave powers (and higher plasma potentials) leads to improved film quality for those substrate biasing approaches. Films fabricated at -25 V do not show significant differences between the two applied MW powers, as here the increase in plasma potential is not as significant compared to the applied substrate bias. Both possess continuous columns through the film and their surfaces are devoid of noticeable porosities. The main difference between the two films are the slightly smaller surface morphology features for the 3×150 W variant.



Figure 43 SEM images of fracture cross-sections and surface morphologies of ZTN films deposited onto floating, grounded and -25 V biased substrates under 3×50 W and 3×150 W MW powers;

4.3.4 Planned next steps

The next steps of the ZTN MAR-HiPIMS study will concern validating the ToF-MS measurements via Langmuir probe and retarding field analyser (RFA) measurements, as well as investigating the ZTN films in greater detail. The structure and optical properties of a "perfect" ZTN structure will be prepared computationally using the density functional theory (DFT). Once the reference model is complete, the deposited ZTN films' lattice parameters will be calculated from the already obtained diffractograms and will be used to follow changes to the materials' optical properties as a function of the selected deposition parameters. Moreover, selected film samples will be prepared for transmission electron microscopy (TEM) investigations to gain more information of the films' crystallographic structure. These further investigations will enable to link the deposition environment phenomena (e.g. species generation, ion energy) more easily with the modifications to the ZTN films.

5

CONCLUSIONS AND OUTLOOK

The aim of this work was to determine the possibilities of improving process control by means of plasma assisted hybrid vapour deposition methods, mainly through the combination of HiPIMS and microwave plasma technologies, by inducing tailored phenomenological decoupling. Three different materials were selected as case studies, with the added incentive of evaluating the flexibility and versatility of the proposed approach. Despite their differences in composition and final application, the contribution of the ionic flux to the film growth is important, as this allows to "move" in the structure zone diagram and finally tailor the film properties. However, going into more detail, each material is characterised by its own issues. In the case of DLC, achieving an significant flux of energetic C⁺ ions, while maintaining a low Ar⁺ ion flux is crucial to produce hard DLC films without causing film delamination or graphitisation. In case of metal-nitrides, producing sufficient reactive nitrogen species beyond the thermal stability of InN, or ensuring controlled co-sputtering of zinc and tin, while being able to access desired chemical compositions and structural orientations, is crucial. It has been shown that the deposition environments resulting from the used HVD processes are complex, however, it is possible to gain valuable insights through in situ diagnostics and to overcome certain material-process limitations. While the impact of the HVD approach on the film quality remained minimal in the case of the pure carbon DLC, the HVD method studies presented in this work demonstrated its strength in the case of metal nitrides, InN and ZTN. With the high nitrogen activation through MW plasma and the possibility of integrating the rather new self-matching Aura-wave sources combined with flexible solid-state microwave power generation, it is possible to overcome several issues related to reactive sputtering. i.e. hysteresis, time-lags, stoichiometry. It may appear secondary, but the flexibility in integration and the ease of use of the above-mentioned microwave technology is important, as it allows to concentrate on the deposition process rather than on the microwave power line.

To improve the understanding of the produced deposition environments and to tune the process phenomena, process development should go hand in hand with technological advances in deposition setups and diagnostic equipment. For example, in the DLC study it was not possible to measure the energies of the incoming species as the tools weren't available at that time. It was only later, as part of a European project with TOFWERK and other industrial and academic partners, that the energy-resolved ToF-MS was developed. On its own, this instrument a mine for process relevant data, as it provides information on which ions hit the substrate surface at which time and with what energy. Combining this tool other diagnostic tools, such as Langmuir probes, retarding field energy analysers,

and modified quartz microbalances, to give only a few examples, will greatly increase the depth of knowledge we can gain. In turn, we can use this information to tailor films for specific applications or to design new material systems.

APPENDICES TO EXPERIMENTAL WORK

A.1 APPENDIX: DIAMOND-LIKE CARBON

Further details on System 2

Assuming a 1 mm gap between the grounded magnetron ring and the ϕ 50 mm target, a 120 sccm flow rate fed through these 3 ring-shaped exits at a pressure of 1 Pa and corresponds to an average speed of 420 m/s. Referring to the surface parallel to the target, the average speed is 34 m/s. In other words, the atoms in front of the target will move approx. 3.4 mm during a 10 µs pulse, which is in the range of the extension of the dense part of plasma (3 to 5 cm). The volume of the reactor is approximately 30 l, therefore a flow rate of 120 sccm would correspond to an exchange of gas volume inside the reactor 5 times per second, assuming a homogeneous gas flow.

DLC substrate cleaning and pre-treatment step

system	ex situ cleaning	in situ cleaning				
		microwave power / W	argon flow / sccm	bias / V	pressure / Pa	time / min
1	compressed air blowing	3×100	100	-100	0.5	1
2	5 min ultrasonic cleaning (acetone, isopropanol)	3×50	10	-600	0.2	10

Table A.1 Cleaning and pre-treatment process summary;

Plasma measurements

Plasma characterisation was only possible for system 2 (HiPIMS-based processes), however, both systems use the same "Aura-wave" microwave sources, therefore plasma properties of *system 1* could be reproduced in *system 2*. It should be noted, however, that plasma densities nearer the microwave sources will be greater. Between 3x45 W and 3x50 W, significant plasma property differences are not expected. Plasma properties for 3x100 W and 3x200 W are shown in Table A2.

MW power / W	V _p / V	kT _e / eV	n_i / m^{-3}	n_e / m^{-3}
3×100	16.60 ± 0.83	2.74 ± 0.01	$9.55 \times 10^{16} \pm 5.74 \times 10^{14}$	$5.97 \times 10^{16} \pm 7.04 \times 10^{14}$
3×200	19.70 ± 0.10	2.90 ± 0.01	$1.43 \times 10^{17} \pm 1.03 \times 10^{15}$	$9.21 \times 10^{16} \pm 1.29 \times 10^{15}$

Table A.2 Microwave plasma properties measured within *system 2* for microwave powers of 3×100 W and 3×200 W;

A.2 APPENDIX: INDIUM NITRIDE

List of selected emission lines

Table A.3 Selected emission lines used for OES species identification, taken from [140-142];

species	In	In ⁺	N_2	N_2^*	N_2^+	Ν
species wavelength / nm	In 271.24 275.63 277.77 283.83 285.95 293.43 295.87 304.18 305.29 325.90	In+ 203.79 256.16 256.27 283.94 286.07 289.19 294.32 296.10 318.92	N₂ 311.90 313.77 315.96 316.07 316.18 336.65 337.08 337.19 337.3 337.4 353.84	N_2^* 575.22 ÷ 610.22 625.42 ÷ 690.36	N ₂ ⁺ 391.58	N 750.33 826.3 851.86
	325.90 410.48	318.92 326.23	353.84 356.62 357.79 357.9			

A.3 APPENDIX: ZINC TIN NITRIDE



ToF-MS contour plots for 3x150 W microwave power

Figure A.1 Time-resolved ToF-MS contour plots for Ar^+ , N_2^+ , N^+ , Sn^+ , SnN_2^+ ion fluxes, with their associated E/Q, obtained during MAR-HiPIMS Sn sputtering under Ar/N_2 gas MW plasma conditions (MW power 3×150 W), scales adapted to the data range;



Figure A.2 Time-resolved ToF-MS contour plots for Ar⁺, N₂⁺, N⁺, Zn⁺, ZnN₂⁺ ion fluxes, with their associated E/Q, obtained during MAR-HiPIMS Sn sputtering under Ar/N₂ gas MW plasma conditions (MW power 3×150 W), scales adapted to the data range;

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- 8. K. Wieczerzak, A. Sharma, <u>C. Hain</u>, J. Michler, *Crystalline or amorphous? A critical evaluation of phenomenological phase selection rules*, *SUBMITTED*
- M. Wątroba, W. Bednarczyk, P. K. Szewczyk, J. Kawałko, K. Mech, A. Grünewald, I. Unalan, N. Taccardi, G. Boelter, M. Banzhaf, <u>C. Hain</u>, P. Bała, A.R. Boccaccini, *In vitro cytocompatibility and antibacterial studies on biodegradable Zn alloys supplemented by a critical assessment of direct contact cytotoxicity assay*, J Biomed Mater Res B Appl Biomater. (2022). https://doi.org/10.1002/jbm.b.35147.
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Conferences and seminars

Posters:

- *Microwave Plasma-Assisted Reactive HiPIMS of Indium Nitride Films,* International Conference on Plasma Surface Engineering, Erfurt, Germany, 2022
- Microwave Plasma-Assisted Reactive High Power Impulse Magnetron Sputtering of Indium Nitride Films, EDMX Research Day, 2022
- Microwave Plasma-Assisted HiPIMS on the Example of Diamond-Like Carbon Films, EDMX Research Day, 2021
- Parametric Study of HiPIMS PVD fabricated Diamond-Like Carbon Films, Empa PhD Symposium, St. Gallen, Switzerland, 2019

Talks:

- Various talks as part of the Plasma Coffee series, BFH, Swizterland, 2019-2022
- *Plasma Behaviour in the Context of Langmuir Probe Measurements*, Evatec, Switzerland, online, 2022
- *Microwave Plasma-Assisted Reactive HiPIMS of Indium Nitride Films*, Empa Seminar, Thun, Switzerland, 2022
- Plasma Environment Analysis During the Deposition of InN Films via Microwave Plasma Assisted Reactive HiPIMS, Szkoła Inżynierii Materiałowej, Kraków, Poland, 2022
- Hybrid Vapour Deposition for Tailored Film Fabrication, ResearchXchange, Biel/Bienne, Switzerland, 2021
- *Hybrid Vapour Deposition Methods for Tailored Film Fabrication*, Empa Seminar, Thun, Switzerland, 2020
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