Process - property relations in reactively sputtered transition metal compounds

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"All I know is that I know nothing (gr: ἐμ οἶδα ὑπὲρ οὐδὲν οἶδα)"

Socrates, 470 BC - 399 BC
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1. Introduction

Thin films are microstructures formed upon deposition of atomic layers of a material on a bulk substrate. Thus, one dimension of the thin film (thickness) is several orders of magnitude smaller than the others. The thin film growth frequently proceeds far from thermodynamic equilibrium. This leads in many cases to physical properties which are different from those of the corresponding bulk materials. In addition, thin films enable the growth of multilayer stacks, the deposition on complex structures and geometries and allow for versatility regarding the structure and composition of the deposited material. Due to these facts, thin films play an important role in a vast range of applications and devices, such as in the fields of microelectronics, optics, data storage and surface protection [1], as shown in Figure 1.1.

![Figure 1.1. Technological applications of thin films.](image)

Nowadays thin films are prepared by the condensation of vapor of a material on a substrate (deposition), at high vacuum conditions (<10^{-5} mbar). Physical, as well as chemical processes can be involved in the generation of the vapor. The corresponding techniques are known as physical and chemical vapor deposition (PVD and CVD), respectively. In chemical vapor deposition, a volatile compound (precursor) of the
material to be deposited reacts with other gases in order to form a solid film on a substrate. The principle of the physical vapor deposition is presented in Figure 1.2. The vapor of the material to be deposited is created by a solid or, sometimes, liquid source (target). The vapor is then transferred through the gas phase to the substrate, where the thin film grows atomistically. The atoms can be removed from the target either thermally or dislodged through impact of gaseous ions. The latter process is known as sputtering and the PVD method as sputter deposition.

The sputtering is a widely used deposition technique, since it combines conceptual simplicity, versatility, and relatively high deposition rates. An additional feature of the sputtering process in the existence of energetic species that bombard the growing film and provide means for the selective control of the film properties. In this work the correlations between the process parameters and the properties of transition metal nitride and oxide films grown by sputtering are investigated. These materials are known for their refractory character and the exceptional properties and have a vast range of technological and industrial applications [2,3].

In chapter 2 the fundamentals of the sputtering process and the technical realization of the sputter deposition are presented. Particular emphasis is put on two modifications of the sputter deposition, the reactive direct current magnetron sputtering and the high power pulsed magnetron sputtering. Moreover, in the same chapter the atomistic mechanisms which determine the formation and the growth of the thin films are outlined.

In chapter 3 the experimental arrangement which is used for the preparation of the thin films is described. In addition, the theory and the experimental realization of the analytical techniques which are employed for determination of the process and film properties are presented.
In chapter 4 the growth of transition metal nitrides by reactive direct current magnetron sputtering is investigated. In particular, the effect of the bombardment by backscattered energetic species on the film properties is manifested.

The chapters 5 and 6 deal with a newly developed sputtering technique, the high power pulsed magnetron sputtering. In chapter 5 the issue of the film deposition rate in high power pulsed magnetron sputtering is addressed. In Chapter 6 the properties of transition metal oxide and nitride films grown by high power pulse magnetron sputtering are studied. Finally, in chapter 7 the outlook of this work is presented.

![Figure 1.2. Principle of physical vapor deposition.](image)
2. An overview of thin film technology and science

2.1. Sputtering process

Sputtering is the removal (ejection) of atoms from a solid surface through bombardment by energetic species. The bombarding particles can be ions and neutrals, as well as electrons. In the sputtering processes employed in thin film technology, ions are exclusively used. Apart from the ejection of the surface atoms, additional phenomena are also observed during sputtering, such as implantation and backscattering of the incident particles, change of the surface structure and morphology, as well as the emission of electrons and photons [4].

The sequence of events which lead to the sputtering of a surface atom is shown in Figure 2.1. The energy of the incident particle is transferred to the atoms of the solid surface. If the energy of the target atoms, after their interaction with the impinging species, exceeds a threshold energy $E_0$, a primary recoil atom is created. Generation of recoils in metals takes place mainly through elastic collisions with the incident particles [5]. The primary recoil can either be ejected from the surface (single knock-on sputtering, Figure 2.1 (a)) or give rise to a recoil cascade, which in turn results to sputtering of surface atoms (linear cascade sputtering, Figure 2.1 (b)). In general, a surface atom is sputtered, if the energy that it gains from the collision process is higher than the surface binding energy ($E_b$). A good estimation for $E_b$ in metals is the heat of sublimation.

![Figure 2.1](image-url)

**Figure 2.1.** Sputtering process in the (a) single knock-on and (b) linear cascade regime (adopted from reference [5]).
The sputtering process is characterized by the sputtering yield, i.e. the number of surface atoms ejected per incident particle. In addition, the atoms are sputtered by a solid surface with a broad distribution in energy [5]. These issues are treated theoretically in the subsequent section.

2.1.1. Theoretical treatment of the sputtering process

A formula for the sputtering yield \( Y \) can be theoretically derived, if one combines results from elastic collision, penetration and linear cascade theories [5-7]. In particular, the sputtering yield as a function of the energy \( E \) of the ions that elastically collide on a planar surface is given by the expression [5],

\[
Y(E) = \lambda \alpha N S_n(E) \quad (2.1)
\]

In equation (2.1) \( \alpha \) is a dimensionless function of the mass ratio \( \frac{M_2}{M_1} \) [5], where \( M_1 \) and \( M_2 \) are the atomic masses of the impinging particles (ions) and of the target atoms, respectively and \( N \) is the atomic density of the target [5]. Moreover, the quantity \( S_n(E) \) is the so-called nuclear cross-section and it is a measure for the energy loss that the ions undergo during their interactions with the target [5]. In fact, \( S_n(E) \) describes the effect of the energy of the impinging ions on the sputtering yield and it is calculated by the equation [5],

\[
S_n(E) = \frac{1}{1 - m} C_m \gamma^{1-m} E^{1-2m} \quad (2.2)
\]

Here, \( \gamma = \frac{4M_1M_2}{(M_1 + M_2)^2} \) is the energy transfer factor for elastic binary collisions. The parameter \( m \) depends on the energy of the impinging ions and ranges from \( m = 1 \) at high energies (keV range) down to \( m = 0 \) at low energies (eV range). Finally, \( C_m \) given by the expression,

\[
C_m = \frac{\pi}{2} \lambda_m a^2 \left( \frac{M_1}{M_2} \right)^m \left( \frac{2Z_1Z_2e^2}{a} \right)^{2m} \quad (2.3)
\]

where \( Z_1e \) and \( Z_2e \) is the nuclear charge of the impinging ions and the target atoms, respectively. Moreover, \( \lambda_m \) is a weak function of the parameter \( m \). The equation (2.3) allows for insight to the physical significance of the parameter \( m \). When \( m = 1 \) (high energy limit) the scattering and the stopping of ions in the target are determined by
the Coulomb interactions (Rutherford scattering) [8]. On the other hand, at the low energy limit \((m = 0)\) the screening of the Coulomb interaction in essential for the ion-target interactions [9,10] Finally, the quantity \(\Lambda\) is calculated as [5],

\[
\Lambda = \frac{3}{4\pi^2} \cdot \frac{1}{NC_0E_b} (2.4)
\]

where \(C_0\) is calculated from equation (2.3) for \(m = 0\).

As mentioned in section 2.1 the sputtered atoms exhibit an energy distribution. The maximum \(E_i\) of this distribution for a given ejection angle can be calculated by the equation [11],

\[
E_i = \frac{U_0}{2(1-m)} (2.5)
\]

It is evident from equation (2.4) that the maximum in the energy spectrum depends only on the target characteristics, while it is insensitive to the ion type and energy.

2.1.2. Direct current (dc) diode sputtering

The sputter deposition can be experimentally realized through the arrangement depicted in Figure 2.2. A noble gas (usually Ar) with a pressure ranging from several tenths of mTorr up to 100 mTorr is introduced into an evacuated chamber. A constant negative voltage (in the kV range) is applied to the target (also referred to as a cathode). This enables the acceleration of natively existing positive ions of the noble gas towards the target. The interactions of the impinging ions with the target lead to removal of target atoms (sputtering), as well as electrons (secondary electrons), as mentioned in section 2.1. The secondary electrons cause generation of new ions, which in turn result in emission of new secondary electrons. This ionization-emission cascade leads to a quasi self-sustained glow discharge. The sputtered atoms are transferred through the gas phase to the substrate (also referred to as an anode), where the thin film is deposited. This deposition technique is known as direct current (dc) diode sputtering.

2.1.3. Principles of glow discharges

The generation and the maintenance of the glow discharge is the core of the sputtering processes. A glow discharge can be described in a first approximation as a plasma [12]. In the following the definition of the plasma and the main processes
which take place in plasmas are presented. Finally, the basic features of dc plasmas are discussed.

2.1.3.1. Definition of plasma. The term “plasma” was first used by Irving Langmuir in 1929 in order to describe an ionized gas [13]. The plasma is an assembly of gas ions, electrons and a much larger number of gas neutrals which exhibit a collective behavior [14]. The ions and electrons in the plasma are created and destroyed pair-wise through collision processes in the gas phase. As a result, the occupied space is free of charge. The latter is known as quasi neutrality of the plasma [12]. The ionized particles have to fulfill two criteria for the gas to qualify as plasma; (i) sufficiently high charge density, so that the long range Coulomb forces determine the statistical properties of the particles and (ii) low enough gas density, so that the Coulomb force of a near neighbor atom is much less than the cumulative Coulomb forces exerted by the many distant particles [14].

![Figure 2.2. Principle of direct current (dc) diode sputtering.](image)

2.1.3.2. Collision processes. The collisions in the gas phase are essential for the generation and the maintenance of the plasma. The gas phase contains electron, ions, neutrals and molecules and ideally one should consider the interactions between all possible pair permutations. However, collisions involving electrons dominate in the plasmas used in the PVD processes [12]. These collisions can be divided in two types namely; elastic and inelastic collision. Elastic collisions involve only the transfer of
kinetic energy, i.e. the internal energy of the colliding particles remains unaffected. The energy that is transferred is determined by the factor \( \gamma = \frac{4M_1M_2}{(M_1 + M_2)^2} \), where \( M_1 \) and \( M_2 \) are the masses of the colliding particles. Thus, a plasma atom or ion remains virtually unaffected, upon the elastic collision with an electron. The electron, on the other hand, changes direction without significant change of velocity, since its mass is much smaller (Figure 2.3).

Figure 2.3. Electron – atom elastic collision (adopted from reference [12]).

All other collisions are inelastic. In this type of collisions there is no restriction regarding the conservation of the kinetic energy, i.e. the internal energies of the colliding particles can also change. The most important of these in sustaining the plasma is the electron impact ionization. In this case a primary electron causes the ejection of an electron from the atom as shown in Figure 2.4 (a). There is an energy threshold for electron impact ionization; the ionization potential of the atom under consideration (e.g. 15.6 eV for Ar [15]). Other ionization processes observed in plasmas occur via ion - neutral and metastable - neutral collisions. In the latter case, ionization occurs if the ionization energy of the atom in the ground state (G) is less than the excitation energy of the metastable atom (A*) according to the process,

\[
A^* + G \rightarrow G^+ + A + e \quad (2.6)
\]

This process is known as penning ionization [16]. The counterpart of the ionization is the recombination, i.e. an electron and an ion coalesce for to form a neutral atom.
Due to the recombination process and the loss of electrons at the chamber walls, an external source for the generation of new electrons is required for the plasma to be sustained. This is role of the negative voltage that is applied to the cathode, as described in section 2.1.2.

A less dramatic transfer of energy to the atoms would cause the bound electron to jump towards a higher energy level. This is the principle of the electron impact excitation, which is depicted in Figure 2.5 (a). The lifetime of the excited states is finite. The electron returns to the ground state and the excess of energy is emitted as photon. This process is known as de-excitation or relaxation (Figure 2.5 (b)). The emitted photons may have energies which correspond to the visible spectral range (1.7 eV – 3.1 eV). As a result of this the plasma glows. In general, detection of the emission energies can provide information about the species present in the plasma, i.e. about the plasma composition. This is the principle of the optical emission spectroscopy, which is described in section 3.2.2.

Figure 2.4. (a) Electron impact ionization and (b) recombination (adopted from reference [12]).

Figure 2.5. (a) Electron impact excitation and (b) relaxation (adopted from reference [12]).
The collision processes described in the current section occur with a certain probability, which is determined by the so-called collision cross-section, which is an energy-dependent quantity [12].

2.1.3.3. Sheath formation at a floating substrate. The plasma is quasi neutral, as mentioned in section 2.1.3.1, i.e. the number of the ions is equal in average to that of the electrons. However, this changes dramatically when the plasma is locally disturbed, e.g. when an electrically isolated (floating) substrate is suspended in the plasma. Initially the substrate is exposed to the flux of charged (electrons and ions) and neutral atoms as shown in Figure 2.6. This flux is equal to $\frac{n\overline{c}}{4}$ [12], where $n$ is the density of the corresponding particles and $\overline{c}$ their average velocity.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig26.png}
\caption{Initial flux of plasma species on a floating substrate.}
\end{figure}

The electrons are much faster than the other plasma species, due to their significantly lower mass. As a result, the floating substrate experiences a much higher electron current density, as compared to the ion current density. This leads to the built up of a negative net charge and hence a negative potential with respect to the plasma. Immediately the random motion of the plasma species is disturbed, since the electrons are repelled by the negative substrate potential. This potential is also referred to as floating potential, $V_f$. The potential of the undisturbed plasma is also called plasma potential, $V_p$, and has the most positive value in the glow discharge. Since the electrons are repelled by the potential difference $|V_p - V_f|$, it follows that the floating substrate acquires a net positive charge around it. This is generally known as space charge and in the context of plasmas it forms a sheath [12]. The electron density in the sheath is lower in comparison to that of the undisturbed plasma. Only electrons with sufficient energy can overcome the barrier $|V_p - V_f|$ and enter into the sheath.
Assuming that the kinetic energy of the electron obeys the Maxwell-Boltzmann distribution, the plasma density in the sheath \( n' \) is equal to [12],

\[
\frac{n'_{e}}{n_{e}} = \exp\left(-\frac{e(V_{p} - V_{f})}{k_{B}T_{e}}\right) \tag{2.7}
\]

Here \( n_{e} \) is the plasma density in the undisturbed plasma and \( T_{e} \) the electron temperature. The potential difference \( V_{p} - V_{f} \) results in a spatial variation of the potential \( \Delta V(x) \) within the sheath which is given by the equation [12],

\[
\Delta V(x) = (V_{p} - V_{f}) \exp(-\frac{x}{\lambda_{D}}) \tag{2.8}
\]

In equation (2.8) \( \lambda_{D} = \left(\frac{k_{B}T_{e}\varepsilon_{0}}{n_{e}e^{2}}\right)^{\frac{1}{2}} \) is the Debye length and \( \varepsilon_{0} \) is the permittivity of the free space [9]. The equation (2.8) is qualitatively plotted in Figure 2.7.

![Figure 2.7. Variation of potential around a perturbation.](image)

The Debye length is a characteristic plasma dimension. According to equation (2.8) any plasma perturbation is reduced to 0.37 \((1/e)\) of its initial value over a distance \( \lambda_{D} \).

Thus, plasma species will practically remain unaffected, if they are located 2 - 3 Debye lengths from the point of the perturbation. Typically \( \lambda_{D} \) is in the order of \( 10^{-4} \) m [12].

2.1.3.4. Dc glow discharges. So far we have been dealing with rather idealized homogeneous plasmas. The dc glow discharges, on the other hand, have a complex structure. Nevertheless, the principles that were presented in the preceding sections can be used for a qualitative description. The voltage distribution in a dc glow discharge is depicted in Figure 2.8. The area between the cathode and the anode has
the most positive potential, i.e. the plasma potential $V_p$. In the vicinity of the two electrodes sheaths are formed, so that the perturbation of the plasma due to the presence of the electric field is restricted in these areas.

![Diagram of voltage distribution in a dc glow discharge](image)

**Figure 2.8.** Voltage distribution in a dc glow discharge (adopted from reference [12]).

Another important issue is the maintenance of the glow discharge. In general, there is loss of electrons due to recombination with ions, at the walls and into the external circuit at the anode. In addition, there is loss of energy due to the impingement of the energetic plasma species on the electrodes and the walls of the chamber and the subsequent heating. The loss of the energy is compensated by the applied electric field. The loss of the electrons, in turn, is compensated by the emission of secondary electrons. This is a general phenomenon which occurs upon the impingement of energetic electrons, ions, and neutrals on the cathode, the anode and the chamber walls [12]. However, in dc glow discharges the main process for emission of secondary electrons is the bombardment of the cathode by positive plasma ions [12]. In the case of secondary electron emission from a clean metal surface two mechanisms exist; the potential and the kinetic emission [17]. The mechanism of potential emission is schematically shown in Figure 2.9 [18-21]. An ion that impinges on the target surface has an electron affinity ($EA_{ion}$) due to his charge. For a singly charged ion $EA_{ion}$ is equal to the ionization potential ($E_i$) of the corresponding neutral atom. When the impinging ion approaches close enough to the target surface, target electrons may tunnel and neutralize the ion. The latter induces an empty state in the electron shell of the target atom (white circle in Figure 2.9), which is subsequently filled by an electron from a higher energy level (red circle in Figure 2.9). This transition is accompanied by emission of a photon with energy $E_{relax}$, equal
to the energy of the electronic transition. If $E_{\text{relax}}$ is higher than the work function ($\Phi$) of the target, a so-called Auger (secondary) electron is emitted. It is evident from this description that potential emission occurs, if the electron affinity (i.e. the ionization potential) of the impinging ion is at least two times higher than the work function of the target. Thus, the emission yield, i.e. the number of the emitted electrons per impinging ion, is independent of the kinetic energy of the ions [18-24] and only depends on the ionization energy $E_i$ of the impinging species and the work function $\Phi$ of the metal surface [22-24].

![Figure 2.9. Potential emission of secondary electron upon the impingement of an ion on a metallic surface.](image)

In the case of the kinetic emission the electrons are ejected via momentum transfer by the impinging ions [17]. The emission yield increases with the energy of the impinging ions [17]. In addition, there is a threshold energy for the activation of this process in the order of $\sim 0.8$ keV [25,26]. The secondary electron emission yield as a function of the energy of the impinging species (ions, as well as neutrals) is presented in Figure 2.10. It is seen that potential emission occurs only for ionized species, while kinetic for both ions and neutrals.
Figure 2.10. Energy dependent secondary electron emission yield of neutrals (A0) and ionized (A+) species impinging on a metallic surface (adopted from reference [17]).

2.1.4. Magnetron sputtering

The dc diode sputtering, described in section 2.1.2, exhibits several drawbacks. The relatively high pressure results in an increased scattering of the sputtered species in the gas phase and thus, a low deposition rate and a poor film quality. In addition, the use of the high target voltage (in the kV range) is energy consuming. Both features lead to a low efficiency of the sputtering process. Moreover, the high cathode voltage has as a consequence the bombardment of the anode by fast electrons, which are repelled from the cathode due to their negative charge. This in turn, causes substantial heating of the growing film; an undesired phenomenon which can crucially affect the obtained film properties. In order to be able to maintain the glow discharge at lower pressures and voltages, an increase of the ionization efficiency is required. The latter can be achieved by combining the existing electric field with a magnetic field. In this case the moving electron experiences a force which is equal to,

$$\vec{F} = -q(\vec{E} + \vec{v} \times \vec{B}) \quad (2.9)$$

Here $\vec{E}$ and $\vec{B}$ are the electric and magnetic field vectors, respectively, $\vec{v}$ the velocity of the electron and $q$ the electron charge. An electron repelled by the negative cathode potential will move helicoidally due to superposition of the electric field force $\vec{F}_e = q\vec{E}$ and the Lorentz force $\vec{F}_L = -q\vec{v} \times \vec{B}$, when $\vec{E}$ lies perpendicular to $\vec{B}$. This situation is schematically depicted in Figure 2.11 and is the operation principle of the
magnetron. Electrons following helicoidal trajectories are confined in the vicinity of the target resulting in an increased ionization. The utilization of magnetrons in sputtering processes led to the magnetron sputtering [1] which is nowadays the most popular physical vapor deposition technique.

![Figure 2.11](image1.png)

**Figure 2.11.** Principle of the magnetron operation (adopted from reference [1]).

The magnetron can be, for instance, technically realized by using two coaxial magnetic rings located at the back side of the target. In the simplest case the strengths of the two rings in the coaxial array are identical. This results in the balanced magnetic field configuration whose lines are mostly located in the target’s vicinity (Figure 2.12 (a)). In 1986 Window and Savvides [27] introduced the unbalanced magnetron. In this case a stronger outer magnetic ring is used, which cannot be compensated by the weaker inner one. As a result, not all the magnetic field lines can be confined at the target area; some of them are extended to the substrate position (Figure 2.12 (b)). The latter enhances the ionization in the substrate vicinity and allows for more intense bombardment of the growing film. As it will be discussed in section 2.2.3 this enables the tailoring of the film properties.

![Figure 2.12](image2.png)

**Figure 2.12.** Magnetic field configuration in an (a) balanced and (b) unbalanced sputtering.

### 2.1.5. Reactive magnetron sputtering

The growth of multicomponent thin films can be achieved in magnetron sputtering, when a compound target is used. This target has to be comprised of the
constituent elements of the material to be deposited. However, in this case the film stoichiometry is confined to values similar to the target composition. Another alternative is the addition of a reactive gas in the sputtering atmosphere. Then, the atoms of the gas react with the sputtered atoms and a compound film is formed on the substrate. This is the principle of the technique known as reactive magnetron sputtering. For instance, when N₂, O₂ and CH₄ are used as reactive gases, metal nitrides, oxides and carbides can be, respectively, deposited. A vast range of film compositions can be obtained by tuning the supply of the reactive gas. Moreover, the change of the composition of the sputtering gas affects also the target stoichiometry (target coverage), since a part of the target’s surface is covered by the same compound. This phenomenon is known as target poisoning. The interactions of the reactive gas with the target and the collecting area of the chamber, i.e. the chamber walls and the substrate have implications on the sputtering process, as shown in Figure 2.13. There the reactive gas partial pressure (Figure 2.13 (a)), the target voltage (Figure 2.13 (b)) and the deposition rate (Figure 2.13 (c)) during the reactive sputtering of Zr-O films at a constant target current are plotted as a function of the O₂ flow [28]. In the low O₂ - flow regime (regime I in Figure 2.13) the reactive gas partial pressure remains low, as the O₂ flow is increased. This can be attributed to the gettering of the reactive gas molecules by the sputtered atoms [29]. This results in a low target coverage and allows for maintenance of the high deposition rates [30]. This sputtering regime is known as the metallic mode and, in this case, results in metallic or understoichiometric oxidic films. The O₂ partial pressure increases abruptly (regime III in Figure 2.13), when the O₂ flow rate exceeds the gettering rate of the reactive gas molecules. This leads to an increase of the target coverage and a drop of the deposition rate. This is a common feature in reactive sputtering and can be explained by the fact that the compounds have in general lower sputtering yields than the corresponding metals [30]. This is explained by the high strength of the covalent/ionic bonds present on the poisoned target surface, as opposed to the metallic bond [30]. This regime is the so - called compound mode and leads to the growth of stoichiometric oxidic films. The transition from the metallic to the compound mode (regime II in Figure 2.13) is frequently abrupt and is often accompanied by a pronounced hysteresis effect. This regime is known as the transition mode. It is also evident from Figure 2.13 (b) that the transition from the metallic to the compound mode has implications on the target voltage. The increase observed in the particular
case of Zr-O is indicative of an increase of the plasma impedance, since the same target current has to be maintained. The latter is explained as being the effect of the lower secondary electron emission yield of the oxide in comparison to the corresponding metal [31]. This is a common feature for the oxides and nitrides of the IVb to VIb transition metal groups [32]. Some other oxides, such as Al₂O₃ [33] and ZnO [34] exhibit a decrease of the target voltage upon transition to the compound mode, which is indicative of a higher secondary electron emission yield, with respect to the corresponding metals. The reason for the peculiar behavior of the secondary electron emission among the various oxides in not yet fully understood. Recent studies by Wittmaack [35] and Depla et al. [36] suggested that differences in the oxidation state of O on the covered target surface may be an explanation.

![Figure 2.13](image.png)

**Figure 2.13.** The effect of the O₂ flow on the (a) O₂ partial pressure, (b) target voltage and (c) deposition rate during the reactive sputtering of Zr-O films at a constant target current (adopted from reference [28]).

### 2.1.6. High power pulsed magnetron sputtering

A special feature of the plasma-based deposition techniques is the bombardment of the growing film by energetic species. This in turn, provides means for tailoring the film properties. Among the various bombarding species, gas and target ions are of particular importance since their energy and trajectories can be altered, when
appropriate electric and/or magnetic fields are utilized. The effect of the ionized plasma species becomes more pronounced as the ion-to-neutral ratio is increased. An increase of ion-to-neutral ratio is achieved by increasing the ionization probability, i.e. by increasing the plasma (electron) density. High plasma densities can be realized by increasing the power applied to the magnetron. In a dc magnetron sputtering process the maximum power is limited by the thermal load which can be delivered on the target. In order to utilize the advantages of the high power, while maintaining a low average power, a new pulsed sputtering deposition technique has been recently introduced [37]: the High Power Pulsed Magnetron Sputtering (HPPMS) [38]. In HPPMS, the power (or the voltage) is supplied to the target in unipolar pulses of low duty cycle (1 % - 10 %) and frequency (0.1 kHz - 2 kHz), as schematically shown in Figure 2.14. This results in high peak target power densities [37], which in turn, lead to the generation of ultra dense plasmas [39] and a high degree of ionization of the sputtered material [37]. HPPMS attractiveness lies in that it provides means for depositing dense and smooth metallic [40] and compound [41,42] films on flat and complex-shaped substrates [40]. HPPMS has also been shown to enhance the adhesion of coatings as a result of the increased metal ion bombardment and implantation [43]. Other areas where HPPMS has been shown to have an advantage compared to conventional techniques are phase tailoring [44-46], and enhancement of film conductivity [44]. Although HPPMS has been shown to be a promising deposition technique, the deposition rate has, since the emergence of this technique, been a point of debate and discussion. In particular, it was shown in a number of papers [41,42,47,48] that the deposition rate for metals is 20 % to 80 % of the rate measured for dcMS deposition.

![Figure 2.14](image-url) Schematic representation of the target voltage during HPPMS. The $t_{on}$ and $t_{off}$ stand for the pulse on - and off – time, respectively.
2.2. Atomistic mechanisms during thin film formation

In section 2.1 the fundamentals and the technical realization of the sputtering process were presented. The sputtering leads to thin film formation and growth by deposition and condensation of atoms from the vapor phase on a substrate. This process is roughly divided in two stages: (i) the early stages of the film deposition, where two-dimensional clusters of atoms (nuclei) are formed and (ii) the growth of the two-dimensional cluster to a continuous film. The atomistic mechanisms involved during these stages are discussed in the current section.

2.2.1. Early stages of thin film formation

The early stages of thin film formation are depicted in Figure 2.15. These include the arrival and accommodation of atoms on the substrate (condensation), their migration along the substrate’s surface (diffusion) and their incorporation into stable two-dimensional clusters of condensed atoms (nucleation). In the following sections these issues are discussed in detail.

![Figure 2.15. Early stages of thin film formation: (a) condensation, (b) surface diffusion and (c) nucleation.](image)

2.2.1.1. Condensation of the impinging atoms. The condensation of the atoms impinging from the vapor phase on the substrate proceeds through dissipation of their initial kinetic energy \(E_{\text{kin}}\) into vibrations of the substrate lattice (phonons). In particular, vapor atoms experience the attractive potential of the surface atoms as they approach the substrate. They gain, thus, energy which is in the order of magnitude of the cohesive energy of the substrate material [49]. The total kinetic energy of an
arriving atom has to be reduced by dissipative mechanisms to a value lower than its adsorption energy ($E_{ad}$), in order for the atom to stick on the surface and not be reflected back to the vapor phase (re-evaporation). The probability for the reduction of the total kinetic energy below the adsorption energy is called sticking coefficient. Theoretical investigations of this problem [50-53] have shown that for nearly equal masses of the impinging atoms and the substrate lattice atoms and for kinetic energies up to 25 times the adsorption energy a unity sticking coefficient should be expected. Sticking coefficients considerably lower than unity are obtained, when lighter atoms or higher substrate temperatures are considered. The residence time of an atom before it re-evaporates is given by the equation [54],

$$\tau_s = \frac{1}{v_0} \exp\left(\frac{E_{ad}}{k_BT}\right) \quad (2.10)$$

Here $v_0$ is the so-called attempt or adatom-surface vibrational frequency, which depends on the adatom-surface combination, and $k_B$ denotes the Boltzmann’s constant. For a given adatom-surface combination large $\tau_s$ values and thus high sticking coefficients are obtained, when $E_{ad} >> k_BT$.

2.2.1.2. Surface diffusion. The surface diffusion is a decisive process at the early stages of film formation, since it provides the mechanisms for the migration of the adatoms to positions which promote the film nucleation and growth. Surface diffusion can be understood as a two-dimensional random walk, during which an adatom jumps from one potential well of the surface to another. The mean square diffusion length of an adatom during its residence time $\tau_s$ can be calculated by the relation [49,54],

$$<\bar{x}^2> = 4D\tau_s \quad (2.11)$$

Here $D$ denotes the surface diffusion coefficient and it is given as,

$$D = \frac{1}{4} l^2 v \quad (2.12)$$

where $l^2$ is the mean square distance covered at a single jump and $v$ the jump rate. Finally, $v$ is given by the equation,

$$v = v_0 \exp\left(-\frac{E_d}{k_BT}\right) \quad (2.13)$$

In equation (2.13) $E_d$ denotes the energy barrier for surface diffusion. It is evident that the surface diffusion depends on the quantities $v_0$ and $E_d$ and it is a thermally
activation processes. These two quantities can be determined both theoretically [55-58] and experimentally [61-63].

2.2.1.3. Nucleation. The basic atomistic mechanisms during nucleation are depicted in Figure 2.16. Atoms which impinge on a substrate form aggregates (nuclei), which either tend to grow in size or dissociate. For a relatively low density of aggregates the growth takes place via surface diffusion of the adatoms.

![Figure 2.16. Atomistic mechanisms during nucleation (adopted from reference [1]).](image)

In a first order approximation the process illustrated in Figure 2.16 can be treated thermodynamically [64]. The change in the total free energy upon formation of a cap-shaped nucleus with a mean size \( r \) is given by,

\[
\Delta G = a_1 r^3 \Delta G_V + a_2 r^2 \gamma_{sf} + a_3 r^2 \gamma_{fs} - a_4 r^2 \gamma_{sv} \tag{2.14}
\]

Here \( \gamma \) is the interfacial energies, while the indices \( v, f, \) and \( s \) stand for the vapor, the film and the substrate, respectively. The quantity \( \Delta G_V \) is the change of the Gibb’s free energy due to the gas-solid transformation. Supersaturation in the vapor phase leads to a negative \( \Delta G_V \) value and it is the driving force for nucleation [1]. Finally, the pre-factors \( a_1, a_2 \) and \( a_3 \) are geometrical constants which are determined by the nucleus-substrate wetting angle \( \theta \) (Figure 2.16). It is evident from equation (2.14) that the formation of a nuclei influences \( \Delta G \) in complex way. The creation of a vapor-film interface results in an increase of the free energy, while loss of the substrate-vapor interface has a negative contribution. The overall dependence of \( \Delta G \) on the nucleus size \( r \) is plotted in Figure 2.17.
Figure 2.17. Dependence on the free energy $\Delta G$ on the nucleus size $r$ (adopted from reference [1]).

The critical nucleus size $r^*$, i.e. the value of $r$ at which $\frac{\partial \Delta G}{\partial r} = 0$ is equal to,

$$r^* = \frac{-2(a_1\gamma_{sf} + a_2\gamma_{fr} - a_2\gamma_{sf})}{3a_3 \Delta G_v} \quad (2.15)$$

and the corresponding $\Delta G$ at $r = r^*$ is,

$$\Delta G^* = \frac{4(a_1\gamma_{sf} + a_2\gamma_{fr} - a_2\gamma_{sf})^3}{27a_3^2 \Delta G_v^2} \quad (2.16)$$

The minimization of the total free energy (Figure 2.17) requires that nuclei with size $r < r^*$ dissociate, while those with $r > r^*$ grow.

Another quantity which is characteristic of the process is the nucleation rate, i.e. the number of stable nuclei formed on the substrate per unit time. It can be shown that the nucleation rate, $\dot{N}$, is equal to [1],

$$\dot{N} = 2\pi r^* a_0 \sin \theta \frac{PN_A}{\sqrt{2\pi MRT}} n_s \exp \left( \frac{E_{ad} - E_d - \Delta G^*}{k_B T} \right) \quad (2.17)$$

The new quantities introduced in equation (2.17) is the pressure of the vapor $P$, the mass of the impinging atoms $M$, the temperature $T$ and the total density of nucleation sites $n_s$. The quantities $E_{ad}$ and $E_d$ have already defined in equations (2.10) and (2.13). It is evident from equation (2.17) that the nucleation rate is a strong function of the nucleation energetics, which is largely contained in term $\Delta G^*$. For a given substrate-film combination, the latter depends on the change of the Gibb’s free energy $\Delta G_v$ and, therefore on the supersaturation and the growth temperature. As a rule of thumb
high nucleation rates encourage the formation of a fined grain or even amorphous structure, while a coarse-gain deposit develops at low values of $N$. However, the growth conditions affect not only the nucleation rate but also the individual nuclei. It is convenient to express this dependence by investigating the effect of the deposition rate $R$ and the growth temperature $T$ on the critical nuclei size $r^*$ and the critical free energy $\Delta G^*$. It is also important to express the change of the Gibb’s free energy due to the gas-solid transformation, $\Delta G_V$, in terms these two quantities [1],

$$\Delta G_V = -\frac{k_B T}{\Omega} \ln \left( \frac{\hat{\kappa}_c}{\hat{\kappa}_r} \right) \quad (2.18)$$

Here $\hat{\kappa}_c$ is the equilibrium evaporation rate from the film nucleus at a temperature $T$ and $\Omega$ the atomic volume. It is worth noting that the nucleation occurs if $\Delta G_V < 0$, which requires that $\hat{\kappa}_c > \hat{\kappa}_r$. By substituting equation (2.18) into equations (2.15) and (2.16), the following relations can be derived [1],

$$\left( \frac{\partial r^*}{\partial T} \right)_{\hat{\kappa}} > 0 \quad (2.19)$$

$$\left( \frac{\partial \Delta G^*}{\partial T} \right)_{\hat{\kappa}} > 0 \quad (2.20)$$

$$\left( \frac{\partial r^*}{\partial \hat{\kappa}_c} \right)_{T} < 0 \quad (2.21)$$

$$\left( \frac{\partial \Delta G^*}{\partial \hat{\kappa}_c} \right)_{T} < 0 \quad (2.22)$$

The relations (2.19) - (2.22) summarize in a nutshell the general trends in thin film deposition and growth. An increase in the growth temperature and a decrease in the deposition rate results in higher $r^*$ and $\Delta G^*$ values. A practical implication of this is that a continuous film takes longer to develop at relatively high temperatures and low deposition rates. In addition, if one associates $r^*$ and $\Delta G^*$ with the crystal size in the continuous film (this issue in discussed in detail in section 2.2.2) low deposition rates and high temperatures lead to the formation of large crystallites or even single crystals.

Despite the qualitative utility of the thermodynamic nucleation theory, its quantitative correctness is poor, when film growth far from equilibrium is considered.
In a more realistic approach one should describe the role of the individual atoms on the nucleation process. This is the concept of the atomistic nucleation theory [65-69]. In the classical approach the rate equations for the areal concentrations of nuclei with \( s \) atoms \( (n_s) \) are considered,

\[
\frac{dn_s}{dt} = \Gamma_{s-1} - \Gamma_s \quad (2.23)
\]

Here \( \Gamma_s \) is the net rate at which \( s+1 \) - nuclei are formed from \( s \) - nuclei and is equal to,

\[
\Gamma_s = \sigma_s D n_s \gamma_{s+1} n_{s+1} \quad (2.24)
\]

where \( \gamma \) is the detachment rate of the adatoms from an \( s \) - nucleus, \( D \) the surface diffusion coefficient and \( \sigma \) is a dimensionless factor that accounts for the propensity of an \( s \) - nucleus to attach an adatom. The equations chain (2.24) is fed by the adatom density,

\[
\frac{dn_1}{dt} = \hat{\Phi} - 2\Gamma_1 - \sum_{s=2}^{\infty} \Gamma_s \quad (2.25)
\]

where \( \hat{\Phi} \) is the deposition rate. In addition, the total density of stable nuclei \( N \) is defined as,

\[
N = \sum_{s=1}^{\infty} n_s \quad (2.26)
\]

If it is assumed that nuclei with size \( s \geq i^*+1 \) (where \( i^* \) is the critical nucleus size) do not decay, while nuclei with \( s \leq i^* \) are unstable, the solution of equations (2.23) - (2.26) deliver the nucleation density \( N \). The most important feature of this solution is that [49],

\[
N \sim \left( \frac{\hat{\Phi}}{D} \right)^x \quad (2.27)
\]

where \( x \) a scaling factor which depends on the nucleus critical size \( i^* \). The equation (2.27) results in the same qualitative trends, as the relations (2.19) - (2.22). However, equation (2.27) contains information about the kinetics of the nucleation process.

The growth of the two dimensional nuclei is of significant importance for the microstructure of the continuous film. Based on the above presented thermodynamic approach, three characteristic growth modes, in the case of epitaxial growth, have been established [70]. The term epitaxy is used here, in order to describe the growth of a crystalline film on a crystalline substrate, where the crystalline orientation imposes an order on the orientation of the deposited film [64,71]. With reference to
When $\gamma_s < \gamma_f + \gamma_{vf}$, the energy balance requires minimization of the area covered by the nucleus. This will cause the nuclei to grow in form of three dimensional islands. This is also called Volmer - Weber growth (Figure 2.18 (a)). When $\gamma_s > \gamma_f + \gamma_{vf}$, the area covered by the nucleus should be minimized. This leads the nuclei to grow smoothly forming one layer a time. In general, the growing layers will be strained due to the different lattice constant between film and substrate. After a few layers the increase of the interfacial stain energy $\gamma_f$ will break the condition for layer - by - layer growth giving rise to island growth. This scenario is known as Stranski - Krastanov growth mode (Figure 2.18 (c)). Finally, in the ideal case of homoepitaxy (i.e. growth of a film on a substrate of the same material and orientation) $\gamma_s = \gamma_f + \gamma_{vf}$. This results in a non - interrupted layer - by - layer growth (Frank - van der - Merwe growth - Figure 2.18 (b)).

In the case of films grown non - epitaxially and far from equilibrium (which is most likely for sputter deposited films) the above classification is not valid. Three - dimensional growth features are frequently observed which are, however, predominantly kinetically controlled and give rise to the formation of polycrystalline films.

Figure 2.18. Growth modes in epitaxial films.
2.2.2. Film growth

The formation of the three dimensional (3D) islands on a substrate lead to the growth of a polycrystalline film. The main growth stages are schematically depicted in Figure 2.19. It is seen that the 3D islands start to grow (Figure 2.19 (a)) until they impinge and coalesce with neighboring 3D islands. (Figure 2.19 (b)). This leads to the formation of polycrystalline islands and channels (Figure 2.19 (c)) and finally, to a continuous film (Figure 2.19 (d)).

![Figure 2.19](image)

*Figure 2.19.* Growth stages of polycrystalline thin films adopted from reference [72]. (a) island growth, (b) island coalescence, (c) formation of polycrystalline islands and channels and (d) growth of continuous film.

In all growth stages illustrated in Figure 2.19 the same atomistic mechanisms are involved; the so-called fundamental structure forming phenomena [73]. These are,

- **The nucleation.** The nucleation is observed in the early stages of thin film formation (primary nucleation), as mentioned in section 2.2.1, or later on a bare film developing upon liquid like coalescence of the islands (secondary nucleation) [73]. Moreover, in the post-coalescence growth stages nucleation occurs locally on the surface of a growing crystal, when the growth is blocked by a covering layer of an impurity phase [73]. This is often referred to as repeated nucleation [74].

- **The crystal growth.** During crystal growth the deposited material is incorporated in the condensed phase. In the case of polycrystalline films two crystal growth processes are observed; (i) growth of discrete crystals dispersed on the substrate surface (island growth) and (ii) growth of crystals which are part of a polycrystalline structure.
The grain growth. In the course of the growth of polycrystalline films two types of grain growth can occur when the grain boundary (GB) mobility has a considerable value; (i) grain growth during the coalescence of the islands and (ii) grain growth via repeated nucleation (referred to as abnormal grain growth).

By considering the dependence of the fundamental structure forming phenomena on the growth conditions, the structural zone models (SZM) for the growth of thin films have been constructed. In the case of physical vapor deposited pure elemental films the microstructure and the growth evolution of the films are classified in terms of the homologous temperature \( \frac{T_s}{T_m} \) [75-81]. Here \( T_s \) is the substrate temperature and \( T_m \) the melting point of the material to be deposited. In general, three \( \frac{T_s}{T_m} \) zones are observed (Figure 2.20, [75]):

- **Zone I** (0 < \( \frac{T_s}{T_m} \) < 0.2). The basic feature for the growth in zone I is the limited adatom mobility. Thus, the lateral grain size is determined by the nucleation density, while the columns preserve the orientation of the initial nuclei. The latter can be predicted by the ballistic deposition models [82,83]. These features result in films with an underdense structure, a weak texture and a roughness which develops with fractal geometry [84].

- **Zone T** (0.2 < \( \frac{T_s}{T_m} \) < 0.4). The film growth in this regime is controlled by the adatom surface diffusion. The growth and the coalescence of small islands leads to grain coarsening, while the GB’s are immobile when a continuous film is formed. During the grain coarsening the orientation selection is incomplete giving rise to weakly textured films at relatively small film thicknesses. The adatom surface diffusion enables local epitaxial growth in the individual grains. On the other hand, anisotropies in the diffusivity determine the dominant orientation [85]. Grains with orientations which exhibit lower surface diffusivity, i.e. higher residence time of the adatoms, grow at the expense of grains with higher surface diffusivity. The dominant grains are observed as V - shaped columns which overgrow kinetically disadvantaged grains as the film thickness increases. This in turn enhances the preferred
orientation. In addition, the surface roughness increases with the film thickness giving rise to open column boundaries.

- **Zone II** ($\frac{T_s}{T_m} > 0.4$). In this temperature regime the bulk diffusion is significant.

This results in GB migration not only during the coalescence state but also during the film thickening. The orientation selection during the coalescence is more pronounced, in comparison to that in Zone $T$, and it is driven by the decrease of the total GB area, as well as the minimization of the interface and surface energy [86]. Secondary nucleation can also take place leading to further enhancement of the preferred orientation. The films grown in this zone exhibit homogenous structure in the growth direction and are composed of columnar crystals with flat surfaces decorated by GB grooves.

![Figure 2.20](image)

**Figure 2.20.** Structural zone model of pure elemental films as a function of the homologous temperature $\frac{T_s}{T_m}$ and the film thickness (adopted from reference [73]).

In the particular case of pure elemental films grown by magnetron sputtering Thorton [87] added an additional parameter to the SZM; the pressure of the sputtering gas. This parameter was used in order to describe the effect of the energetic bombardment; an inherent property of the sputtering process. The model proposed by Thorton predicts that the decrease of the sputtering pressure will shift the transition from zone $I$ to zone $T$ or from zone $T$ to zone $II$ to lower $\frac{T_s}{T_m}$ values due to the increase of the energy transferred to the film by the energetic plasma species.

The extension of SZM’s in the case of multicomponent and/or multiphase films provides means for understanding the film growth in reactive deposition processes,
e.g. in reactive magnetron sputtering. The construction of a SZM for reactively deposited polycrystalline films requires, similarly to the pure elemental films, the determination of the dependence of the fundamental structure forming phenomena on the growth conditions. In this case, apart from the substrate homologous temperature \( T_s \), an additional deposition parameter should be considered; the concentration of the contaminant species and their effect on the fundamental structure forming phenomena [73]. It should be pointed out here, that the term “contaminant species” does not only imply the impurities, which unintentionally contaminate the growing film, but also atoms of a reactive gas or a second element, which are incorporated in the host material for the formation of the compound or the second phase, respectively. Contaminant species impinging on the growing films can be adsorbed and segregated on the growing crystal faces or dissolved in the crystal lattice [88-90]. Experimental results have shown that active contaminant species can either promote or inhibit the operation of the fundamental structure forming phenomena [91,92]. A representative example is the growth of O-containing Al films at room temperature. This \( T_s \) value corresponds to the zone II in the pure Al-SZM [93]. The effect of the O concentration on the microstructure of the growing film is summarized in Figure 2.21 [73]. Oxygen has in general low solubility in the Al lattice and segregates on the surface and at the GB’s. At these sites 2-dimensional oxide layers are formed, which inhibit the surface diffusion and the GB migration. At low O/Al arrival rate ratios \( (J_O/J_{Al} \sim 10^{-3}) \) O is accumulated at the GB’s inhibiting the GB migration. This gives rise to zone II films with a worse texture, compared to the pure Al films (Figure 2.21 (a) and (b)). At higher O concentrations \( (J_O/J_{Al} \sim 10^{-2}) \) the coarsening during the coalescence is partially suppressed leading to randomly oriented grain, i.e. zone T films (Figure 2.21 (c)). An oxygen concentration in the range of \( J_O/J_{Al} \sim 0.1 – 1 \) leads formation of oxide layer on islands of all possible orientation. This in turn leads to a periodical interruption of the growth grain and secondary nucleation, which gives rise to nanosized grains (Figure 2.21 (d)). This microstructure is also referred to as zone - III structure and is also predicted by the SZM’s models for elemental films, when growth temperatures close to the melting point of the deposited film are utilized [75]. Finally, when the O atoms are the majority of the deposited species \( (J_O/J_{Al} \sim 2 - 5) \) the film consists mainly of aluminum oxide which is an amorphous material at room temperature (Figure 2.21 (e)).
2.2.3. **Effect of energetic species on the growing film during sputtering**

An inherent property of the sputtering processes is the bombardment of the growing film by energetic plasma species. These species can be positive and negative ions, as well as neutrals [1]. The effect of a species on the growing film depends on its energy and its flux. In particular, the energy determines the nature of the interactions between the film and the bombarding species [4]. The energetic species - film interactions and their energy ranges are illustrated in Figure 2.22. It is seen that the energy spans over five orders of magnitude. In fact, the exact energy values depend on extrinsic factors, such as the material and the surface condition of the growing film, as well as the growth conditions. However, five energy regimes can be
considered in general [4]. Species with energies below 0.1 eV are thermalized and do not affect the growing film. The lower limit for activation of surface processes is at 0.1 eV, where physisorption of bombarding species is possible. An order of magnitude higher, at 1 eV, is the onset for the chemisorption. The typical energy values, above which the surface characteristics of the films are affected, is in the range of tenths of electronvolts. Finally, bombarding species with energies in the range of hundreds of electronvolts are able to influence the bulk of the growing film.

The surface and the bulk effects are the most important for the thin film science, since they provide additional means for tailoring film properties. In the energy range of the surface effects, the energetic bombardment can affect both film nucleation and growth [4,72]. An important feature of the energetic bombardment in this energy regime is the enhancement of the adatom mobility. The latter can be achieved by (i) direct transfer of kinetic energy to single adatoms or clusters by the bombarding species, (ii) bombardment induced phonons which are coupled to an adatom and (iii) shallow collision cascade which affects an adatom [4]. The effect of the bombardment - induced adatom mobility has been demonstrated in the case of transition metal nitride films [94-99]. It has been shown that the increase of the flux [94-98] and of the energy [99] of the bombarding species lead to smoother film surfaces and change of the preferred orientation from (111) to (100) orientation. In addition, the microstructure of the films is also affected. Films grown at low energetic bombardment exhibit a columnar structure with inter- and intracolumnar voids [100] (Zone I in SZM). An increase of the energy and the flux of the energetic species lead to a zone T microstructure [94].

![Figure 2.22](image.png)

**Figure 2.22.** Energy range of the interactions of energetic species with thin films.

A further increase of the bombarding energy leads to implantation of the energetic species at the subsurface side of the growing film which gives rise to bulk effects [4].
These effects are depicted in Figure 2.23. Implantation often creates lattices defects, such as displacement of lattice atoms to interstitial positions and vacancy formation. These phenomena lead to the generation of residual compressive stresses in the thin film, as discussed in detail in section 2.2.4. In some cases, the implantation can also cause a collision cascade, which in turn results in sputtering, i.e. resputtering, or affects the film surface by creation of mobile adatoms. Moreover, highly energetic charged species can also penetrate deep in the growing film. This is the so-called channeling mechanism. In this case the ballistic damage is significantly reduced and the bombarding species loose energy via electronic excitations. Not all the energetic species are implanted in the film. Some of them are backscattered. In particular, when these species are ionized the backscattering is accompanied by neutralization [101]. Finally, the interactions of the bombarding species with the film surface can lead to electron and photon emission.

![Diagram of bulk effects](image)

**Figure 2.23.** Bulk effects during energetic bombardment of a growing film.

The energetic bombardment in the energy regime of the bulk effects has also been shown to have implications on the microstructure of transition metal nitride films, grown by reactive magnetron sputtering [72]. In the particular case of TiN films [102-106], it has been reported that an increase in the energy of the implanted species leads to film densification, while the preferred orientation can be tailored. For even higher energies (typically > 400 eV) interruption of the individual grain growth and renucleation takes place [72]. However, in all these cases the films exhibit a high density of lattices defects and compressive stresses [102,104,105], while significant incorporation of inert gas atoms is observed [106].
2.2.4. Generation and evolution of residual stresses in thin films

Thin films grown epitaxially, forming perfect single crystals on substrates with identical lattice constant are free of stresses. However, this growth mode is extremely unlikely for physical vapor deposited films, as discussed in the preceding sections. The real films grow far from thermodynamic equilibrium, while the growth is predominantly kinetically controlled. In addition, the growing films frequently experience an intense energetic bombardment. These features result in films with high defect density leading to residual stresses. The residual stresses are often responsible for malfunction of thin-film devices. For instance, high residual stresses can lead to films peeling off and cracking, as well as in a change of the film properties. In general, the residual stresses can be tensile and compressive. Conventionally the tensile stresses are considered to be positive, while the compressive stresses are considered to be negative. The residual stresses are generated as a result of the requirement for the maintenance of mechanical equilibrium (net force and bending moment) between thin film and substrate, when the in-plane dimensions of the film change (in-plane strain) [1]. The sequence of event that leads to the generation of tensile and compressive stresses in thin film/substrate systems is schematically depicted in Figure 2.24 (a) and (b), respectively.

![Figure 2.24](image)

**Figure 2.24.** Sequence of events which leads to generation of (a) tensile and (b) compressive stresses in thin films (adopted from reference [1]).

Film shrinkage leads to tension in the film due to its compatibility to the substrate. The substrate contraction, in turn, leads to compression of the substrate. To achieve equilibrium in the bending moments the film/substrate system is bent concavely upward, as shown in Figure 2.24 (a). Similarly, film expansion leads to
compression of the film and downward convex bending of the film/substrate system (Figure 2.24 (b)). It is noteworthy that this model is general, regardless of the mechanism which leads to the expansion or shrinkage of the film.

The mechanisms which cause film strain and thus, lead to generation of residual stresses can act (i) in the film and (ii) at the film/substrate interface [107]. In the followings these mechanisms are briefly presented. It should be pointed out here that this discussion refers to polycrystalline films in the post-coalescence growth stages (section 2.2.2).

2.2.4.1. Stress generation in the film. In polycrystalline films the grain boundaries (GB) can be a source of tensile stresses. This issue was first introduced and described by the grain boundary relaxation model proposed by Hoffman [108]. According to this model the individual grains interact in order to close any existing gap. This leads the GB’s to shrinkage which in turn causes tensile stresses. The magnitude of the tensile stresses induced by the shrinkage of the GB’s can be calculated by the equation [108],

\[ \sigma_{GB} = \frac{E_f}{1-v_f} \frac{D}{L_g} \] (2.28)

Here \( E_f \) and \( v_f \) is the elastic modulus and the Poisson’s ratio of the film, respectively, \( L_g \) the grain size and \( D \) the grain boundary relaxation distance. In a similar way, shrinkage of the film volume due to recrystallization, phase transformations and defect annihilation also causes tensile stresses [109].

Compressive stresses are generated in the film due to the expansion of the crystal lattice. In ionized physical vapor deposited films, the lattice expansion is caused by direct implantation of bombarding species in the film or by displacement of film atoms to interstitial positions caused by the energetic bombardment, as explained in section 2.2.3. A correlation between the bombardment conditions, i.e. energy and flux of bombarding species, and the resulting compressive stresses is manifested in the models proposed by Windischmann [103,110] and Davis [105]. These models are based on three assumptions [111]: (i) displacement of atoms to interstitial positions is a result of forward sputtering by the energetic species, (ii) the mass transport and the defect mobility in films grown at low temperature is sufficiently low to freeze the volumetric distortion caused by the displacement of the atoms, (iii) the volumetric
distortion is proportional to the fraction of atoms that are displaced from equilibrium position. The formalization developed by Windischmann [110] led to the following expression for the compressive stresses,

$$\sigma_{\text{exp}} \propto F_p \sqrt{E_p Q} \quad (2.29)$$

where $F_p$ and $E_p$ is the flux and the energy of the bombarding species, respectively. The term $Q$ represents the elastic energy stored due to the volumetric distortion. The equation (2.29) implies that the volumetric distortion caused by the displacement of lattice atoms is proportional to the square root of the energy ($\sqrt{E_p}$), i.e. the stress generation is a momentum transfer process. An additional effect, which is frequently observed, is the relaxation of the compressive stresses, when the energy and/or the flux of the bombarding species are high [105]. This is caused by the intense local heating of the film ("referred to as thermal spike" [112]), which provides the energy for the implanted and displaced atoms to move from their metastable positions towards the film surface (outdiffusion). The number of atoms, $n_a$, which are set in motion by a thermal spike has been calculated by Seitz and Köhler to be [113],

$$n_a \propto \left(\frac{E_p}{E_a}\right)^{3/2} \quad (2.30)$$

where $E_a$ is the activation energy required for the motion of atoms from their metastable positions. Based on this considerations Davis [102] suggested the following equation for the compressive stresses in thin films,

$$\sigma_{\text{exp}} \propto \frac{\sqrt{E_p}}{F_i / F_p + k_a (E_p)^{3/2}} \quad (2.31)$$

Additional quantities in equation (2.31), in comparison to equation (2.29) is the flux of the atoms condensed on the film’s surface ($F_i$), as well as the term $k_a$, which is related to the energy barrier $E_a$. 

In summary, it is evident that the sign of residual stresses in the film depends on the energy transferred to the adatoms. Three energy regimes can be ideally considered (Figure 2.25 [111]): (i) low energy regime (0.1 - 1 eV/at) where tensile stresses due to GB shrinkage are dominant, (ii) moderate energy regime (1 - 20 eV/at) where a transition from tensile to compressive stresses takes place due the implantation and atom displacement and (iii) high energy regime (>25 eV/at) where stress relaxation due to thermal spikes is observed.
2.2.4.2. Stress generation at the substrate/film interface. The substrate/film interface contributes to the residual stresses of the film, when the film is deposited at a temperature different than the ambient/operation temperature. This is the so called thermal stress \([111]\) which is calculated by the equation,

\[
\sigma_{th} = \frac{E_f}{1-v_f}(a_s - a_f)\Delta T \quad (2.32)
\]

where \(\Delta T = T_a - T_d\) is the difference between deposition \((T_d)\) and ambient temperature \((T_a)\), \(a_s\) and \(a_f\) the thermal expansion coefficients of the substrate and the film. Depending on the sign of the term \(\Delta T\) and the difference of the thermal expansion coefficients the thermal stresses can be either tensile or compressive.
3. Analytical methods and experimental facilities

3.1. The sputter deposition setup

The film growth in this work was carried out in a home made magnetron sputtering deposition setup which is shown in Figure 3.1. This deposition setup is a cylindrical stainless-steel deposition chamber. It is evacuated by an Alcatel pumping system that consists of a turbo-molecular pump connected to a membrane pump. Moreover, a baking belt that enables to heat up the chamber up to a temperature of ~80 °C is used for outgassing. The combination of the pumps and the backing belt enables to achieve base pressures ($p_b$) in the order of $10^{-6}$ mbar. The chamber can be equipped with up to 6 cathodes. The substrate holder is a rotating metallic plate that allows for simultaneous loading of 24 substrates with maximum size of 76 x 24 mm. A shutter is located between the substrate holder and the target. This is a metallic plate with a single 24 x 76 mm hole that is put above the center of the target. The rotation of the substrate holder enables the sequential exposure of the 24 substrate positions to the target. For the depositions in the dc magnetron sputtering mode (chapter 4) the power was supplied to the target by an ELAN dc generator. In high power pulsed magnetron sputtering depositions (chapter 5 and 6) an Advanced Energy Pinnacle dc power supply coupled to a Melec SPIK 2000A pulsing unit [114] was used (Figure 3.2). The dc power supply enables the independent control of the average values of target current and power and allows for operation either at a constant current or at a constant power mode. The pulsing unit supplies unipolar pulses with minimum on- and off-time of 25 µs and can support peak target currents up to 200 A. The experimental setup in Figure 3.2 is also equipped with a LEM LA205-S current transducer and a LEM CV3-1500 voltage transducer, which are used to measure the target current and voltage, respectively. A TDS 2014 digital oscilloscope is used as a monitoring device. An additional feature of the pulsing unit is the rectangular voltage pulsed, i.e. the target voltage is constant throughout the pulse on-time, as shown in Figure 3.3.
Figure 3.1. The magnetron sputtering deposition setup.

Figure 3.2. The Advanced Energy Pinnacle dc power supply coupled to the Melec SPIK 2000A pulsing unit.
3.2. Plasma characterization

The properties of the glow discharge (plasma) crucially affect the growing film and are correlated with a number of process parameters, such as the target power, the working pressure and the composition of the sputtering gas. Thus, the plasma characterization is of utmost importance in order to unravel the influence of the deposition conditions on the film. In this section two methods which are widely employed for plasma diagnostics are presented; the electrostatic probe measurements and the optical emission spectroscopy.

3.2.1. Electrostatic probe measurements

The electrostatic probes are used to measure the electrical characteristics of the glow discharge. A dc voltage \( V \), which spans from negative to positive values, is applied to the probe and the induced probe current \( I \) is recorded. A typical probe current - voltage \( (I - V) \) curve is shown in Figure 3.4 [115]. The application of a high negative voltage leads to suppression of the electron current to the probe, while the positively charge plasma ions are only attracted. In this case the ion saturation current, \( I_{si} \), is measured. On the other hand, when a high positive voltage is applied to the probe the electron saturation current, \( I_{se} \), is obtained. As mentioned in section 2.1.3.3 \( I_{se} \) is by several orders of magnitude higher than \( I_{si} \) [12].
The analysis of the probe $I - V$ curve enables the determination of plasma-relevant quantities [116]. The floating potential $V_f$ is equal to the voltage at which $I = 0$. In addition, the plasma potential $V_p$ is determined by the equation,

$$\frac{d^2 I_e}{dV^2} = 0 \quad (3.1)$$

The electron energy (speed) distribution function (EEDF) can be calculated as,

$$g_e(V) = \frac{2m}{e^2 A_{pr}} \left( \frac{2eV}{m} \right)^{\frac{1}{2}} \frac{d^2 I_e}{dV^2} \quad (3.2)$$

Here $m$ is the electron mass, $A_{pr}$ the probe collecting area and $V = V_p - V_{pr}$ is the potential difference between plasma and probe. The electron density can be then determined as,

$$n_e = \int_0^{\infty} g_e(\varepsilon)d\varepsilon \quad (3.3)$$

where $\varepsilon$ is the potential difference $V$ multiplied by the elementary charge $e$. Finally, the mean electron energy and the corresponding mean (effective) electron temperature are obtained by the respective equations,

$$\langle \varepsilon \rangle = \frac{1}{n_e} \int_0^{\infty} \varepsilon g_e(\varepsilon)d\varepsilon \quad (3.4)$$

$$k_B T_{\text{eff}} = \frac{3}{2} \langle \varepsilon \rangle \quad (3.5)$$

Despite the conceptual simplicity of the electrostatic probe measurements there are some practical complications. In particular, the presence of a floating or a biased object in the glow discharge causes a local perturbation of the plasma [12]. In order to
minimize this effect and to be able to measure the bulk plasma properties a thin cylindrical probe is used. The latter is also known as Langmuir probe [117] and is schematically depicted in Figure 3.5 (a).

![Figure 3.5. (a) Cylindrical and (b) flat electrostatic probe.](image)

An additional plasma parameter which can be determined by the electrostatic probe measurements is the ion saturation current, as shown in Figure 3.4. This together with the potential difference, $V_f - V_p$ provides information about the bombardment of the growing film by the positively charged plasma species. The measured ion current depends on the probe collecting area. In the case of the Langmuir probe the latter is determined by the sheath thickness, which in turn is a function of the applied voltage [12]. Thus, the accuracy of the ion current values measured with the Langmuir probe is marginal. Alternatively a flat probe can be utilized (Figure 3.5 (b)). In this experimental arrangement the collecting area is independent of the sheath thickness [116]. In the present work home - made Langmuir and flat electrostatic probes are used. Details of the probe construction can be found in reference [118].

### 3.2.2. Optical emission spectroscopy

Glow discharges emit light due to the excitation and the subsequent relaxation of the plasma species, as explained in section 2.1.3.2. The frequency of the emitted light spans over a broad spectral range from the near infrared to the ultra violet (300 – 850 nm). This frequency is for given species equal to the energy difference between the excited and ground state. The emitted intensity for a wavelength $\lambda$ that corresponds to a transition $\text{p} \rightarrow \text{k}$ is given by the expression [119],

$$I_{pk} = n_n \cdot n_e \cdot X_{i,0} (\sigma(E), n_e, f(E)) \quad (3.6)$$
Here, \( n_n \) is overall density of the species, \( n_e \) is the electron density and \( X_{i,0} \) is the emission rate coefficient. The emission rate coefficient \( X_{i,0} \) is a function of the electron-impact excitation cross section \( \sigma(E) \), the electron density and the electron energy distribution function \( f(E) \). It is evident from equation (3.6) that by knowing the emission intensity one can draw conclusions about the density of the corresponding species, i.e. about the plasma composition [119].

![Figure 3.6](image)

**Figure 3.6.** Experimental arrangement used for the optical emission spectroscopy measurements (adopted from reference [120]).

The experimental arrangement used for the OES measurements in this work is depicted in Figure 3.6. The light is collected by a fiber mounted from the one side on the deposition chamber and from the other side on the entrance slit of the spectrometer. The spectrum in the range from 200nm to 930 nm is then created from the collected light by using an *Andor Mechelle 5000* spectrograph. The structure of the spectrograph is schematically shown in Figure 3.7. The incident light is collected and collimated by lenses. Then it passes through a prism that provides vertical dispersion. Afterwards it falls onto an *Echelle* grating which creates dispersion in the horizontal direction. The spectrum is finally relayed by focusing mirrors onto the detector. The detector is an *iStar* intensified charge-coupled device (ICCD) camera, shown in Figure 3.8. Photoelectrons are emitted, when a photon strikes the photocathode. These electrons are accelerated by a high voltage in the intensifier tube. Photoelectrons with sufficient energy can dislodge secondary electrons from the walls of the intensifier which are then detected by the CCD sensor. With the ICCD arrangements signal gains of up to \( 10^4 \) can be achieved, allowing measurements at low integration times to be made. The intensifier is controlled by high speed electronics that enable ultra-fast gating and real time measurements on a \( \mu \text{s} \) scale.
3.3. Determination of atomic composition in thin films

The determination of the atomic composition of the thin films in this work was realized by means of the Rutherford backscattering spectroscopy (RBS). RBS is based on the elastic (back) scattering of particles (ions) with energies in the MeV range from the sample under investigation. The elastic collision of a moving ion of a mass $M_1$ and incident energy $E_0$ with a stationary target atom of a mass $M_2$ is depicted in Figure 3.9. The conservation of the energy and the momentum can be expressed as,

$$\frac{1}{2} M_1 v_0^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2 \quad (3.7)$$

$$M_1 v_0 = M_1 v_1 \cos \theta - M_2 v_2 \cos \phi \quad (3.8)$$

$$0 = M_1 v_1 \sin \theta - M_2 v_2 \sin \phi \quad (3.9)$$
Here $v_0$ is the velocity of the primary ion, $v_1$ and $v_2$ are the velocities of the backscattered ion and the target atom, respectively. The angles $\theta$ and $\phi$ are measured with respect to the direction of incidence. By eliminating $v_2$ and $\phi$ and considering that $M_1 < M_2$ the following expression can be derived,

$$
\frac{E_1}{E_0} = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right]^2
$$

(3.10)

The energy ratio, which is called kinematic factor $k = \frac{E_1}{E_0}$, depends on the ion and the target mass atoms and the scattering angle $\theta$ and can be used for the identification of the elements in the sample under investigation.

For the quantitative analysis of the film composition the number of the backscattered ions is considered. This is described by the detection yield $Y$, i.e. the number of the atoms measured by the detector and is given by the expression [121],

$$
Y = \sigma \cdot \Omega \cdot Q \cdot N_s \cdot E_0 \cdot E_0
$$

(3.11)

where $N_s$ is the number of the atoms in the target, $\sigma$ the scattering cross-section, $\Omega$ the solid angle of the detector used and $Q$ the total number of the incident particles. The equation (3.11) can be used for the quantitative determination of the film composition. For this purpose the backscattering yield has to be normalized with respect to the scattering cross-section. Finally, the composition profile as a function of the film thickness can be determined by the energy loss $\frac{dE}{dx}$ which is given by the expression [121],

$$
-\frac{dE}{dx} = \frac{4\pi Z_i e^4 n}{M_1 v_0^2} \ln \frac{2M_1 v_0^2}{I} \quad (3.12)
$$

Here $n$ is the electron density of the sample, $Z_i$ the atomic number of the incident ions, $e$ the electronic charge and $I$ the average excitation energy of the electrons in the sample atoms. From Equation (3.12) one can calculate the film thickness $\Delta x$ if the total energy loss $\Delta E$ is known.
In this work, RBS measurements were performed by using a 1.4 MeV $^4\text{He}^+$ beam with a current of 14 nA provided by a Tandetron accelerator. The backscattered particles were detected by a semiconductor detector with a resolution of 10 keV, placed at an angle of 170° with respect to the incident beam direction. A representative RBS measurements of a 100 nm thick CrN film deposited on graphite substrate is presented in Figure 3.10.
3.4. Investigation of film microstructure

The term film microstructure includes properties such as, the crystalline quality and the structural defects, the density and the porosity, as well as the surface topography. In order to determine these properties, analytical techniques, in which an appropriate probe is utilized, are employed. Frequently X-rays and electrons are used as probes. In the followings X-ray and electron based characterization techniques used in this work are demonstrated.

3.4.1. X-ray based techniques

3.4.1.1. Microscopic interactions of the X-rays with matter. In a microscopic scale the most fundamental interaction is the scattering of the X-rays from a single electron, as depicted in Figure 3.11. For the theoretical description of the process an incident X-ray beam with an electric field vector \( \vec{E}(\vec{r}, t) = \vec{E}_0 \exp[i(k \cdot \vec{r} - \omega \cdot t)] \) is considered, where \( \vec{k} \) is the wavevector along the direction of propagation of the electromagnetic wave. In the case of elastic scattering the wavelengths of the incident and scattered beams are equal, i.e. \(|\vec{k}| = |\vec{k}'|\), where \( \vec{k}' \) is the wavevector of the scattered wave (Figure 3.11). This process is also known as Thomson scattering. The change of the propagation direction upon scattering implies that there is momentum transfer to the electron which is,

\[
\hbar \vec{k} - \hbar \vec{k}' = \hbar \vec{Q} \quad (3.13)
\]

The vector \( \vec{Q} \) in equation (3.13) is referred to as wavevector transfer or scattering vector.
A single electron is structureless. The simplest structure is that consisting of two electrons. One is located at an origin point O and the second at a position \( \vec{r} \) with respect to the origin, as shown in Figure 3.12. Considering again elastic scattering the phase difference between incident and scattered wave is

\[
\phi = (\vec{k} - \vec{k}') \cdot \vec{r} \equiv \vec{Q} \cdot \vec{r} \quad (3.14).
\]

From the scattering triangle in Figure 3.12 it is evident that

\[
|\vec{r}| = \frac{4\pi}{\lambda} \sin \theta \quad (3.15)
\]

Here \( \lambda \) is the wavelength of the electromagnetic wave and \( \theta \) is the scattering angle. The scattering amplitude can be then written as [122],

\[
A(\vec{Q}) = -r_0 (1 + \exp(i\vec{Q} \cdot \vec{r})) \quad (3.16)
\]

From the definition (3.16) it follows that the intensity of the scattered beam is,

\[
I(\vec{Q}) = |A(\vec{Q})A(\vec{Q})^*| = 2r_0^2 (1 + \cos(\vec{Q} \cdot \vec{r})) \quad (3.17)
\]

The prefactor \( r_0 = 2.82 \times 10^{-5} \, \text{Å} \) in equations (3.16) and (3.17) is known as Thomson scattering length or classical electron radius [122]. According to equation (3.17) the structure of the two-electron system, i.e. \( \vec{r} \), can be calculated by measuring the intensity \( I(\vec{Q}) \).
If one considers a system with more than two electrons the scattering amplitude can be calculated as,

\[
A(\mathbf{Q}) = -r_0 \sum_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (3.18)
\]

where \( \mathbf{r}_j \) denotes the position of the \( j^{th} \) electron. In the case of continuously distributed electrons with a charge density \( \rho(\mathbf{r}) \) the sum must be replaced by an integral. Then the scattering amplitude is equal to,

\[
f^0(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \quad (3.19)
\]

in units of \(-r_0\). The quantity \( f^0(\mathbf{Q}) \) is also referred to as atomic form factor.

The next level of complexity is scattering from a group of atoms organized into a molecule. If the atoms are labeled by \( j \) the scattering amplitude of a molecule is given by,

\[
f^{mol}(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (3.20)
\]

Crystalline materials may be characterized by periodicity, i.e. they consist of a regularly repeated structure unit known as unit cell. The points that define the unit cell form a lattice. Thus the crystal can be constructed by specifying the lattice and then associating each lattice point with a collection of atoms or molecules, known as basis. In the 3-dimensional case, a lattice is described by the vector

\[
\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (3.21)
\]

Here \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are the unit cell vectors and \( n_1, n_2, n_3 \) are integers. In general, the scattering occurs from atoms that lie within the same family of planes in the crystal. The Miller indices (h,k,l) are the most convenient way to specify these planes and are defined by the plane located closest to the origin of the unit cell with
intercepts \( \frac{h}{d_1}, \frac{k}{d_2} \) and \( \frac{l}{d_3} \) with the axes \( d_1 \), \( d_2 \) and \( d_3 \), respectively. Having introduced a way for describing the crystal one can calculate the scattering amplitude. The position of the \( j \)th atom can be expressed as \( R_j = R_0 + r_j \) where \( R_0 \) specifies the origin of the unit cell and \( r_j \) the position of \( j \)th atom relative to that origin. Then,

\[
f^{\text{crystal}}(Q) = \sum_{r_j} f^{\text{mod}}(Q) \exp(iQ \cdot r_j) \sum_{R_n} \exp(iQ \cdot R_n) \tag{3.22}
\]

The first term in equation (3.22) is known as unit cell structure factor and the second one as lattice sum. The sum of the phase factors \( \exp(iQ \cdot R_n) \) is negligible unless the scalar product \( Q \cdot R_n \) is \( 2\pi \) or a multiple thereof. The problem is then to solve the equation,

\[
Q \cdot R_n = 2\pi \times \text{integer} \tag{3.22}
\]

To find a solution a lattice with vectors \( a^*_i \) that fulfill the condition

\[
a^*_i \cdot a^*_j = 2\pi \delta_{ij} \tag{3.23}
\]

is introduced, where \( \delta_{ij} = 1 \), if \( i=j \) and zero otherwise. It can be shown that [123],

\[
\begin{align*}
\frac{r^{*}_1}{a_1} &= \frac{2\pi}{V} \frac{r}{a_2} \times \frac{r}{a_3} \\
\frac{r^{*}_2}{a_2} &= \frac{2\pi}{V} \frac{r}{a_3} \times \frac{r}{a_1} \\
\frac{r^{*}_3}{a_3} &= \frac{2\pi}{V} \frac{r}{a_1} \times \frac{r}{a_2}
\end{align*} \tag{3.24}
\]

Here \( V \) is the volume of the primitive cell. It is apparent from the definition (3.24) that the vectors \( a^*_i \) have units of reciprocal length. Thus, the so-called reciprocal lattice can be defined with vector

\[
G = ha^{*}_1 + ka^{*}_2 + la^{*}_3 \tag{3.25}
\]

It is evident that \( G \) fulfills the condition (3.22) since,

\[
G \cdot R_n = 2\pi(hn_1 + kn_2 + ln_3) \tag{3.26}
\]

In other words the scattering amplitude from a crystal is not vanishing if,

\[
Q = G \tag{3.27}
\]

The expression (3.27) is known as Laue condition.

3.4.1.2. X-ray diffraction. On a mesoscopic scale the interaction of the X-rays with a lattice can be treated as diffraction. It can be proven that scattering and diffraction are absolutely equivalent. This is shown for the case of a two-dimensional square lattice
in Figure 3.13. With reference to Figure 3.13 (a), X-rays are specularly reflected from atomic planes with a spacing $d$. In order for diffraction to be observed, the path difference of the two beams must be an integer multiple of their wavelength. This leads to Bragg’s law of the form,

\[ n\lambda = 2d \sin \theta \quad (3.28) \]

In Figure 3.13 (b) the reciprocal cell with lattice spacing \( \frac{2\pi}{d} \) is depicted. The Laue condition requires the scattering vector to be equal to the reciprocal lattice vector, i.e. \( \mathbf{Q} = \mathbf{G} \). From the scattering geometry it is evident that

\[ |\mathbf{Q}| = 2|\mathbf{k}| \sin \theta \quad (3.29) \]

In addition,

\[ |\mathbf{Q}| = \frac{2\pi}{d} \quad (3.30) \]

The combination of the equations (3.29) and (3.30) yields the Bragg’s law.

![Figure 3.13. Scattering geometry of X-rays from (a) a real and (b) a reciprocal 2-dimensional square lattice (adopted from reference [122]).](image)

3.4.1.3. X-ray diffraction measurement geometries. According to the discussion in the preceding sections the intensity of the diffracted X-rays is non-vanishing only for lattice planes (hkl) that fulfill the Bragg’s condition. In practice the diffraction intensity is measured as a function of the angle \( \theta \) and the so-called X-ray diffraction pattern is constructed. This technique is known as X-ray diffractometry (XRD) and it is used to obtain structural information for both bulk samples and thin films. The XRD pattern is a unique fingerprint of the crystal structure. The angular position of the intensity maxima enables the determination of the interplanar spacing $d_{hkl}$ by using the equation (3.28). Depending on the variation of the angular position of the sample...
and the detector, which is used for measuring the diffraction intensity, with respect to the incident beam direction, the following XRD geometries exist (Figure 3.14).

**Figure 3.14.** Schematic representation of the (a) Bragg-Brentano, (b) grazing incidence and (c) rocking curve XRD geometry. The capital letters T, S, and D stand for the X-ray tube, the sample and the detector, respectively.

- **Bragg-Brentano geometry (BB).** With reference to Figure 3.14 (a) the sample angle is $\omega = \theta$, whereas the detector’s angle is $2\theta$, with respect to the incident beam direction. In addition, the angular speed of the sample $\vartheta_s$ and the detector $\vartheta_d$ are linked through the relation $\vartheta_d = 2\vartheta_s$. This geometry enables detection of diffraction from lattice planes with scattering vector parallel to the surface vector, i.e. planes parallel to the sample surface.

- **Grazing incidence geometry (GI).** In this case the sample angle $\omega$ is kept constant and only the detector angle $2\theta$ is varied (Figure 3.14 (b)). With GI X-rays diffracted from planes which are randomly oriented with respect to the sample surface are detected. This measurement geometry is widely used for the characterization of thin polycrystalline films.

- **Rocking curve geometry.** The detector angle $2\theta$ is fixed at the position of an intensity maximum, while the sample angle $\omega$ is varied around the value
ω = θ (Figure 3.14 (c)). Thus, the deviation of the lattice planes’ orientation with respect to the sample surface is measured.

3.4.1.4. X-ray reflectivity. The interactions of X-rays with matter have been described so far on an atomic level. On the other hand, X-rays are electromagnetic waves and macroscopic phenomena characteristic for waves, such as reflection and refraction can also occur. An X-ray beam reflected by the surface of the sample under investigation provides information for its density and its surface roughness. Moreover, in the case of single- or multilayer thin films deposited on a bare substrate the reflected beam carries also information for the distance between the interfaces (i.e. film thicknesses) and their roughness.

In practice, X-rays impinge onto a surface with an angle θi. The intensity of the specularly reflected beam (θr = θi, where θi the angle of reflection) is detected as a function of the angle θi. This technique is known as X-ray reflectometry (XRR) and its principle is depicted in Figure 3.15

![Figure 3.15. Principle of X-ray reflectometry.](image)

In the X-ray region matter is transparent, since the frequency of the X-rays is much higher than the resonance frequency of the bound electrons [124]. In this case, the index of refraction of the material can be written as [125],

\[ \tilde{N} = 1 - \delta + i\beta \] (3.31)

where δ is in the order of 10^{-5} and β (absorption coefficient) is several orders of magnitude lower. By neglecting the absorption it can be shown that [125],

\[ \delta = \frac{\lambda^2}{2\pi} r \rho \] (3.32)
where \( \rho_e \) is the electron density, \( \lambda \) the wavelength of the X-rays and \( r_0 \) the classical electron radius. It is evident from equation (3.31) that the refractive index \( n = 1 - \delta \) is slightly less than unity. Due to this fact the X-ray beam is totally reflected for incident angles lower than a critical value \( \theta_c \). For \( \theta_i = \theta_c \), Snell’s law yields,
\[
\cos \theta_c = 1 - \delta \quad (3.33)
\]
Here the refractive index of air is \( n_{\text{air}} = 1 \). For relatively low \( \theta_c \) values, the left hand side if equation (3.33) can be approximated as,
\[
\cos \theta_c = 1 - \frac{\theta^2}{2} \quad (3.34)
\]
Combining the equations (3.32) - (3.34) it is obtained that,
\[
\theta^2 = \frac{\lambda^2}{\pi} r_0 \rho_e \quad (3.35)
\]
The electron density \( \rho_e \) is linked to the mass density of the material \( \rho_m \) via the relation,
\[
\rho_e = \frac{A \rho_m}{N_A Z} \quad (3.36)
\]
The equations (3.35) and (3.36) enable the calculation of the mass density of the sample under investigation by measuring the critical angle for total external reflection \( \theta_c \), provided that the stoichiometry of the material is known.

The reflectivity measured from an ideally smooth surface changes as \( R(\theta_i) \sim \theta_i^{-4} \) when \( \theta_i >> \theta_c \) [125]. On the other hand, the real surfaces are in general non-ideal exhibiting roughness, which causes reflection of the incident beam to non-specular directions resulting thus, in a lower detected specular reflectivity. In many cases the height of the surface \( h \) can be described by a Gauss distribution (Figure 3.16). The standard deviation of this distribution (also referred to as root mean square roughness \( \sigma_{\text{rms}} \)) is used to quantify the vertical surface roughness. It can be shown [125] that the reflectivity of the non-ideal surface with respect to that of the ideal one is given by the expression,
\[
R_{\text{non-ideal}}(\theta_i) = R_{\text{ideal}}(\theta_i) \left[ \exp\left(-\frac{4\pi}{\lambda} \sin \theta_i \sigma_{\text{rms}}\right)^2 \right] \quad (3.37)
\]
According to equation (3.37) the surface roughness can be calculated by measuring the decay of the X-ray reflectivity as a function of the angle \( \theta_i \).
When XRR is employed for the investigation of a sample consisting of a film on a thick substrate and \( \theta_i > \theta_c \), part of the beam is transmitted (refracted) into the film, as shown in Figure 3.15. The transmitted beam may undergo multiple reflections at the film/air and at film/substrate interfaces before finally being reflected to the detector. The optical path difference between primary reflected and transmitted and subsequently reflected at the film/substrate interface beams gives rise to interference phenomena, which are observed as oscillations (known also as Kiessig Fringes) of the measured reflected intensity. This is shown in Figure 3.17 where a characteristic XRR curve is plotted. The angular separation of the intensity maxima enables the determination of the film thickness. In particular, it can be shown that [126],

\[
d = \frac{\lambda}{2} \frac{1}{\theta_{m+1} - \theta_m}, \text{ for } \theta >> \theta_c \quad (3.38)
\]

where \( \theta_{m+1} \) and \( \theta_m \) are the angular positions of two successive intensity maxima.

**3.4.1.5. The Phillips X’Pert diffractometer.** The X-ray measurements in this work were performed at a Phillips X’Pert Pro Diffractometer, which is shown in Figure 3.18. The diffractometer is equipped with a Cu X-ray source that provides an X-ray beam of a wavelength \(~1.54\ \text{Å} \). The size, the shape and the angular divergence of the beam can be adjusted by an array of masks and slits located at the exit of the X-ray tube. The sample is fixed by permanent magnets on a holder. The holder can be rotated around three different axes (with respective angles \( \Psi, \phi \) and \( \omega \)) and moved along three directions (X, Y, and Z) as shown in Figure 3.18. The diffracted/ reflected beam is focused on the detector by an array of slits. Two detectors are used for the
measurements: (i) A PW 3011/2, which is a Xe filled proportional counter and provides high angular resolution and (ii) a PW3015/20 X Cel erator which can measure over an angular range of 1.56° simultaneously providing high acquisition speeds. The XRR and the GI-XRD scans were performed by the PW 3011/2 detector, while the BB-XRD patterns were recorded by the PW3015/20 X Cel erator detector.

![Figure 3.17. A characteristic XRR curve.](image)

![Figure 3.18. The Phillips X’Pert diffractometer.](image)

### 3.4.2. Transmission electron microscopy

*Transmission electron microscopy* (TEM) is used in order to obtain structural information from samples that are thin enough to transmit electrons. The principle of
TEM is schematically shown in Figure 3.19 [1]. Electrons are thermionically emitted by a gun and are accelerated to energies of 100 keV or higher. The electron beam is projected to the sample by a condenser lens system. During their passage through the sample the electrons experience a variety of scattering processes. For TEM only elastic scattering, which gives rise to diffraction effects, is of interest. The primary transmitted and the diffracted beams are made to pass through an arrangement of post-sample lenses, which lead to the formation of the image. In fact, images can be formed by several ways. The bright-field image is obtained by blocking all diffracted beams by an aperture and only allowing the primary transmitted one to pass through. When both the transmitted and one diffracted beam are used, then the so-called dark field images are obtained. In the third imaging mode the primary beam is made to recombine with one or more diffracted ones. This technique is employed in high resolution lattice imaging. In this work TEM images were recorded using a Philips CM 20 transmission electron microscope, operated at 200 kV.

![Figure 3.19. The principle of transmission electron microscopy (adopted from reference [127]).](image)

### 3.4.3. Scanning electron microscopy

Scanning electron microscopy (SEM) is by far the most widely employed thin-film and surface coating characterization technique [1]. The principle of SEM is depicted in Figure 3.20. Electrons with energies of several tens of keV are emitted either by a filament (W or LaB₆) or by a field emission gun. The electron beam is
focused on the sample and scans a rectangular area. Upon impinging on the sample
the primary electrons transfer energy by elastic and inelastic collisions. This results in
emission of secondary electrons and X-rays from the sample, as well as in
backscattering of electrons from the primary beam. The number of the secondary and
backscattered electrons depends on the structure and the surface topography. These
are captured by a detector consisting of a scintillator-photomultiplier combination.
The output of the detector serves to modulate the intensity of cathode ray tube (CRT),
which is synchronized with the primary beam. This leads to the image generation. The
magnification is then defined by the ratio of the scan length on the CRT to that of the
primary beam on the sample. The energy and the intensity of the emitted X-rays are
characteristic of the atoms and their concentration in the material under investigation,
respectively. This technique is known as X-ray energy dispersive analysis (EDX). In
this work the SEM measurements were carried out on a Joel JSM-7400F microscope.

Figure 3.20. The principle of scanning electron microscopy (adopted from reference [128]).

3.5. Determination of residual stresses in thin films

Residual stresses are commonly observed in physical vapor deposited films, as
already mentioned in section 2.2.4. The precise determination of their magnitude is
essential for thin film analysis, since it provides valuable information for the growth
mechanisms. Here two techniques for residual stress determination are presented; the wafer curvature and the \( \sin^2 \psi \) method. The wafer curvature method enables the direct measurement of the stress in the film. On the other hand, in the \( \sin^2 \psi \) method the measured quantity is the film strain. The stress can be then determined given that the elastic constants of the films are known. It should be also pointed out here that these methods only enable the determination of biaxial stresses, i.e. stresses in the plane of the film.

### 3.5.1. The wafer curvature method

The wafer curvature method was originally introduced by Stoney [129] and is based on the measurement of the substrate’s curvature. As explained in section 2.2.4 residual stresses in the film induce bending of the film/substrate system. If \( R_s \) and \( R_f \) are the curvatures of the substrate prior and after the film deposition, respectively, the residual biaxial stress can be calculated from the relation [1],

\[
\sigma = \frac{E_s d_s^2}{6(1-v_s)d_f} \left( \frac{1}{R_f} - \frac{1}{R_s} \right) \quad (3.39)
\]

Here \( \frac{E_s}{(1-v_s)} \) is the substrate’s biaxial elastic modulus, \( d_s \) the substrate thickness and \( d_f \) the film thickness. The main advantage of this technique is that only the elastic constants of the substrate are required for the determination of the magnitude of the residual stresses.

The substrate curvature and thus the residual stresses were determined in this work by using a home made setup based on the scanning laser beam method [130]. The top view of the setup is shown in Figure 3.21. A He-Ne laser (1) emits a monochromatic beam. The intensity of the beam is adjusted by a rotating polarizer (2) and then reflected by a mirror (3) onto a galvanometer (4). From the galvanometer the beam is reflected to a beam splitter (5), passes through a convex lens (6) to additional lenses (7) which direct it to the sample (8). Upon reflection by the sample the beam passes again by the splitter and ends up on a position sensitive detector (PSD) (9). The motion of the beam on the PSD enables the determination of the substrate’s curvature.
3.5.2. The $\sin^2 \psi$ method

This method is based on the measurement of the spacing between crystallographic planes by X-ray diffraction, as a function of the orientation of these planes with respect to the sample surface [131], as shown in Figure 3.22. This enables the determination of the strain and consequently, the stresses in the thin film [131]. In the particular case of biaxial stresses then stress-strain relation is given by the equation [131],

$$
\varepsilon = \frac {d^\psi_{hkl} - d^0_{hkl}} {d^0_{hkl}} = \frac {1 + \nu} {E} \sigma \sin^2 \psi - 2 \frac {\nu} {E} \sigma \quad (3.40)
$$

where $\varepsilon$ is the strain, $d^\psi_{hkl}$ is the d-spacing of the (hkl) planes oriented at various tilt angles $\psi$ with respect to the Bragg-Brentano geometry, $d^0_{hkl}$ is the d-spacing value obtained by the Bragg-Brentano geometry ($\psi = 0$, planes parallel to the surface), $\nu$ and $E$ are the Poisson’s ratio and the elastic modulus of the film, respectively, and $\sigma$ is the value of the residual stresses. Equation (3.40) implies that $\sigma_{xx} = \sigma_{yy} = \sigma$. Here $\sigma_{xx}$ and $\sigma_{yy}$ are the two components of the in-plane biaxial stresses. By measuring the d-spacing for a number of tilt angles $\psi$ one can calculate the stresses from the slope of the $d - \sin^2 \psi$ line. In this work, the Phillips X’Pert diffractometer, presented in section 3.4.3, was used in order to implement the $\sin^2 \psi$ method.

Figure 3.21. The stress measurement setup.
Figure 3.22. The principle of the $\sin^2 \psi$ method.

### 3.6. Optical properties in thin films

The light - matter interactions, i.e. the optical response of the materials can be solely described by the complex dielectric function $\tilde{\varepsilon}(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$, where $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ are the real and the imaginary parts, respectively and $\omega$ is the angular frequency of the electromagnetic plane wave, i.e. the light [124]. The complex dielectric function is linked to the complex index of refraction $\tilde{N}(\omega) = n(\omega) + ik(\omega)$ through the relation,

$$\tilde{\varepsilon}(\omega) = \tilde{N}^2(\omega) \quad (3.41)$$

where $n$ is the refractive index and $k$ the extinction coefficient. These quantities describe the dispersion and the absorption of the electromagnetic radiation in the matter, respectively [119]. It is evident from Equation (3.41) that,

$$\varepsilon_1 = n^2 - k^2 \quad (3.42)$$

$$\varepsilon_2 = 2nk \quad (3.43)$$

Spectroscopic ellipsometry is a technique which is widely used for the determination of the dielectric function of bulk materials and thin films [132]. Polarized light (normally linearly) is reflected from the surface of the sample under investigation, as depicted in Figure 3.23. This technique is also referred to as reflection ellipsometry. By determining then polarization state of the reflected beam (which is in the general case elliptical), one can derive the dielectric function of bare substrates and thin films, as explained in sections 3.6.1 and 3.6.2, respectively.
3.6.1. Spectroscopic ellipsometry in bulk materials

For the calculation of the dielectric function of a bulk material from the ellipsometric measurement Maxwell’s electromagnetic theory must be used, in order to describe the reflection and the refraction of the electromagnetic radiation [132]. The incidence of a plane electromagnetic wave (Figure 3.24) at the interface between two semi infinite media (0 and 1) is considered, as shown in Figure 3.25. The electric field vector can be written as,

\[
\mathbf{E}(r,t) = \mathbf{E}_0 \exp\left(i\frac{2\pi \tilde{N} \mathbf{r} \cdot \mathbf{r}}{\lambda} \right) \exp(-i\omega t) \tag{3.44}
\]

Here \( k \) is the wavevector in the direction of propagation, \( \tilde{N} \) is the complex index of refraction of the medium, \( \lambda \) is the wavelength of light in vacuum, \( \omega \) is the angular frequency of the wave and \( \mathbf{E}_0 \) is a complex vector which specifies both the amplitude
and the polarization of the electric field. With reference to Figure 3.25 $E_0$ and thus
the polarization can be resolved to a component parallel ($E_p$) and to a component
perpendicular ($E_s$) to the plane of incidence. The latter is defined as the plane parallel
to the reflected beam and the surface normal, i.e. it is the plane of the paper.

![Figure 3.25. Incidence of a plane electromagnetic wave on the surface of a bulk material](image)

The Snell’s law for the refraction of incident beam yields

$$\tilde{N}_0 \sin \phi_0 = \tilde{N}_1 \sin \phi_1 \quad (3.45)$$

where $\tilde{N}_0$ and $\tilde{N}_1$ are the complex indices of refraction of two media. The angles
$\phi_0$ and $\phi_1$ stand for the angle of incidence and refraction, respectively and they are in
general complex quantities. Let ($\tilde{E}_p, \tilde{E}_i$) and ($\tilde{E}_p, \tilde{E}_r$) be the complex components
of the incident ($i$) and the reflected ($r$) electric field vector in the $p$ and $s$ directions.

By matching the tangential electric fields at the interface one obtains [132],

$$\tilde{r}_p = \frac{\tilde{E}_r}{\tilde{E}_i} = \frac{\tilde{N}_1 \cos \phi_0 - \tilde{N}_0 \cos \phi_1}{\tilde{N}_1 \cos \phi_0 + \tilde{N}_0 \cos \phi_1} \quad (3.46)$$

$$\tilde{r}_s = \frac{\tilde{E}_r}{\tilde{E}_i} = \frac{N_0 \cos \phi_0 - N_1 \cos \phi_1}{N_0 \cos \phi_0 + N_1 \cos \phi_1} \quad (3.47)$$

where $\tilde{r}_p$ and $\tilde{r}_s$ are the complex Frensel reflection coefficients. In order to investigate
the effect of the reflection on the amplitude and the phase separately one can write the
electric field vector as $\hat{E} = |E| \exp(i\theta)$, where $|E|$ is the amplitude and $\theta$ the phase. Then the Frensel coefficients can be expressed as,

$$\tilde{r}_p = \left( \frac{E_{r_p}}{E_{i_p}} \right) \frac{\exp(i\theta_{r_p})}{\exp(i\theta_{i_p})} = \left( \frac{E_{r_p}}{E_{i_p}} \right) \exp(i\theta_{r_p} - \theta_{i_p}) = |r_p| \cdot \exp(i\delta_p) \tag{3.48}$$

$$\tilde{r}_s = \left( \frac{E_{r_s}}{E_{i_s}} \right) \frac{\exp(i\theta_{r_s})}{\exp(i\theta_{i_s})} = \left( \frac{E_{r_s}}{E_{i_s}} \right) \exp(i\theta_{r_s} - \theta_{i_s}) = |r_s| \cdot \exp(i\delta_s) \tag{3.49}$$

The ratio $\bar{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \frac{|r_p|}{|r_s|} \exp(i(\delta_p - \delta_s))$ is known as complex ellipsometric ratio and is the quantity which is obtained by reflection ellipsometry. Alternatively $\bar{\rho}$ can be written as,

$$\bar{\rho} = \tan \psi \exp(i\Delta) \tag{3.50}$$

where $\tan \psi = \frac{|r_p|}{|r_s|}$ and $\Delta = \delta_p - \delta_s$. It is therefore evident, that $\psi$ and $\Delta$ express the differential changes in the amplitude and the phase, respectively, that the electric field experiences upon reflection. These quantities are also referred to as ellipsometric angles and are directly obtained by the measurement. By substituting equation (3.50) into (3.46) and (3.47) and using Snell’s law (equation (3.45)) and equation (3.41)) one can calculate the dielectric function of the medium 1 (sample), when the angle of incidence $\phi_0$ and the dielectric function of the medium 0 (ambient) $\tilde{\varepsilon}_0(\omega)$ are known, i.e.,

$$\tilde{\varepsilon}_1(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) = \tilde{\varepsilon}_0(\omega) \sin^2 \phi_0 \left\{ 1 + \left( \frac{1-\tilde{\rho}}{1+\tilde{\rho}} \right)^2 \tan^2 \phi_0 \right\} \tag{3.51}$$

### 3.6.2. Spectroscopic ellipsometry in thin films

A case of considerable importance for spectroscopic ellipsometry is that in which polarized light is reflected from a substrate covered by a transparent film. As shown in Figure 3.26 a film with parallel boundary planes and a thickness $d$ is considered. The film (medium 1) is sandwiched between two semi-infinite media, i.e. the ambient (0) and the substrate (2). A plane wave incident at the 0 - 1 interface at angle $\phi_0$ will give rise to a specularly reflected and a refracted beam in medium 1 with an angle $\phi_1$. The refracted beam will suffer multiple reflections at the 0 - 1 and 1 - 2 interfaces. These reflections are in general not perfect, i.e. a part of the beam is refracted in the
two semi infinite media, i.e. the substrate and the ambient. It can be shown that the complex Frenzel coefficients for the total reflected beam in the p and s directions are,

\[ \tilde{R}_p = \frac{\tilde{r}_{01p} + \tilde{r}_{12p} \exp(-i2\beta)}{1 + \tilde{r}_{01p} \tilde{r}_{12p} \exp(-i2\beta)} \] (3.52)

\[ \tilde{R}_s = \frac{\tilde{r}_{01s} + \tilde{r}_{12s} \exp(-i2\beta)}{1 + \tilde{r}_{01s} \tilde{r}_{12s} \exp(-i2\beta)} \] (3.53)

Here \( \tilde{r}_{01} \) and \( \tilde{r}_{12} \) are the respective reflection coefficients at the 0 - 1 and 1 - 2 interfaces and \( \beta \) the phase change of the plane wave as it transverses between the two interfaces of the film. The latter is equal to,

\[ \beta = 2\pi \left( \frac{d}{\lambda} \right) \left( \tilde{N}_1^2 - \tilde{N}_0^2 \sin^2 \phi_0 \right)^{1/2} \] (3.54)

Similarly to section 3.6.1, the complex reflection coefficients can be expressed in terms of their amplitude and their phase, i.e.,

\[ \tilde{R}_p = |R_p| \exp(i\Delta_p) \] (3.55)

\[ \tilde{R}_s = |R_s| \exp(i\Delta_s) \] (3.56)

Then the complex ellipsometric ratio can be calculated,

\[ \tilde{\rho} = \frac{\tilde{R}_p}{\tilde{R}_s} = \left| \frac{R_p}{R_s} \right| \exp(i(\Delta_p - \Delta_s)) = \tan \psi \exp(i\Delta) \] (3.57)

where \( \tan \psi = \left| \frac{R_p}{R_s} \right| \) and \( \Delta = \Delta_p - \Delta_s \). In this case the measured ellipsometric angles contain information for the optical response of the entire film/substrate system. Thus, the quantity calculated by using the equation (3.51) is called effective- or pseudodielectric function \( < \tilde{\varepsilon}(\omega) > \)[134], namely,

\[ < \tilde{\varepsilon}(\omega) >= \varepsilon_r(\omega) + i \varepsilon_i(\omega) = \tilde{\varepsilon}_0(\omega) \sin^2 \phi_0 \left\{ 1 + \left( \frac{1 - \tilde{\rho}}{1 + \tilde{\rho}} \right)^2 \right\} \tan^2 \phi_0 \] (3.58)

In order to extract the optical constants of the thin film by the measured pseudodielectric function, the optical response of the film/substrate system must be mathematically described. The optical constants of the substrate are known, while the optical properties of the films can be modeled by using a dispersion relation (section 3.6.3). Then by fitting the measured spectrum to the model one can calculate the optical constants of the thin film.
3.6.3. Dispersion relations

The dispersion relations are used, in order to parameterize the optical response of materials. The choice of an appropriate relation is of utmost importance for the accurate calculation of the thin film’s optical constant from the ellipsometric measurement. In general, there are three categories of dispersion relations; (i) empirical (ii) classical and (iii) quantum – mechanical ones. These are briefly presented in the following sections.

3.6.3.1. Empirical dispersion relations. The empirical dispersion relations are mathematical expressions which are used in order to describe the optical response of the materials. The parameters used in these expressions have no physical meaning. An empirical dispersion relation which is widely employed is the Cauchy model [133]. This model considers fully transparent films for which \( k = 0 \) and the refractive index changes according to the expression,

\[
n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{3.59}
\]

Here \( A, B \) and \( C \) are constants and \( \lambda \) the wavelength of the radiation used. Typically \( A \) has values between 1 and 2, while \( B \) and \( C \) are in the order of \( 10^{-1} \) and \( 10^{-2} \) respectively [133]. This model enables the calculation of the refractive index, as well as the thickness of transparent materials with high accuracy [133].
3.6.3.2. Classical dispersion relations. The classical dispersion relations treat the propagating light in the medium as an electromagnetic wave, while electrons and atoms are modeled as classical dipole oscillators. This approach can be used in order to describe atomic vibrations (phonons), electronic (interband) transitions, as well as free electrons [135]. In the followings the classical approach for electronic transitions is presented. This approach is also known as the Lorentz model [124].

The electrons are held at a constant orbit due to the binding with a much larger and, thus, stationary nucleus. This situation is represented as a mass connected to a much larger one by a spring (Figure 3.27). By assuming small displacements ($r$) from the equilibrium position, the differential equation of motion for the bound electron can be written, i.e.,

$$m\frac{d^2r}{dt^2} + m\Gamma \frac{dr}{dt} + m\omega_0^2 r = -eE_{\text{loc}}$$  (3.60)

Here $m$ is the electron mass, $e$ the magnitude of the electron charge and $E_{\text{loc}}$ the local electrical field which acts as driving force for the electron motion. The term $m\Gamma \frac{dr}{dt}$ represents damping and accounts for loss of the energy of the dipole due to interactions with phonons in the crystal. Finally, the term $m\omega_0^2$ represents the restoring force and $\omega_0$ is the resonance frequency of the oscillator.

![Figure 3.27. Electron bound to a stationary nucleus.](image)

In the concept of the electronic transitions, $\omega_0$ corresponds to the quantized transition energy from a filled to an empty electronic state. If the electric field varies with the time as $\exp(-i\omega t)$ it can be shown that the solution of the equation (3.60) is [124],
The displacement of the electron induces a dipole moment $\vec{p}$ which is equal to,

$$\vec{p} = -e \vec{r} = \frac{-e^2 E_{loc} / m}{(\omega_0^2 - \omega^2) - i\Gamma \omega} \quad (3.62)$$

The electric field causes small displacement of the electron from the equilibrium position. As a result a linear relationship between $\vec{p}$ and $E_{loc}$ can be considered, i.e.,

$$\vec{p} = \tilde{a}(\omega) \frac{1}{i} E_{loc} \quad (3.63)$$

where $\tilde{a}(\omega)$ is the frequency dependent atomic polarizability. By combining the equations (3.62) and (3.63) it is found that,

$$\tilde{a}(\omega) = \frac{e^2 / m}{(\omega_0^2 - \omega^2) - i\Gamma \omega} \quad (3.64)$$

If we consider N atoms per unit volume, the macroscopic polarization is then written as,

$$\vec{P} = N < \vec{p} >= N \tilde{a}(\omega) < \frac{1}{i} E_{loc} > \quad (3.65)$$

It can be assumed that the macroscopic electrical field $\vec{E}$ is equal to the average value of the local field over all atomic positions [124], i.e. $< \frac{1}{i} E_{loc} >= \vec{E}$. Based on this approximation the complex electric displacement $\vec{D}$ can be expressed in terms of the electrical field and the polarization vector through the relation,

$$\vec{D} = \varepsilon_0 \tilde{\varepsilon}(\omega) \vec{E} = \varepsilon_0 \vec{E} + \vec{P} \quad (3.66)$$

Here $\tilde{\varepsilon}(\omega)$ is the complex dielectric function of the material and $\varepsilon_0$ the vacuum dielectric constant. By combining the equations (3.64) - (3.66) one can calculate,

$$\tilde{\varepsilon}(\omega) = 1 + N \varepsilon_0^2 \frac{1}{\varepsilon_0 m (\omega_0^2 - \omega^2) - i\Gamma \omega} \quad (3.67)$$

The spectral dependence of the complex dielectric function (real and imaginary part) is presented in Figure 3.28. It is seen that except of a narrow $\omega$ range the real part $\varepsilon_r$ increases with increasing frequency. This is called normal dispersion. However, for $\omega = \omega_0$ the $\varepsilon_r$ decreases when the frequency is increased, a behavior that is known as
anomalous dispersion. In the same range the absorption occurs, i.e. $\varepsilon_i$ exhibits a maximum.

Figure 3.28. Spectral dependence of the complex dielectric function according to the Lorentz model.

3.6.3.3. Quantum - mechanical dispersion relations. The quantum - mechanical dispersion relations provide a more sophisticated description of the light - matter interactions. In these relations the effect of quantum - mechanical aspects, such as the band gap, the electron mass and the defect states [136,137] on the absorption and the dispersion are considered. One of the most frequently used dispersion relations is the Tauc - Lorentz model introduced in 1996 by Jellison et al. [136]. This model arises by the combination of the Tauc density of states [138] which describes the absorption at the band edge and the Lorentz model which describes the interband transitions as presented in section 3.6.3.2. According to the Tauc - Lorentz model the imaginary part of the dielectric function is given by the expression [136],

$$
\varepsilon_i(\omega) = \begin{cases} 
\frac{A\omega_0\Gamma(\omega - \omega_g)^2}{(\omega^2 - \omega_0^2)^2 + \Gamma^2\omega^2}, & \omega \geq \omega_g \\
0, & \omega < \omega_g 
\end{cases} 
$$

(3.68)

Two new quantities have been introduced in equation (3.68) with respect to the Lorentz model (equation (3.67)), the oscillator strength $A$ that accounts for the probability of the interband transition and the band gap $\omega_g$. Moreover, no absorption is considered for photon energies below the band gap. The real part of the dielectric function can be then calculated by using Kramer - Kronig integration which is based in the principle of causality [124]. The spectral dependence of $\varepsilon_i(\omega)$ as obtained by
the Tauc - Lorentz model is presented in Figure 3.29, together with the \( \epsilon_i(\omega) \) curve which corresponds to the Lorentz model, for comparison. It is seen that the introduction of the band gap in the Tauc - Lorentz model affects merely the band edge resulting in an asymmetric curve.

3.6.4. The Woollam M2000-UI rotating compensator ellipsometer

The ellipsometric measurements in this work were performed using a Woollam M2000-UI rotating compensator ellipsometer. The arrangement of the optical components in the beam path is depicted in Figure 3.30 [139]. The incident beam path consists of the source, a fixed polarizer and a continuously rotating compensator. The source provides randomly polarized light. In the M2000 - UI two lamps are used; a deuterium discharge lamp for the near infrared spectral range (0.73 eV - 1.3 eV) and a halogen lamp for the visual and ultraviolet range (1.3 eV - 5.13 eV). The fixed polarizer has an azimuth angle of 45° with respect to the plane of incidence and polarizes the incident light equally to the -s and -p directions. The compensator is in general a retarder which induces a phase shift between the two components of the electric field. The combination of the polarizer with a compensator that has a time dependent azimuth angle \( P \) results in a continuously changing elliptically polarized beam [140]. A second fixed polarizer (analyser) is used after the sample in order the again polarize linearly the reflected beam. Finally a time - dependent light intensity is measured by the detector. The detector is a CCD array camera that enables the simultaneous measurement of all wavelengths in the observed spectral range and thus, allows for ultra fast acquisition. For the determination of the ellipsometric angles \( \psi \) and \( \Delta \) the time dependent intensity is Fourier analyzed to obtain the Fourier coefficients [133], i.e.,

\[
I_D \propto 1 + a \sin(4P) - 2\beta \cos(4P) \quad (3.69)
\]

where \( a \) and \( \beta \) are the Fourier coefficients and \( P=\omega t+\delta \) is the time dependent azimuth angle of the compensator. The ellipsometric angles \( \psi \) and \( \Delta \) can be calculated by the Fourier coefficients [133], i.e.,

\[
\tan(\Psi) = \frac{1+\alpha}{\sqrt{1-\alpha^2}} \quad (3.70)
\]

\[
\cos(\Delta) = -\frac{\beta}{\sqrt{1-\alpha^2}} \quad (3.71)
\]
Figure 3.29. Spectral dependence of the imaginary part of the complex dielectric function according to the Tauc – Lorentz (black curve) and the Lorentz (red curve) models.

Figure 3.30. Arrangement of the optical components in Woollam M2000-UI rotating compensator ellipsometer.
4. The effect of the backscattered energetic species on the growth of reactively sputtered transition metal nitride films

4.1. Introduction

The nitrides of the IVb to VIb transition metal groups (e.g. TiN, VN, ZrN, CrN) have been established as a category of very important technological materials, since they exhibit a refractory character, chemical stability and a vast range of optical and electronic properties [3,141]. In thin film form they are widely used as single [142] and superlattice (e.g. TiN/CrN, TiN/VN) [143] protective coatings, as decorative coatings [144,145], as metal diffusion barriers [146,147] and gate electrodes [148] in microelectronics. One of the most widely used techniques for the growth of transition metal nitride films is the reactive magnetron sputtering from an elemental metallic target in an Ar-N\textsubscript{2} atmosphere. By varying the composition of the working gas, i.e. the partial pressures of Ar and N\textsubscript{2}, films with different stoichiometries and phase compositions can be obtained [142,149]. An additional inherent characteristic of the magnetron sputtering, which crucially affects the properties of the growing film, is the energetic bombardment by the neutral and the charged plasma species, as explained in section 2.2.3. The bombardment regime during growth, i.e. the energy and the flux of species that impinge on the growing film, can be tailored by varying deposition parameters, such as the target-to-substrate distance, the working gas pressure, and the target power. Moreover, the energy and the trajectory of ionized plasma species can be manipulated by the use of an electric field (e.g. substrate bias voltage) allowing thus, for selective control of the films properties. Considerable effort has been spent in order to understand the effect of the bombardment by positively charged ions on the film properties [96,101,142,150]. It has been shown that by tuning the energy and the flux of the bombarding ions the crystallographic orientation [96,101,150], the surface roughness and topography [142], as well as the nanomechanical properties of the transition metal nitride films [101,142,151] can be tailored. Negatively charged ions may also act as a source of energetic bombardment during sputtering. This has been observed during reactive magnetron sputtering of metal oxides. In this case, negatively charged O\textsuperscript{-} ions are formed on the oxidized target surface [152,153] and
accelerated by the negative target potential towards the growing film. Recently, Ngaruiya et al. [154] showed that these ions have a significant influence on the structure formation of reactively sputtered transition metal oxides. The barrier energy for the formation of a negative ion from a metal compound is proportional to the difference between the ionization potential, $IP_M$, of the cation (metal) and the electron affinity, $EA_A$, of the anion (e.g. O) [154]. This is illustrated in Figure 4.1. In the particular case of N, $EA_N < 0$ [155]. This implies that the formation of N$^-$ ions is energetically unfavorable, even if the term $IP_M - EA_N$ has a finite value. Therefore, the existence of N$^-$ ions during reactive sputtering of transition metal nitrides is unlikely.

Finally, the gas composition can also affect the bombardment regime during growth. Petrov et al. [101] showed that in Ar-N$_2$ discharges N$_2^+$ ions become the dominant charged species, when the N$_2$ partial pressure exceeds 75 % of the total working pressure. In addition, Wang et al. [156] reported that N$_2^+$ ions undergo dissociative neutralization, when they impinge on the target, giving rise to two N atoms, which are, then, backscattered. The energy of the impinging ions depends on the target voltage, which is between 300 V and 500 V for most dc magnetron sputtering processes. Upon collision with the target, and depending on the mass of the target atoms and the impinging ions, a fraction of this energy is transferred to the backscattered species [101,156]. Petrov et al. [101] suggested that the backscattered N species have much higher energies than the sputtered atoms. However, the effect of the backscattered species on the growth of transition metal nitride films and the resulting film properties is not yet established. In addition, the dependence of the flux and energy of the backscattered N species on the composition of the sputtering gas and consequently their effect on the film properties are yet to be investigated.

In section 4.2 the chromium nitride material system (CrN) is used in order to manifest the role of the backscattered energetic species on the growth of transition metal nitride films deposited by reactive magnetron sputtering. Simulations based on Berg’s model [30] for reactive deposition are employed in order to link the target and the film properties. The results of these simulations are combined with computations using the TRIM freeware [157] in order to investigate the interactions of the plasma ions with the target. Moreover, Langmuir probe measurements are performed in order to obtain information about the energy of the ionized plasma species that impinge on the growing film. Finally, TRIM computations are also used to study the interactions of the plasma species with the growing films. This enables the identification of the
relationship between the working gas composition, the bombarding of the growing film by backscattered energetic species and the resulting film structural properties. Then, in section 4.3 VN_x (x ≤ 1) films are grown employing reactive magnetron sputtering for different compositions of the Ar and N_2 gases. The simulation procedure, which is used for the case of CrN films, is also employed, in order to estimate the energy of the backscattered plasma species and study their interactions with the growing film for various deposition conditions. The plasma composition is studied and correlated to the observed changes in film properties, such as the residual stresses and the surface roughness. The effect of the backscattered energetic atoms on the stress generation and the surface morphology of reactively sputtered VN_x films is thus, established.

![Energy barrier for the formation of a free negative ion (anion) from a metal compound](image)

**Figure 4.1.** Energy barrier for the formation of a free negative ion (anion) from a metal compound (adopted from reference [154])
4.2. The role of the backscattered energetic species in thin film growth in reactive magnetron sputtering of chromium nitride

4.2.1. Experimental procedure

CrN$_x$ (x≤1) films were deposited on Si (100), glass and graphite substrates using the deposition system described in section 3.1. The magnetic field strength was 200 Gauss at the center of the target and the zero magnetic field distance was calculated using the FEEM freeware [158] to be ~40 mm. A Cr target (cathode) with a diameter of 76 mm and a purity of 99.95% was used. The substrates were placed at 70 mm above the center of the target and were grounded. Prior to deposition the chamber was evacuated to a base pressure of $p_b \sim 10^{-6}$ mbar. The depositions were carried out in a mixed Ar - N$_2$ ambient. The N$_2$ flow ($q_{N2}$) was varied between 0-50 sccm and the Ar flow was adjusted in order to hold a constant working pressure of $8 \times 10^{-3}$ mbar. The target was operated at a constant current of 0.9 A. The substrate temperature was measured by a pt - 100 thermo-resistor clamped on the substrate holder and was found to be ~160 °C at all deposition conditions.

The composition of the films for the various $q_{N2}$ values was determined by Rutherford Backscattering Spectroscopy (RBS - section 3.3). The RBS measurements were performed for samples grown on graphite substrates in order to decrease the overlap of substrate and film spectra and to improve the resolution capability for low cross-section elements like N. The corresponding spectra were analyzed using the XRUMP [159] software.

X-Ray measurements were carried out for samples grown on Si (100) as well as glass substrates using the Philips X’Pert Diffractometer, described in section 3.4.1.5. X-Ray Reflectometry (XRR - section 3.4.1.4) was employed in order to determine the film thickness and consequently also the deposition rate. In addition, XRR was used for the calculation of the film density and the roughness both at the surface and at the interface. The crystal structure and the phase composition of the films were investigated by means of X-Ray Diffraction (XRD - section 3.4.1.2). The XRD measurements were performed in both Bragg-Brentano (BB) and grazing incidence (GI) geometry.

The residual stresses of the films were also investigated. In general, the residual stresses can be either compressive or tensile as explained in section 2.2.4. The
compressive stresses are related to the energetic bombardment and caused both by the
direct subplantation of bombarding species in the film or by the displacement of film
lattice atoms to interstitial positions [103,105]. The tensile stresses are generated due
to the shrinkage of the grain boundaries [108]. In addition, the magnitude of the
residual stresses can be affected by the growth temperature. The deposition of thin
films at temperatures different than the ambient temperature causes the so called
thermal stresses \( \sigma_{th} \) which can be calculated by the equation (2.28). The residual
stresses for the CrN films were determined by analyzing films grown on 150 \( \mu \)m glass
substrates with a biaxial modulus of 92 GPa. The substrate curvature was measured
before and after deposition and the stresses were calculated using Stoney’s formula
[129]. The effect of the residual stresses on the film strain was investigated utilizing
the \( \sin^2 \psi \) method [131] (equation (3.40)).

In order to investigate the discharge characteristics, plasma characterization was
carried out, at 40 mm from the target surface, using a cylindrical Langmuir probe
(section 3.2.1) consisting of a tungsten wire of length \( l_{pr} = 5.0 \pm 0.5 \) mm and radius \( r_{pr} = 0.05 \pm 0.01 \) mm. Voltage values \( V \) between -15 V and 15 V were applied to the
probe and the probe current \( I \) was measured over a resistor of 100 \( \Omega \). The probe \( I - V \)
curves were analyzed using the second derivative method proposed by Lieberman and
Lichtenberg [116], and plasma characteristics, such as the plasma (electron) density
and the plasma potential were obtained.

4.2.2. Simulation of the growth process

The target-discharge-film interactions upon the reactive sputtering of the CrN\(_x\)
films are depicted in Figure 4.2. It is shown that a fraction of the target surface is
covered (nitrified) by Cr-N compound. In general, it is known that in the reactive
sputtering the composition of the target surface (target coverage) and the sample
stoichiometry differ [30,160,161]. In particular, at the same deposition conditions, a
lower fraction of the reactive element atoms is expected on the target surface than in
the film, [30,160,161]. In order to support the validity of this statement, the Berg’s
model for reactive deposition was used [30]. Process characteristics, such as the target
voltage (\( V_T \)), the deposition rate (derived from XRR) and the sample stoichiometry
(derived from RBS) as a function of the \( N_2 \) flow were fitted to the rate equations, as
described by Berg et al. [30,162] and the target coverage \( \theta_i \) was obtained for the
different N$_2$ flows. Other fundamental processes during the reactive sputtering of CrN$_x$ films, such as the impingement of plasma ions (Ar$^+$ and N$_2^+$) on the target (solid arrows), are also depicted in Figure 4.2. Upon impingement these ions are neutralized via an inverse Auger process [101] and backscattered (dotted arrows). In addition, atoms from the target surface are sputtered (dashed arrows). The flux of the backscattered and sputtered species is transmitted through the plasma gas undergoing collisions with the plasma particles. Finally, the transmitted species impinge on the growing film.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.2.png}
\caption{Target-discharge-film interactions upon the reactive sputtering of CrN$_x$ films.}
\end{figure}

The dynamics of the interactions described in Figure 4.2 were studied using a three-stage simulation process based on the TRIM freeware [157], which are described in detail in the following paragraphs:

(i) The results of the analysis based on the Berg’s model were combined with TRIM computations in order to study the interactions of the plasma ions with the target. In these simulations the deposition conditions (N$_2$ flow and target voltage) which
correspond to the growth of stoichiometric CrN films were considered. In particular, a CrN \( x \) target with mass density \( \rho = \theta_i \rho^{CrN} + (1-\theta_i)\rho^{Cr} \) was considered. Here \( x = \theta_i \) is the target coverage at the deposition conditions of CrN films, calculated by the analysis based on the Berg’s model. In addition, \( \rho^{Cr} \) and \( \rho^{CrN} \) are the bulk densities of Cr [163] and CrN [164], respectively. Upon incidence of the Ar\(^+\) and the \( \text{N}_2^+ \) ions on the CrN\( x \) target the backscattered particles were studied. The energy of the incident Ar\(^+\) and \( \text{N}_2^+ \) ions was considered to be equal to the target voltage, i.e. \( eV_T \). Furthermore, the \( \text{N}_2^+ \) ions are treated according to Wang et al. [156], who showed that the \( \text{N}_2^+ \) ions with an energy \( eV_T \) much higher that the dissociation energy of the \( \text{N}_2 \) molecule (9.7 eV) [165,166] dissociate upon impinging on the target and are backscattered as two \( \text{N} \) neutrals (see Figure 4.2). For incident ions with energies greater than 100 eV, the dissociation probability approaches unity [156]. Therefore, we considered in our calculations that an impinging \( \text{N}_2^+ \) ion can be replaced by two \( \text{N} \) projectiles with energy \( eV_T/2 \), as proposed by Petrov et al. [101] and Wang et al. [156]. The computations provided the energy distributions of the backscattered species and their ratio, with respect to the total number of the impinging ions.

(ii) The interactions of the backscattered species with the glow discharge were studied using TRIM simulations. The glow discharge was described as a gaseous Ar-N \( \text{N}_2 \) “target”. The width of this target was 70 mm, equal to the actual target-to-substrate distance. An Ar-N\( \text{N}_2 \) target composition was considered, due to the nearly equal partial pressures of the two gases for the deposition conditions of CrN. The mass density of the Ar-N\( \text{N}_2 \) gaseous target that corresponds to a working pressure of \( 8\times10^{-3} \) mbar was calculated to be \( 1.14\times10^{-8} \) g cm\(^{-3} \). The computations provided the ratio of the transmitted species with respect to the number of the backscattered species and their energy distributions.

(iii) TRIM computations were utilized in order to study the effect of the transmitted species on the growing films. A CrN film with mass density equal to the value determined by XRR (see section 4.2.3) was considered. In these computations, the number of lattice interstitials induced per incident particle was calculated. In addition, the ratio of the impinging particles that are subplanted was determined. The subplantation is a process of shallow implantation of hyperthermal species below the growing film’s surface introduced by Lifshitz et al. [167]. The subplantation occurs
whenever the projected range of an incident bombarding particle in the film is larger than the width of the film surface [167]. A physically reasonable estimation for the width of the film surface is the thickness of the first monolayer [99]. Here the monolayer thickness was considered to be equal to the CrN primitive cell size [164].

It has to be mentioned here that the above presented simulation process merely provides a qualitative description of the target-plasma-film interactions during the reactive sputtering process. The quantities obtained by the simulations are combined with experimental findings regarding the plasma characteristics and the film properties in order to demonstrate trends in the energetic bombardment of the films and to identify the role of the backscattered energetic atoms upon film growth. For reference, the dynamics of the film-discharge-target interactions for the growth of Cr films were also studied by using the previously described analysis.

4.2.3. Results

4.2.3.1. Film and plasma properties. The variation of the film composition \( x = [\text{N}]/[\text{Cr}] \) ratio, obtained from the RBS measurements, upon the increase of \( q_{\text{N}_2} \) is presented in Figure 4.3. It was observed that the ratio \( x \) increases with increasing \( q_{\text{N}_2} \) up to \( \sim 30 \) sccm, where \( x \sim 1 \). After this point, saturation is observed, i.e. stoichiometric CrN films are obtained. The microstructure of a stoichiometric CrN film grown at \( q_{\text{N}_2} = 30 \) sccm was investigated by means of grazing incidence XRD. The corresponding GI-XRD pattern is presented in Figure 4.3. The reflections in Figure 4.3 are assigned to the rocksalt crystal structure of the CrN phase [164].

![Figure 4.3. Variation of film composition \( x = [\text{N}]/[\text{Cr}] \) ratio as a function of N\(_2\) flow \( q_{\text{N}_2} \). The vertical dotted line is guide to the eye.](image)
Other properties of the film grown at $q_{N2} = 30$ sccm, such as the density and the residual stresses were also investigated. The XRR analysis and the wafer curvature method revealed a density of 6.1 g cm$^{-3}$ ($\rho^{bulk} = 6.14$ g cm$^{-3}$ [164]) and compressive stresses of 2.66 GPa, respectively. The results are summarized in Table 4.1, where the corresponding results for pure Cr are also listed for reference.

![Figure 4.4. Grazing incidence XRD pattern of CrN film grown at $q_{N2}=30$ sccm. The reflections are assigned to the rocksalt crystal structure of the CrN phase.](image)

Alternatively, the residual stresses of the films were determined by the $d$-$\sin^2\psi$ method. The results for a CrN film grown at $q_{N2} = 30$ sccm are presented in Figure 4.5 (a). The open squares correspond to the experimental data and the dotted line to their least square linear fit. The $d$-spacing values for CrN were calculated from the angular position of the CrN (200) reflections. The negative slope of the $d$-$\sin^2\psi$ line in Figure 4.5 (a) is indicative of compressive stresses. The magnitude of the stresses was calculated by substituting the slope of the $d$-$\sin^2\psi$ line and the elastic constants of CrN [149] in equation (3.40). The calculation yielded compressive stresses of 2.32 GPa that are in good agreement with those obtained by the Stoney’s method (2.66 GPa). The solid straight line in Figure 4.5 (a) corresponds to $d^{\psi}_{hkl}$ values calculated from equation (3.40) using as $d^0_{hkl}$, i.e. $d^{\psi}_{hkl}$ for $\psi = 0^\circ$, the interplanar spacing of the (200) planes in unstrained bulk CrN crystal [164] and as $\sigma$ the residual stresses which were obtained by the wafer curvature method. This corresponds to films under in-plane biaxial stresses, according to the analysis presented by Janssen et al. [168]. Cr films were also studied with the $d$-$\sin^2\psi$ method (Figure 4.5 (b)). The analysis yielded tensile stresses of 1.33 GPa. Moreover, in both Figure 4.5 (a) and (b) the solid straight lines are shifted to lower values with respect to the $d$-spacing determined experimentally.
Finally, the plasma properties at the CrN deposition conditions \((q_{N2} = 30 \text{ sccm})\) were determined by means of Langmuir probe measurements. The plasma (electron) density, \(n_e\), was found to be \(4.8 \times 10^{15} \text{ m}^{-3}\). This value is typical for dc magnetron processes. In addition, the plasma potential, \(V_p\), was 0.25 V. Similar values were also found for the pure Ar plasma employed to grow Cr films.

![Figure 4.5](image)

**Figure 4.5.** Interplanar spacing \(d\) versus the sin\(^2\)ψ of the tilt angle ψ of the sample with respect to the Bragg-Brentano geometry for (a) CrN and (b) Cr films. The points are the experimental data and the dotted lines their least-square linear fit. The solid lines are calculated \(d_{hkl}^\prime\) values for the stress values obtained by the wafer curvature method and the \(d_{hkl}^\prime\) value for unstrained bulk CrN and Cr, respectively.

<table>
<thead>
<tr>
<th>(q_{N2}) (sccm)</th>
<th>Crystal structure/Phase</th>
<th>Density [bulk values] (gcm(^{-3}))</th>
<th>Residual stresses (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>rocksalt/CrN</td>
<td>6.1 ± 0.01 [6.14]</td>
<td>-2.66 ± 0.02</td>
</tr>
<tr>
<td>0</td>
<td>bcc/Cr</td>
<td>6.75 ± 0.02 [7.2]</td>
<td>+1.55 ± 0.02</td>
</tr>
</tbody>
</table>

**4.2.3.2. Growth process simulation.** The target coverage \(\theta_t\) at \(q_{N2} = 30 \text{ sccm}\), i.e. at the CrN growth conditions, was found by the calculations based on the model proposed by Berg et al. [30] to be \(\theta_t = 0.4\). This confirms the expectation that the N fraction on the target surface is lower than the N fraction in the sample. The calculated \(\theta_t\) value was used as composition of the Cr-N target in the TRIM computations which were employed to study the backscattered Ar and N species (stage (i) in section 4.2.2). In the same computations the target voltage, i.e. the energy of the plasma ions that
impinge on the target, was \( V_T = 504 \) V. The energy distributions of the backscattered Ar and N species, as obtained by the TRIM computations, are plotted in Figure 4.6 (a) and (c), respectively. It is evident that the backscattered N species have, in average, a higher energy than the corresponding Ar species, with respective mean energies of \( \sim 63 \) eV and \( \sim 11 \) eV. Furthermore, backscattering ratios \( (R_{\text{back}}) \) of \( \sim 3 \% \) and \( \sim 13 \% \) were calculated for Ar and N species, respectively. The results presented above are summarized in Table 4.2. It should be pointed out here that for the calculations of the target coverage, which is used in stage (i) of the simulation procedure, the contribution of the \( \text{N}_2^+ \) and \( \text{N}^+ \) ions to the sputtering process [160], as well as the implantation of the reactive gas ions in the target [161] were not considered. This affects the accuracy of the calculated \( \theta_t \) value [160,161], which in turn determines the average mass of the target atoms and consequently, affects the energy of the backscattered species [101,156], as further discussed in section 4.2.4. However, the same \( \theta_t \) values are used to study both Ar and N backscattered atoms (see section 4.2.2). As a result, the previously presented trends for the energy of these species will be the same irrespective of the target coverage considered. Simulations of the interactions of the backscattered species with the plasma (stage (ii) of the simulation procedure) revealed transmission ratios, \( R_{\text{tr}} \), with respect to the number of the backscattered neutrals, of \( \sim 40 \% \) and \( \sim 80 \% \) for the Ar and N species, respectively. The energy distributions for the transmitted Ar and N species are presented in Figure 4.6 (b) and (d), respectively. Similarly to the backscattered species, the transmitted N species have in average higher energies than the transmitted Ar species, with calculated mean values \( (E_{\text{tr}}) \sim 57 \) eV and \( \sim 10 \) eV, respectively. The results for the transmitted species are summarized in Table 4.3. Finally, simulations of the effect of the transmitted species on the growing film showed that the Ar species have a subplantation ratio of \( \sim 0.3 \% \) and do not induce lattice interstitials. On the other hand, the N species have a much higher subplantation ratio of \( \sim 48 \% \) and induce 0.4 interstitials per impinging neutral. It shall be pointed out here that the subplantation ratio strongly depends on the monolayer thickness. The latter, in turn, depends on the orientation of the crystallographic planes which are considered. In the present calculations, the goal is to compare the subplantation ratio of the N and the Ar species in a CrN film. For this reason, the size of the primitive CrN cell is used as a
monolayer thickness. These results are summarized in Table 4.4. In all cases (Table 4.2-4.4) the corresponding results for Cr films are also listed for reference.

Table 4.2. Results of TRIM computations for the interactions of the plasma ions with Cr-N and Cr targets. $R_{\text{back}}$ is the ratio of the backscattered species with respect to the number of the impinging ions and $E_{\text{back}}$ their energy.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{back}}$</th>
<th>$E_{\text{back}}$ (eV)</th>
<th>$R_{\text{back}}$</th>
<th>$E_{\text{back}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-N</td>
<td>0.02695</td>
<td>11.74</td>
<td>0.1337</td>
<td>63.19</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0361</td>
<td>9.48</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3. Results of TRIM computations for the interactions of the backscattered species with the plasma. $R_{\text{tr}}$ is the ratio of the transmitted species with respect to the number of the backscattered species and $E_{\text{tr}}$ their energy.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{tr}}$</th>
<th>$E_{\text{tr}}$ (eV)</th>
<th>$R_{\text{tr}}$</th>
<th>$E_{\text{tr}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN</td>
<td>0.402</td>
<td>9.99</td>
<td>0.8034</td>
<td>57.97</td>
</tr>
<tr>
<td>Cr</td>
<td>0.423</td>
<td>10.76</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4. Results of TRIM computations regarding the effect of the transmitted neutral species on the film. $R_{\text{sub}}$ is the subplantation ratio of the impinging species in the film and $I$ the number of lattice interstitials that they induce.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{sub}}$</th>
<th>$I$ (/species)</th>
<th>$R_{\text{sub}}$</th>
<th>$I$ (/species)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN</td>
<td>0.0322</td>
<td>0</td>
<td>0.4865</td>
<td>0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>0.12</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.6. Energy distribution of (a) backscattered Ar, (b) transmitted Ar (c) backscattered N and (d) transmitted N species as provided by the TRIM computations.

4.2.4. Discussion

It was shown in section 4.2.3 that CrN films exhibit high compressive stresses and a density similar to the bulk value. These properties are typical for films grown
under energetic bombardment, e.g. for films grown on negatively biased substrates [151]. In the depositions described in this section, all substrates were grounded. As a consequence, the energy that ionized particles gain upon deposition is $eV_p$, where $V_p$ is the plasma potential which was determined to be 0.25 V. Furthermore, the number of the ionized species in a dc magnetron sputtering discharge is very low (< 1%) [169]. In addition, it is known that the mean energy of the sputtered particles ranges from 2 to 6 eV [170-173] and the majority of them are thermalized. Therefore, the observed CrN film properties cannot be attributed to bombardment by plasma ions or sputtered atoms. Moreover, from equation (2.31) the thermal stresses of the CrN films can be calculated. Using the growth temperature of 160 °C, the elastic constants of CrN [149], and the thermal expansion coefficient for Si [155] and CrN [174], compressive thermal stresses of 0.02 GPa were calculated. This value is significantly lower than the value of the measured compressive stresses (2.66 GPa). Hence, a different mechanism has to be invoked, in order to explain the observed film properties.

TRIM computations showed that the N$_2^+$ species which are backscattered from the target in the form of atomic N have a significantly higher energy than the backscattered Ar species. These findings can be understood within a binary collision model, which describes the normal incidence of a moving plasma ion on a stationary target atom. In particular, the ratio of the energy transferred to the backscattered ion ($E_b$) with respect to the energy of the incident ion ($E_i$) is given by the equation,

$$\frac{E_b}{E_i} = \left(\frac{m_i - m_L}{m_i + m_t}\right)^2 \quad (4.1)$$

Here $m_i$ and $m_t$ are the masses of the impinging ions and the target atoms respectively. By using the atomic masses $m_{Ar} = 40$ amu and $m_N = 14$ amu for the ions and $m_{CrN0.4} = (m_{Cr}+0.4m_N)/1.4 = 41.14$ amu for the CrN$_{0.4}$ target, we have calculated that the energy transfer ratio for Ar is 1 %, while the transfer ratio for N is 24 %. The results based on the binary collision model are consistent with the results obtained by the simulations. The significantly higher energy of the backscattered N species is due to their relatively smaller mass in comparison to the mass of the Ar species, with respect to the mass of the target atoms. In addition, the trends which are manifested by the TRIM simulations and the binary collision model are also in good agreement with earlier results reported by Petrov et al. [101].
The interaction of the backscattered particles with the plasma species can also be elucidated by employing the same collision model. In that case the energy loss of a backscattered particle with energy $E_i$ and mass $m_i$ upon collision with a stationary plasma particle with mass $m_t$ is given by the equation,

$$\frac{E_i}{E_t} = \frac{4m_i m_t}{(m_i + m_t)^2}$$  \hspace{1cm} (4.2)

where $E_t$ is the energy of the plasma particle after the collision. The calculations based on equation (4.2) showed that the energy loss for the Ar and N species is 99% and 82%, respectively. For the calculations we used the corresponding atomic masses for the Ar and N species. In addition, a mass $m_{ArN2} = (m_{Ar} + m_{N2})/2 = 34$ amu for the the Ar-N$_2$ plasma, was used. The total energy loss of a transmitted particle depends on the number of collisions that this particle undergoes moving from the target towards the growing film, which in turn depends on the mean free path for momentum transfer, $\lambda$. This is given by the equation [116],

$$\lambda = \frac{1}{4\sigma_p n_g}$$  \hspace{1cm} (4.3)

Here $n_g$ is the molecular density of the plasma gas and $\sigma_p$ the momentum transfer collision cross-section of the plasma particles. The collision cross-section depends on the size of the gas particles and in a first approximation $\sigma_p = \pi d^2$, where $d$ is the diameter of the particle. The gas density is $n_g = p/kT$, where $p = 8 \times 10^{-3}$ mbar is the sputtering pressure. By assuming that the plasma consists of Ar atoms with a diameter of 3 Å [155], a mean free path of ~13 mm was calculated. That means that the sputtered and backscattered particles undergo in average ~5 collisions as they move from the target towards the substrate, since the substrate-to-target distance is 70 mm. If we assume that the energy loss is the same for each collision, we can calculate the fraction of the initial energy that a particle possesses after the fifth collision:

$$\left(1 - \frac{E_i}{E_t}\right)^5.$$  

By using the $\frac{E_i}{E_t}$ values for backscattered Ar and N species, which were calculated from equation (4.2), it was found that N atoms posses a $1.5 \times 10^{-4}$ fraction of their initial energy. This value is higher by 7 orders of magnitude than the corresponding values for the Ar species. These findings manifest the same trends as the simulation results for the transmitted species (Table 4.3), which suggested that 40% and 80%, respectively, of the backscattered Ar and N particles are transmitted. In
particular, both the binary collision model and the simulations show that the Ar species are scattered more efficiently than the N species during their transmission through the plasma gas.

Based on the above presented analysis we suggest here that the backscattered N atoms are the major bombarding species during the growth of CrN films. In addition, it is seen that the simulation results regarding the effect of the backscattered species on the CrN films (Table 4.4) correlate well with the experimental findings. In particular, it was found that the backscattered species (mainly N) are subplanted in the film and cause interstitials. The direct subplantation and/or the displacement of lattice atoms to interstitial positions lead to out-of-plane lattice expansion [175,176] and generation of compressive stresses [98,100]. Compressive stresses were found experimentally, both by the wafer curvature and the \(d\sin^2\psi\) methods. In addition, the existence of out-of-plane lattice expansion is clearly illustrated in Figure 4.5 (a). It shall be pointed out here that the film stresses obtained both by the wafer curvature and the \(d\sin^2\psi\) methods are in-plane biaxial stresses and the out-of-plane strain that they cause is included in equation (3.40). Nevertheless, in Figure 4.5 (a) an offset of the experimental \(d_{hkl}^\psi\) values with respect to the \(d_{hkl}^\psi\) values which correspond to a biaxial stressed lattice (solid lines) is observed. This is indicative of an additional out-of-plane lattice expansion. Since the bombarding efficiency of the ionized species and sputtered atoms is low, we attribute the out-of-plane lattice strain and the compressive stresses to the bombardment by the backscattered (mainly N) plasma species.

The same effect, i.e. additional out-of-plane lattice expansion, is also observed in the case of the Cr films (Figure 4.3 (b)). However, these films exhibit tensile stresses. This contradiction can be elucidated in light of the additivity of the stress components [168], i.e. tensile stresses generated by the shrinkage of the grain boundaries [108] and compressive stresses generated by the atomic peening [102,105] are additive in nature. The dominant stress component determines the stress sign of the film. In our case, the TRIM computations show that a fraction of the backscattered Ar\(^+\) ions is subplanted in the Cr films. We argue that this is the reason for the observed out-of-plane lattice expansion and which, in turn induces a compressive stress component. On the other hand, the low deposition temperature (~160 °C), the relatively low energetic bombardment and the fact that Cr is a low mobility metal [107] can explain
the low density of the Cr films. Low density structures, on the other hand, exhibit
voids and extended grain boundaries [99], which lead to tensile stresses [108]. The
positive (tensile) stress sign in our Cr films implies that the tensile stress term caused
by the shrinkage of the grain boundaries cannot be compensated by the compressive
stress term caused by the subplantation of the backscattered Ar species.

4.3. The effect of backscattered energetic species on stress formation
and the surface morphology of reactively sputtered vanadium nitride
thin films

4.3.1. Experimental procedure
VN\(_x\) (x≤1) films were deposited on c-Si (100), glass, and graphite substrates
employing the deposition system described in section 3.1. A vanadium target
(cathode) with a diameter of 76 mm and a purity of 99.99% was used. Prior to
deposition, the chamber was evacuated to a base pressure of \(\sim 10^{-6}\) mbar. The
substrates were placed at a distance of 70 mm above the center of the target and were
grounded. Depositions were carried out for a number of Ar-N\(_2\) mixtures by varying
the N\(_2\) flow \((q_{N2})\) from 0 to 50 sccm, while the Ar flow was varied from 45 to 12
sccm, in order to hold the working pressure constant at \(8\times10^{-3}\) mbar. All depositions
were performed at a constant target current of 0.9 A.

In general, the composition of the sputtering gas in reactive sputtering affects the
target coverage, i.e. the composition of the target surface [30]. The change in the
target coverage results in changes in the target voltage [30], which in turn have
implications on the plasma species, both ionized and neutrals, and thus, on the
growing films’ properties, as explained in section 4.2. In order to elucidate this
process, the simulation procedure, described in section 4.2.2, was used. For
convenience the main stages of this simulation procedure are also described here. At
first, deposition characteristics, such as the deposition rate and the sample
stoichiometry, which were determined experimentally as functions of the N\(_2\) flow,
were fitted to the rate equations as described by Berg \etal\. [30,158] and the
dependence of the target coverage \(\theta_t\) on \(q_{N2}\) was obtained. Then, a first set of TRIM
[157] computations was performed, in order to study the incidence plasma species Ar\(^+\)
and N\(_2^+\) on the V-N target with a coverage \(\theta_t\). The energy of the Ar\(^+\) was considered to
be $eV_T$, where $V_T$ is the target voltage. The $N_2^+$ ions were treated according to Wang et al. [156] who showed that these ions are dissociated upon impingement on the target giving raise to two N projectiles. As a consequence, $N^+$ ions with energy $eV_T/2$ were considered. The same considerations were taken by Petrov et al. [101] in order to describe the incidence of $N_2^+$ ions on the target during deposition of TiN. From the computations the sputtering yields for the N and the V atoms $Y_{s}^{N}$ and $Y_{s}^{V}$, respectively, by both $Ar^+$ and $N_2^+$ ions were calculated. Moreover, the computations provided the energy of the backscattered Ar and N species and their backscattering ratio with respect to the number of the incident atoms. In these computations the target coverage and the ion energy were varied simultaneously. In order to study the effect of these two quantities on the sputtering yield separately, a second set of TRIM computations was performed. There $Y_{s}^{N}$ and $Y_{s}^{V}$ were calculated for the same ion energies, as in the first set of computations, while the V-N target coverage was kept constant at $\theta_t = 1$. Thereupon, the interactions of the backscattered species with the plasma gas were simulated by the TRIM computations. For simplicity, the plasma gas was described as an Ar-N gaseous “target”. The composition and the density of the gaseous “target” were equal to the corresponding values of the Ar-N$_2$ gas mixtures for which the depositions were performed. The results provided the energy of the backscattered species which were transmitted through the plasma gas. Finally, TRIM computations were utilized in order to study the incidence of the transmitted species on the film. V-N films with densities equal to those determined experimentally for films grown at the corresponding deposition conditions were considered and the ratio of the bombarding species which are subplanted in the film, with respect to the number of the incident species, was calculated. Here, it was considered that the subplantation occurs, whenever the vertical range of the bombarding species in the films exceeds the monolayer thickness, which was for these calculations equal to the size of the primitive cell [177]. Once again, it has to be mentioned here that the simulation procedure presented above merely provides a qualitative description of the target-plasma-film interactions during the reactive sputtering process. The calculated, by the simulations, quantities are combined with experimental findings regarding the plasma characteristics and the film properties in order to demonstrate trends in the energetic bombardment by backscattered species and investigate their effect on the growth of the VN$_x$ films.
The effect of the working gas composition on the plasma composition was investigated by means of optical emission spectroscopy (OES). Spectra were recorded in the spectral range from 200 to 935 nm using the Mechelle spectrometer equipped with an intensified charge-coupled device camera for optimized signal count (section 3.2.2). Light emission was collected using a glass fiber that was placed at 30 cm from the target surface, at an angle of 45°.

In order to study the film properties for the various deposition conditions, a number of analytical techniques were employed. These include Rutherford Backscattering Spectroscopy (RBS), which was used in order to determine the sample composition. Similarly to the CrN films (section 4.2.1), the RBS analysis was performed for VN films deposited on graphite substrates in order to improve the resolution capability for low cross-section elements like N. The RBS spectra were analyzed using the XRUMP [150] software. Furthermore, X-ray reflectometry (XRR) was used for the determination of film density and roughness both at the surface and the interface, as well as the film thickness and consequently the deposition rate. X-ray diffraction (XRD) in both Bragg-Brentano (BB) and grazing incidence (GI) geometry was employed in order to identify the phase composition and the crystalline structure of the films. Finally, in order to determine the residual stresses, films grown on glass substrates were analyzed. The curvature of the substrates before and after the deposition of the films was measured and the residual stresses were calculated using Stoney’s formula [129].

4.3.2. Results

4.3.2.1. Deposition characteristics and simulation results. The effect of the working gas composition on the target voltage $V_T$, the deposition rate $R_d$ and the sample stoichiometry is demonstrated in Figure 4.7 (a), (b) and (c), respectively. It is seen that the target voltage increased and the deposition rate decreased, as $q_{N_2}$ was increased. These changes are related to changes of the target’s surface composition, i.e. changes of the target coverage, as discussed by Berg et al. [30]. The changes in the target coverage in turn, have implications on the film composition [27]. The latter is demonstrated in Figure 4.7 (c), where the ratio $x = [N]/[V]$ increased linearly up to a $N_2$ flow of ~ 5 sccm. Above this point, the change of $x$ was less pronounced, and nearly stoichiometric films ($x \approx 1$) were deposited at $q_{N_2} > 10$ sccm.
The calculated target coverage $\theta_t$ as a function of the N$_2$ flow is presented in Figure 4.8. In the same graph the experimentally determined film composition (squares) and the curves calculated by the iteration process (dashed line) are also plotted for reference. It is seen that a fair agreement between calculated and experimental sample stoichiometry is obtained. Moreover, the increase of N$_2$ flow induced an increase of the target coverage by the V-N compound up to a value $\theta_t = 0.75$ at $q_{N2} = 30$ sccm.

The effect of the target coverage on the interactions of the plasma species with the target were studied by TRIM computations. The analysis provided a mean energy of ~ 7 eV for neutralized Ar$^+$ ions, which are backscattered as Ar species, for all deposition conditions. Furthermore, the backscattering ratio of the Ar atoms was calculated to
decrease from 3 % to 1.5 % as $q_{N\text{2}}$ increased from 3 to 30 sccm. The mean energy of the backscattered N neutrals was found to be $\sim 28$ eV, while the increase of $q_{N\text{2}}$ from 3 to 30 sccm resulted in a decrease of their backscattering ratio from 15 % to 10 %. Moreover, the analysis provided the sputtering yields for V ($Y_s^{V}$) and N ($Y_s^{N}$) both by Ar$^+$ and N$_2^+$ ions. The results are presented in Figure 4.8, where the ratio $Y_s^{N}/Y_s^{V}$ is plotted versus $q_{N\text{2}}$ (left and bottom axes). It is seen that $Y_s^{N}/Y_s^{V}$ ratio increased as $q_{N\text{2}}$ was increased. However, this increase was more pronounced for $q_{N\text{2}} < 15$ sccm, while a saturation was observed for $q_{N\text{2}} > 20$ sccm. On the other hand, no significant effect of $V_T$ on the $Y_s^{N}/Y_s^{V}$ ratio was observed, when a V-N target with constant composition was considered (right and top axes in Figure 4.9). The simulation of the transmission of the backscattered species through the plasma using the TRIM freeware revealed mean energies of $\sim 6.5$ eV and $\sim 25$ eV for Ar and N species, respectively. Finally, TRIM computations revealed that the Ar and N species had different effects on the growing films. In particular, it was found that Ar species had a subplantation ratio of $\sim 1.2$ % on the VN$_x$ films at all deposition conditions. The corresponding values for the N species were calculated to be $\sim 22$ %.

4.3.2.2. Plasma composition. A representative OES scan recorded at $q_{N\text{2}} = 40$ sccm in the spectral range from 200 to 935 nm is presented in Figure 4.10 (a). Among the emission lines presented in Figure 4.10 (a), N$^0$ lines are of significant importance, since they provide information for the atomic N in the glow discharge. Two representative N$^0$ lines at 818.49 nm and 821.62 nm [156] are depicted in the inset of Figure 4.10 (a), where the spectral range 815-825 nm is highlighted. In order to compare the N$^0$ emission intensity for various $q_{N\text{2}}$ values, the intensity of the peak at 821.62 nm was normalized with respect to the intensity of the Ar$^0$ peak at 763.52 nm [155], recorded at the same deposition conditions. This peak is designated by a solid arrow in Figure 4.10 (a). The normalized N$^0$ intensity is plotted in Figure 4.10 (b) as a function of N$_2$ flow. Almost constant values are observed up to a N$_2$ flow of 20 sccm. A steep increase in the normalized N$^0$ emission intensity is seen for $q_{N\text{2}} > 20$ sccm. In this $q_{N\text{2}}$ range values up to $\sim 20$ folds higher than the values found for $q_{N\text{2}} < 20$ sccm were obtained.
Figure 4.9. Ratio $Y_s^N/Y_s^V$ of the target sputtering yield for N ($Y_s^N$) and V atoms ($Y_s^V$) by (a) Ar$^+$ and (b) N$_2^+$ ions as a function of the N$_2$ flow (squares - left and bottom axes) and as a function of the target voltage, i.e. ion energy, for a V-N target with a coverage of $\theta_t = 1$ (circles - right and bottom axes).

4.3.2.3. Film properties. The structure, the residual stresses and the surface roughness of the VN$_x$ films were investigated as functions of the N$_2$ flow, in order to correlate the obtained film properties with the changes in the target coverage and plasma composition, manifested in the previous sections. Bragg-Brentano and grazing incidence XRD scans of a sample deposited at $q_{N2} = 3$ sccm are presented in Figure 4.11 (a) and (b), respectively. The peaks at $\sim 37.9^\circ$ and $\sim 43.9^\circ$ in Figure 4.11 were assigned to the respective (111) and (200) reflections of the rocksalt-VN phase [177]. These reflections were observed for all samples deposited at $q_{N2} > 3$ sccm. This fact in combination with the film composition (Figure 4.7 (c)) implies that a
substoichiometric rocksalt-VN$_x$ phase with a [N]/[V] ratio varying from ~ 0.8 to ~ 0.95 was formed for the deposition conditions used in this work.

The residual stresses of the VN$_x$ films as a function of $q_{N2}$ are presented in Figure 4.12 (a). It was found that the compressive stresses in films sputtered for $q_{N2} < 18$ sccm exhibited low values (maximum value ~0.8 GPa) and a weak dependency on N$_2$ flow. On the other hand, for films sputtered for $q_{N2} > 18$ sccm the compressive stresses increased with N$_2$ flow and reached a value of ~ 2.5 GPa at $q_{N2} = 30$ sccm. In Figure 4.12 (b) the surface roughness, $\sigma_s$, of films calculated from XRR measurements is plotted. It is seen that at low N$_2$ flows films with high roughness, of ~ 3.8 nm were obtained. The roughness dropped continuously with N$_2$ up to a value of ~ 1.2 nm at $q_{N2} = 20$ sccm. Above this N$_2$ flow $\sigma_s$ remained constant.

Figure 4.10. (a) OES recorded at an N$_2$ flow of 40 sccm in the spectral range 200 - 935 nm. The inset presents a highlight of this scan in the spectral range 815 - 825 nm, where representative N$^0$ emission lines at 818.49 nm and 821.62 nm are manifested. (b) Normalized N$^0$ emission intensity with respect to the emission intensity of the Ar$^0$ line at 763.52 nm as a function of the N$_2$ flow.
Figure 4.11. XRD scans of a film deposited at $q_{N2} = 3$ sccm recorded in (a) Bragg-Brentano and (b) grazing incidence geometry. The peaks at ~37.9° and ~43.9° are assigned to the (111) and (200) reflections of the rocksalt-VN phase, respectively.

4.3.3. Discussion

The increase of the residual compressive stresses and the decrease of the surface roughness with increasing $q_{N2}$ (Figure 4.12) are indicative of an increasing energetic bombardment [4]. Moreover, from the results presented in Figure 4.12, two growth modes can be recognized. In the first mode ($q_{N2} < 20$ sccm), the increase of the N$_2$ flow and of the energetic bombardment mostly affect the roughness, i.e. the surface of the films. In the second mode ($q_{N2} > 20$ sccm), the increase of $q_{N2}$ influences only the residual compressive stresses, which are a bulk characteristic of the film. These growth modes have been proposed by Greene et al. [94] and Patsalas et al. [99], when the effects of energy and the flux of positively ionized bombarding species on the properties of reactively sputtered TiN films are considered. In particular, it was shown [94,99] that when the energy of the incident ions is lower than the subplantation threshold of the material [167,178], the surface diffusion length of the adatoms is affected [4] and, therefore, the surface roughness [4,72]. On the other hand, the ions are subplanted when their energy exceeds the subplantation threshold. The latter in turn, is known to be related to the generation of residual compressive stresses [103,105,178].

In the current study the depositions were performed on grounded substrates. The energy that the positive plasma ions gain upon impingement on a grounded substrate is equal to the plasma potential, which is up to ~2 V and independent of the working gas composition for dc magnetron Ar-N$_2$ glow discharges [101]. This is also the energy range of the sputtered atoms in dc magnetron plasmas [169]. As a
consequence, neither the bombardment by the positive plasma ions nor the bombardment by the sputtered atoms can explain the existence of the two growth modes. On the other hand, the TRIM computations provided evidence that the backscattered N species have higher energies than those of the plasma ions. The number of the N species in the plasma is proportional to the intensity of the N$^0$ emission lines in Figure 4.10, as explained in section 3.2.2. In general there are two mechanisms which lead to generation of N atoms in dc magnetron sputtering discharge: (i) sputtering of N atoms from the target and (ii) dissociative neutralization of N$_2^+$ ions upon impingement on the target, which are then backscattered as N atoms [156]. The amount of the N atoms that are sputtered from the target depends on the total sputtering yield $Y_{s}^{tot}$, as well as on the $Y_{s}^{N}/Y_{s}^{V}$ ratio. The drop of the deposition rate shown in Figure 4.7 (b) implies that the target erosion rate and thus, $Y_{s}^{tot}$ decrease as the N$_2$ flow is increased. This in turn results in a decrease of the total number of V and N atoms sputtered from the target. The $Y_{s}^{N}/Y_{s}^{V}$ ratio was found by the TRIM computations to increase with increasing $q_{N2}$, while it was not significantly affected by the target voltage when the target coverage was held constant (Figure 4.9). These findings clearly show that the $Y_{s}^{N}/Y_{s}^{V}$ ratio is mainly determined by the target composition. The saturation of the $Y_{s}^{N}/Y_{s}^{V}$ ratio at $q_{N2} > 20$ sccm presented in Figure 4.9 is, therefore, consistent with the saturation of the target coverage in the same N$_2$ flow range shown in Figure 4.8. The previous analysis suggests that neither an increase of the total sputtering yield nor the preferential sputtering of N atoms can explain the increase of the N$^0$ emission intensity as N$_2$ flow is increased in Figure 4.10 (b) and in particular the steeper increase at $q_{N2} > 20$ sccm. Therefore, this increase can only be attributed to an increase of the number of the backscattered N species, which in turn indicates an increase in the flux of these species to the growing film. The non-linear dependence of the N$^0$ emission intensity and subsequently of the flux of backscattered N species on N$_2$ flow can be qualitatively explained by earlier results reported by Pertov et al. [101]. They showed that the fraction of N$_2^+$ ions during sputtering of TiN films in an Ar-N$_2$ ambient is negligibly small below a critical value of N$_2$ partial pressure (or N$_2$ flow). Only above this value considerable fractions of N$_2^+$ ions are measured, which increase exponentially with N$_2$ flow.

The analysis presented above enables us to establish two bombarding regimes. In the first regime ($q_{N2} < 20$ sccm) the backscattered N species do not contribute significantly to the energetic bombardment, since only weak N$^0$ OES intensities were
detected in this $q_{N2}$ range (Figure 4.10 (b)). As a consequence, in this regime the major bombarding species are the backscattered Ar neutrals, as well as the positive plasma ions and the sputtered atoms. The simulation results (section 4.3.2.1) showed that bombarding species with energies of several electron volts, i.e. the bombarding species in this regime, have a very low subplantation ratio. This implies that most of their energy is transferred to the surface of the growing film. In the second regime ($q_{N2} > 20$ sccm) the increase of the $N_2$ flow resulted in an increase in the flux of the backscattered N species to the growing film. This in combination with the simulation results implies that the energy which is transferred from the bombarding species to the growing film increases with increasing $q_{N2}$. In addition, the part of the energy which is dissipated in the bulk of the film is also higher, since a higher subplantation ratio was calculated for the backscattered N species. The two bombarding regimes correlate well with the two growth modes demonstrated in Figure 4.12. In particular, the low compressive stresses for $q_{N2} < 18$ sccm in Figure 4.12 (a) are consistent with the fact that most of the energy of the bombarding species affects the surface of the films. The drop of the roughness in the same $q_{N2}$ range (Figure 4.12 (b)) implies that the energy transferred to the surface of the film as $q_{N2}$ was increased [4]. Nevertheless, no evidence for an increase in the energy and the flux of bombarding species was found in this regime. On the other hand, it was shown in Figure 4.7 (b) that the deposition decreased by ~ 50 % when $q_{N2}$ was increased up to a value of 20 sccm. This means that the energy per deposited atom (adatom) increased, since the ratio of the bombarding species to the adatoms arriving on the substrate increases. This is, in turn, consistent with the drop of the surface roughness [4,72]. For films grown in the second bombarding regime ($q_{N2} > 20$ sccm) the increase of the compressive stresses correlates well with the increase of the flux of the N neutrals to the growing film with increasing $N_2$ flow and the subsequent increase of the number of the subplanted species [103,105,178].

4.4. Conclusions

In section 4.2 experimental techniques and simulations were used in order to study the role of the backscattered plasma species upon film growth in reactive magnetron sputtering of CrN. It was shown that the neutralized plasma ions that are backscattered by the target impinge on the substrate with significantly higher energy
than the corresponding ionized plasma species. In addition, it was found by simulations that the energy of backscattered of $N_2^+$ species, in form of atomic N, is significantly higher than that of the Ar species. This was explained by the lower mass of N with respect to the mass of the target atoms and the plasma species compared to that of Ar. Out-of-plane lattice strain and compressive stresses were found experimentally for the CrN films. This was attributed to the subplantation of backscattered N species, as simulations results showed. Cr films were also studied for reference. A less intense bombardment by the backscattered Ar ions, compared to the CrN films, was found by the simulations. This is consistent with the formation of underdense film and the tensile stresses found experimentally. Furthermore, simulations showed that a fraction of the backscattered Ar species is subplanted in the film. This can explain the out-of-plane lattice expansion, which was also observed experimentally for Cr films. It was argued that the positive stress of the Cr films implies that the dominant stress component is tensile and it cannot be compensated by the compressive one caused by the subplantation of the Ar species.

In section 4.3 the effect of the bombardment by backscattered Ar and N neutral species on the stress formation and the surface roughness of reactively sputtered VN$_x$ films was investigated. Based on simulation results and experimental findings two bombarding regimes of the growing films were manifested depending on the N$_2$ flow. In the first regime ($q_{N_2} < 20$) the contribution of the backscattered N species to the bombardment was not significant. The major bombarding species were backscattered Ar species, as well as plasma ions and sputtered atoms with energies of several electron volts. The simulations showed that bombarding species in this energy range had low subplantation ratio and thus, their energy was mostly transferred to the surface of the growing film. Evidences for a higher energy and a higher subplantation ratio were found for the backscattered N species, which were the major bombarding species in the second regime ($q_{N_2} > 20$ sccm). Furthermore, in this regime the increase of N$_2$ flow resulted in an increase of the flux of the N species to the growing film. These results were combined with measurements of the residual stresses and the surface roughness of the films and enabled us to establish the relationship between the bombardment by backscattered energetic species and the above mentioned film properties. Films that were grown for $q_{N_2} < 20$ sccm exhibited low compressive stresses. This fact was consistent with the low subplantation ratio of the bombarding species in this regime. In addition, a drop of the surface roughness was observed with
increasing \( q_{N_2} \). This was attributed to the increase of the energy transferred per adatom, due to the steep drop of the deposition rate, and the subsequent decrease of the adatom arrival rate. An increase of the residual compressive stresses was found when the \( N_2 \) flow was increased, for films grown at \( q_{N_2} > 20 \) sccm. This was correlated with the increase of the flux of the N atoms in this regime and the subsequent increase of the number of the subplanted species.

**Figure 4.12.** (a) Residual compressive stresses and (b) surface roughness of \( VN_x \) films as a function of \( N_2 \) flow.
5. Control, modeling and enhancement of the deposition rate in high power pulsed magnetron sputtering

5.1. Introduction

High power pulsed magnetron sputtering (HPPMS) is a promising deposition technique, as mentioned in section 2.1.6. The increased ionization of the sputtered material and the subsequent increase of ion flux towards the substrate have been shown to result in films with improved properties in comparison to those deposited by conventional sputtering techniques, such as dc magnetron sputtering (dcMS) [48]. However, the deposition rate in HPPMS has been considered to be the major drawback. Using a constant average target power, rates varying between 20% - 80% of those achieved by dcMS for non-reactive [47,48], as well as reactive [41,42] depositions have been reported in the literature.

This chapter deals with the issue of deposition rate in HPPMS. In section 5.2 the effect of pulse characteristics, such as the pulse frequency and the pulse duty cycle on the deposition rate in non-reactive HPPMS is investigated. In section 5.3 a theoretical description of the deposition process in a non-reactive HPPMS is presented, which enables the development of a model that explains and predicts the dependency of the deposition rate on the pulse parameters. Finally, in section 5.4 the deposition rate during reactive HPPMS is treated. In particular, the effect of the pulse parameters and the reactive gas flow on the deposition rate of zirconium oxide films is studied.

5.2. Pulse configuration effect on the discharge characteristics and the deposition rate in non-reactive high power pulsed magnetron sputtering

The deposition rate is a quantity of significant technological and industrial importance. This was a motivation for a number of workers to deal with this issue trying to unravel the reason for the lower rates achieved in HPPMS. Originally Christie [47] and then Vlcek et al. [179] developed a model that explained the loss of the deposition rate to be a result of the self-sputtering phenomenon [48], i.e.
sputtering of the target by ionized target material, as shown schematically in Figure 5.1.

![Figure 5.1. Deposition process in HPPMS and self-sputtering phenomenon, according to the model proposed by Christie (adopted from reference [47]).](image)

The self-sputtering is more pronounced in HPPMS, than in dcMS, due to the increased ionization of the sputtered species. The latter is accompanied by a target voltage ($V_T$) higher than the dcMS one. This leads to a lower average target current ($I_{Tav}$) in HPPMS, when a constant average power has to be maintained. Both the target voltage and current affect the deposition rate. In particular, $V_T$ determines the energy of the sputtering ions and thus, the sputtering yield, while $I_{Tav}$ determines the ion flux towards the target and thus, the total target erosion rate. This reveals the complexity of the process, when a constant average power is utilized.

In order to easier control and better understand the HPPMS process, a constant average target current was used for the deposition of Cr films. High power unipolar pulses of a few hundreds of kW were applied to a Cr target of 76 mm in diameter and 6 mm in thickness. Both the pulse on- and off-time ($t_{on}$ and $t_{off}$, respectively) were varied in order to obtain pulses with duty cycles ranging between ~ 1 % and ~ 10 %. Here the duty cycle $a$ is given by the ratio $\frac{t_{on}}{t_{on} + t_{off}}$. The power was supplied using an Advanced Energy Pinnacle dc power supply coupled to a SPIK 2000A pulsing unit from Melec GmbH. The target current and voltage were measured using a LEM LA205-S current transducer and a LEM CV3-1500 voltage transducer, respectively, and were monitored in a TDS 2014 digital oscilloscope (section 3.1). Depending on
the pulse configuration, peak target current densities (\(I_{Tpd}\)) ranging from 90 to 2600 mA×cm\(^{-2}\) were calculated. Films were grown at a distance of 70 mm from the target using an Ar gas of purity 99.999% and a pressure of 0.8 Pa. The film thicknesses and consequently the deposition rates were determined with Å precision using X-ray reflectometry (XRR-section 3.4.1.4). The ion flux to the growing films was quantified by measuring the ion saturation current at different deposition conditions, using a flat probe, while the plasma (electron) density was determined using a Langmuir probe (section 3.2.1). In order to investigate the changes in the plasma composition with changing deposition conditions, time-resolved optical emission spectroscopy (OES) measurements were performed using the Mechelle 5000 spectrograph, demonstrated in section 3.2.2. The light emitted by the plasma was collected by an optical fiber placed 30 mm above the target at an angle of 45°. The OES spectra were recorded by measuring the emission intensity in the spectral range from 200 nm - 900 nm, for a total time of 70 µs from the beginning of the pulse and a time resolution of 2 µs. The measurements were carried out by measuring the emission intensity corresponding to the four wavelengths 487.89, 696.53, 283.56 and 301.73 nm, representing Ar\(^+\), Ar\(^0\), Cr\(^+\), and Cr\(^0\) species \[155\], respectively.

In order to investigate the deposition rate, depositions were performed for a number of average target current values using HPPMS and dcMS. The results (not shown here) demonstrated that the HPPMS deposition rate was equal to the dcMS deposition rate for low average current values but deviated from it for higher average current values. Further analysis showed that the deposition rate changed as a function of the peak target current, even when the average target current, \(I_{Tav}\), was kept constant. This indicated that the peak target current density, \(I_{Tpd}\), was the more appropriate parameter to use for deposition rate (\(R_d\)) investigations. Figure 5.2 shows deposition rates for two HPPMS pulse configurations 50/950 and 50/2450 (i.e., \(t_{on} = 50\) µs and \(t_{off} = 950\) and 2450 µs, respectively) and for the dcMS-grown films. It is seen that a deviation from the dcMS rates (dotted lines) started at the same well defined \(I_{Tpd}\) value of \(~ 570\) mA×cm\(^{-2}\), for both pulse configurations.
Figure 5.2. The deposition rate ($R_d$) vs the target current peak density ($I_{tpd}$) for two HPPMS pulse configurations. Comparison with dc magnetron sputtering deposition rates (dotted lines) shows a rate decrease for both pulses starting at $I_{tpd}=570$ mA cm$^{-2}$.

In order to better understand the mechanisms responsible for the deposition rate loss, $I_{tpd}$ was investigated as a function of the target voltage, $V_T$. Figure 5.3 presents $I_{tpd}$ versus $V_T$ in a log-log scale, for three pulse configurations, using the same pulse on-time of 50 µs. The slopes of the $I_{tpd}$ - $V_T$ curves changed at well defined positions (knees) corresponding to the $I_{tpd}$ values of ~ 360, ~ 570 and ~ 1900 mA cm$^{-2}$. The same knee positions were found when the pulse on-time was changed to 25 µs and 100 µs (not shown). A comparison between these finding and Figure 5.2 shows that above $I_{tpd} = 570$ mA cm$^{-2}$, i.e. above the second knee of the $I_{tpd}$ - $V_T$ curve, $R_d$ falls below the dcMS value. This indicates that specific changes in the sputtering process occurred at this point, which will be further investigated in the following.

In dcMS, the relationship between the target current, $I_T$, and the target voltage, $V_T$, obeys the power law [180] $I_T = \alpha V_T^\beta$, with $\beta$ ranging between 5 < $\beta$ < 15. The corresponding value in our dcMS measurements was $\beta = 8.5$, which is in accordance with the literature [180]. In HPPMS, a similar relation between the peak target current density and the target voltage is valid, i.e., $I_{tpd} \propto V_T^\delta$. The exponent $\delta$ was determined for different regions of the $I_{tpd}$ - $V_T$ curves and for the different pulse configurations. It was found that $\delta \approx 18$ for $I_{tpd}$ lower than 360 mA cm$^{-2}$ (part 1 in Figure 5.3). This indicates that the discharge is dc-like with low plasma impedance, allowing $I_{tpd}$ to increase for a small increase of $V_T$. As $I_{tpd}$ was increased above 360 mA cm$^{-2}$ (from part 1 to part 2 in Figure 5.3), the plasma became HPPMS like with ion flux densities at the substrate reaching 20-50 times dcMS flux densities, as determined by flat probe
measurements. As a consequence, $\delta$ decreased from 18 to 1. Similar observations were made by Ehiasarian et al. [181], who proposed this to be the effect of the loss of magnetron confinement. However, in our experiments, the $\delta$ value increased further when $I_{Tpd}$ was increased (part 3), which suggests that the explanation for the slope change at this stage must lie otherwise. In order to unravel the origin of the change of the $I_{Tpd} - V_T$ slope, time resolved optical emission analysis for different plasma conditions were performed.

![Figure 5.3](image)

**Figure 5.3.** Target peak current density, $I_{Tpd}$, vs target voltage, $V_T$, for three pulse on/off time configurations. Changes in the relationship $I_{Tpd} \sim V_T^\delta$ are seen at well defined $I_{Tpd}$ values for all pulse configurations.

The optical emission spectra (OES) are displayed in Figure 5.4, where $I_{Tpd}$ is increased as we move from Figure 5.4 (a) to Figure 5.4 (d). In Figure 5.4 (a), the pulse configuration with a 50 $\mu$s on-time and a 950 $\mu$s off-time (50/950), and an average current $I_{Tav} = 0.35$ A was used. In Figure 5.4 (b), $I_{off}$ was increased to 2450 $\mu$s, i.e. the duty cycle was decreased from $\sim 5\%$ to $\sim 2\%$, while $I_{Tav}$ was kept at 0.35 A. As a consequence, $I_{Tpd}$ increased from 270 to 500 mAXcm$^{-2}$. In Figure 5.4 (c) and (d), the same pulse configuration (50/2450) was used, while the average target current, $I_{Tav}$, was increased to 1 A ($I_{Tpd} = 1600$ mAXcm$^{-2}$) and 2 A ($I_{Tpd} = 2800$ mAXcm$^{-2}$), respectively. Figure 5.4 (a) shows that the intensity of the Ar$^+$ and Ar$^0$ lines increased during the pulse on-time. However, as $I_{Tpd}$ increased (Figure 5.4 (b)- Figure 5.4 (d)), Ar$^+$ and Ar$^0$ signal intensities increased only at the beginning of the pulse ($t < 10 \mu$s) but decreased for $t > 10 \mu$s, most notably for Ar$^0$. This is an indication of the depletion of the Ar species (rarefaction [180]), especially neutrals, from the area close to the
Rossnagel and Kaufman [180] showed that during dc sputtering, the gas in front of the target is heated by collisions with the energetic sputtered atoms from the target, resulting in rarefaction. In HPPMS, rarefaction is more pronounced, since the instantaneous sputtering rate during the pulse on-time (50 µs) is 1-3 orders of magnitude higher than the dc sputtering rate. This is estimated from the magnitude of $I_{Tpd}$ which is 1-3 orders of magnitude higher than the target current density in dcMS. Furthermore, $V_T$ is generally higher in HPPMS than in dcMS resulting in particles’ energy distributions with broader high energy parts and higher average energy, as was shown by Lattemann et al. [182]. As a result, the rarefaction is enhanced further, which causes an increase of the plasma impedance and consequently an increase of the target voltage. This is illustrated in Figure 5.3, part 2, where it is seen that the $\delta$ - value in the $I_{Tpd} - V_T$ curve decreases to $\delta \sim 1$. Analysis of the corresponding regions in Figure 5.2 shows that the rarefaction of the gas species does not affect the deposition rate.

Numeric integration over the emission curves in Figure 5.4 showed that when $I_{Tpd}$ was increased by 2, 6, and 10 folds (part 2, 3, and 4, respectively), the Cr$^0$ emission count increased by 1.5, 6, and 12 folds, while the Cr$^+$ emission intensity increased by 33, 150, and 400 folds, respectively. A substantial increase of the ionization is, thus, demonstrated notably for parts 3 and 4. Ion saturation measurements revealed that for HPPMS with $I_{Tpd} = 700$ mA×cm$^{-2}$, an ion current of ~ 2 orders of magnitude higher than in a dcMS discharge was obtained. The increased ion flux is a result of the increased electron density, $n_e$, which was found to be $2.3 \times 10^{17}$ m$^{-3}$ in the substrate vicinity, which is ~ 2 orders of magnitude higher than in conventional dcMS. The substantial increase of the plasma charge density causes a decrease of the plasma impedance, and consequently, an increase of the exponent $\delta \sim 7.5$, as seen in part 3 of Figure 5.3. Furthermore, it is seen in Figure 5.2 that deposition rate decreases in this region ($I_{Tpd} > 570$ mA×cm$^{-2}$). The mechanisms behind the deposition rate loss in HPPMS have been studied by other workers [47,48] and are shown to be a result of self-sputtering (i.e., Cr performing the sputtering rather than Ar).
Figure 5.4 Temporal optical emission spectroscopy for 4 pulse on/off-time configurations during high power pulsed magnetron sputtering. The peak target current density increases from 270 in (a) to 500, 1600, and 2800 mA×cm$^{-2}$ (b), (c), and (d), respectively, resulting in an increase of the Cr$^+/\text{Cr}^0$ ratio, and indicating an increased ionization degree. Ar$^+$ and Ar$^0$ emission intensities decrease as a result of rarefaction in (b)-(d).

Finally, as the $I_{tpd}$ increased above 1900 mA×cm$^{-2}$, the target voltage increased ($V_T > 640$ V in Figure 5.3, part 4). As a result, the magnetic field was too weak to keep the highly energetic plasma particles in the vicinity of the target, leading to a loss of plasma confinement and an increase of plasma impedance as illustrated by the drop in the delta value ($\delta \approx 1.5$) in Figure 5.3.
5.3. Theoretical description and modeling of the deposition rate in a non-reactive high power pulsed magnetron sputtering discharge

5.3.1. Introduction and motivation

The target voltage \( (V_T) \) in HPPMS is higher than that in dcMS, as explained in section 5.2. The latter results in a lower average target current \( (I_{Tav}) \) in HPPMS, when a constant average power is utilized. The differences in the \( V_T \) and the \( I_{Tav} \) affect the energy and the flux, respectively, of sputtering ions and thus, the deposition rate. Moreover, in the same section it was shown that the average power, pulse frequency and pulse duty cycle crucially affect the plasma composition in the target’s vicinity. This in turn, determines the nature of the ionized species that impinge onto the target and has also implications on the deposition rate. In order to reduce the dimensionality of the problem, the use of a constant average target current was suggested. In this case the flux of the sputtering ions towards the target remained constant. This allowed for an easier control over and a better understanding of the process during the HPPMS deposition of Cr films.

In the present section a theoretical treatment of the HPPMS deposition process, when a constant \( I_{Tav} \) is used, is presented. This enables the development of a model that describes the deposition rate as a function of process parameters, such as the pulse frequency and the pulse duty cycle. Furthermore, the effect of these parameters on the deposition rate of various materials is studied experimentally. Finally, the equations of the model are fitted to the experimental data and the physical relevance of the model parameters is discussed.

5.3.2. Experimental procedure

The deposition rate was studied experimentally for copper (Cu), chromium (Cr) and carbon (C) films grown by HPPMS and dcMS, for reference. For the deposition of the films Cu, Cr and C targets with a purity of 99.95% and a diameter of 76 mm were used. The targets were operating at a constant average target current \( I_{Tav}=0.3 \) A using the experimental setup which is described in section 3.1. The films were deposited at a working pressure of \( 8 \times 10^{-3} \) mbar on c-Si (100) substrates placed at a distance of 70 mm above the target surface. For the HPPMS depositions the pulse on-
time \((t_{on})\) was kept constant at 50 µs, while the pulse frequency and duty cycle were varied by varying the pulse off-time \((t_{off})\) from 200 µs to 12000 µs.

It was shown in section 5.2 that in HPPMS the used pulse on/off time configuration affects the electrical characteristics of the target, such as the relationship between the target voltage \((V_T)\) and peak target current \((I_{Tp})\). These quantities \((V_T\) and \(I_{Tp}\)) determine the plasma-target interactions and the target composition in the target’s vicinity and have, therefore, implications on the deposition rate. In order to study these relationships, \(I_{Tp-V_T}\) curves were recorded for the C, Cr and Cu targets by varying of the average target current and the pulse off-time. Furthermore, the plasma composition in the target’s vicinity at the various deposition conditions was investigated employing time-resolved optical emission spectroscopy (OES) using the experimental procedure which is described in section 5.2. For the analysis the temporal evolution of characteristic \(\text{Ar}^0\), \(\text{Ar}^+\), target atoms \((\text{M}^0)\) and ions \((\text{M}^+)\) lines was tracked. Finally, the thickness of the films at the various deposition conditions was investigated by means of X-ray reflectometry (XRR).

5.3.3. Theoretical description of the deposition process

A schematic representation of the target-discharge interactions during sputtering is displayed in Figure 5.5. \(\text{Ar}^+\) ions with a current density \(j_{\text{Ar}^+}\) impinge on the target causing sputtering of target atoms, \(\text{M}\). A fraction of the species \(\text{M}\) is ionized close to the target and subsequently, a number of the \(\text{M}^+\) ions are attracted back to the target with a current density \(j_{\text{M}^+}\). In dcMS the target ion current consists mostly of \(\text{Ar}^+\) species, due to the low ionization of the sputtered material [160], i.e.

\[
j_{\text{AMS}} = j_{\text{AMS} \text{Ar}^+} \quad (5.1)
\]

In HPPMS the ionization of the sputtered material is considerably higher [37,183], i.e.

\[
j_{\text{NRRMS}} = j_{\text{NRRMS} \text{Ar}^+} + j_{\text{NRRMS} \text{M}^+} \quad (5.2)
\]

In general, the deposition rate \(R_d\) is proportional to the target erosion rate \(\Phi\), i.e.

\[
R_d \propto \Phi \quad (5.3)
\]

The erosion rate \(\Phi\) in turn, can be calculated as

\[
\Phi = j_i \cdot Y(E) \quad (5.4)
\]
where \( Y(E) \) is the sputtering yield, which is a function of the energy of the sputtering ions. In both dcMS and HPPMS discharges the fraction of the singly charged ions is at least one order of magnitude higher than that of the doubly charged ones [179,182]. This implies that, on average, the energy of the sputtering ions can be considered to correspond to the target voltage. Based on equation (5.4) one can derive the target erosion rates \( \Phi_{dcMS} \) and \( \Phi_{HPPMS} \):

\[
\Phi_{dcMS} = j_{dcMS} \cdot Y_{dcMS} \left( E_0 \right) \quad (5.5)
\]

where \( E_0 \) corresponds to the target voltage in dcMS mode. In dcMS the ion current mainly consists of \( \text{Ar}^+ \) ions (equation (5.1)), which implies that

\[
Y_{dcMS} \left( E \right) \approx Y_{\text{Ar}^+} \left( E \right) \quad (5.6)
\]

By combining the equations (5.1), (5.5) and (5.6) the following expression for \( \Phi_{dcMS} \) can be derived,

\[
\Phi_{dcMS} = j_{dcMS} \cdot Y_{\text{Ar}^+} \left( E_0 \right) \quad (5.7)
\]

In HPPMS the ionized sputtered species (\( M^+ \)) also contribute to the sputtering process. Thus the corresponding target erosion rate \( \Phi_{HPPMS} \) can be calculated as

\[
\Phi_{HPPMS} = j_{n_{\text{M}^+}} \cdot Y_{\text{Ar}^+} \left( E \right) + j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right) - j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right) \quad (5.8)
\]

The additional term at the right hand side of the equation (5.8) \( - j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right) \) accounts for the self-sputtering phenomenon, i.e. sputtering of the target by ionized target species. By combining the equations (5.7) and (5.8) one can calculate the following expression for the \( \frac{\Phi_{HPPMS}}{\Phi_{dcMS}} \) ratio,

\[
\frac{\Phi_{HPPMS}}{\Phi_{dcMS}} = \frac{j_{n_{\text{Ar}^+}} \cdot Y_{\text{Ar}^+} \left( E \right) + j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right) - j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right)}{j_{dcMS} \cdot Y_{\text{Ar}^+} \left( E_0 \right)} \quad (5.9)
\]

As mentioned in section 5.3.2 a constant average target current is utilized, which implies that

\[
j_{ dcMS } = j_{ HPPMS } \quad (5.10)
\]

The substitution of equation (5.10) into Eq. (5.9) yields,

\[
\frac{\Phi_{HPPMS}}{\Phi_{dcMS}} = \frac{j_{n_{\text{Ar}^+}} \cdot Y_{\text{Ar}^+} \left( E \right) + j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right) - j_{n_{\text{Ar}^+}} \cdot Y_{\text{M}^+} \left( E \right)}{j_{dcMS} \cdot Y_{\text{Ar}^+} \left( E_0 \right)} \quad (5.11)
\]

If we define the relative factions of \( \text{Ar}^+ \) ions \( M^+ \) currents as
\[ f^{Ar^+} = \frac{j_{Ar^+}}{j_{i}} = \frac{j_{Ar^+}}{j_{Ar^+} + j_{M^+}} \quad (5.12) \]

\[ f^{M^+} = \frac{j_{M^+}}{j_{i}} = \frac{j_{M^+}}{j_{Ar^+} + j_{M^+}} \quad (5.13) \]

then equation (5.11) turns to,

\[ \frac{\Phi^{HPPMS}}{\Phi^{dcMS}} = f^{Ar^+} \cdot \frac{Y^{Ar^+}(E)}{Y^{Ar^+}(E_0)} + f^{M^+} \cdot \frac{(Y^{M^+}(E)-1)}{Y^{M^+}(E_0)} \quad (5.14) \]

In the following analytical expressions for the parameters \( f^{Ar^+} \), \( f^{M^+} \), \( Y^{Ar^+}(E) \) and \( Y^{M^+}(E) \) in equation (5.14) are derived.

\[ \text{Figure 5.5. Target-plasma interactions during the sputtering process. The solid and dotted arrow indicate the average current density of } \text{Ar}^+ \text{ (} j^{Ar^+} \text{) and ionized sputtered species, } M^+ \text{ (} j^{M^+} \text{), respectively.} \]

5.3.3.1. Calculation of the target sputtering yield. An analytical expression for the sputtering yield (\( Y(E) \)) as a function of the ion energy was presented in section 2.1.1, equation (2.1). If one uses the definitions (2.2) and (2.3), the equation (2.1) can be rewritten in the following compact form,

\[ Y(E) = A \cdot E^b \quad (5.15) \]

where \( A = \frac{3}{4\pi^2} \cdot \frac{C_m}{C_0} \cdot \frac{\alpha}{1-m} \cdot \frac{1}{U_0} \) and \( b = 1 - 2m \).
In order to calculate the parameters $A$ and $b$ in equation (5.19) and to obtain analytical expressions for the sputtering yields, $Y^{Ar^+}(E)$ and $Y^{M^+}(E)$ were calculated using the TRIM freeware [157] for the three targets (C, Cr and Cu) used in this work and for ion energies between 200 and 1000 eV. These energies correspond to the typical target voltage range in dcMS and HPPMS (section 5.2). Then, the parameters $A$ and $b$ were determined by fitting the calculated sputtering yields using Levenberg-Marquardt algorithm [184,185] to the equation (5.15).

5.3.3.2. Estimation of the relative ion current fractions. The relative ion current fractions $f^{Ar^+}$ and $f^{M^+}$ depend on the ion current densities $j^{Ar^+}$ and $j^{M^+}$, as it is seen in equations (5.12) and (5.13). If $n_{Ar^+}$ and $n_{M^+}$ are the densities of the Ar$^+$ and M$^+$ ions, respectively in the target’s vicinity, the current densities $j^{Ar^+}$ and $j^{M^+}$ can be expressed as,

$$j^{Ar^+} = a_{Ar^+} \cdot n_{Ar^+} \quad (5.16)$$

$$j^{M^+} = a_{M^+} \cdot n_{M^+} \quad (5.17)$$

Here $a_{Ar^+}$ and $a_{M^+}$ are proportionality factors that account for the fraction of the Ar$^+$ and M$^+$ ions, respectively, which are re-attracted and impinge onto the target. The substitution of the equations (5.16) and (5.17) into the equations (5.12) and (5.13) yields

$$f^{Ar^+} = \frac{a_{Ar^+} \cdot n_{Ar^+}}{a_{Ar^+} \cdot n_{Ar^+} + a_{M^+} \cdot n_{M^+}} \quad (5.18)$$

$$f^{M^+} = \frac{a_{M^+} \cdot n_{M^+}}{a_{Ar^+} \cdot n_{Ar^+} + a_{M^+} \cdot n_{M^+}} \quad (5.19)$$

It is, therefore, evident from equations (5.18) and (5.19) that the quantification of the Ar$^+$ and M$^+$ ion densities is required in order to obtain analytical expressions for the relative ion current fractions $f^{Ar^+}$ and $f^{M^+}$. For this purpose the optical emission spectroscopy (OES) can be used, since the intensity Ar$^+$ and M$^+$ emission lines depends also on the density of the corresponding species, as explained in section 3.2.2. In HPPMS time-dependent spectra were obtained, as mentioned in section 5.3.2. It was observed the measured time dependent intensities $I(t)$ were strong
functions of the used pulse configuration. In order to be able to compare measurements performed at different deposition conditions, $I(t)$ curves, similar to those plotted in Figure 5.4, were integrated over the acquisition time. Based on equation (3.6) it can be shown that the integrated intensity for $\text{Ar}^+$ and $\text{M}^+$ species is equal to [119,186]

$$I_{\text{Ar}^+} = C_0 \cdot S(\lambda) \cdot n_{\text{Ar}^+} \cdot n_e \cdot X_{\text{Ar}^+} \quad (5.20)$$

$$I_{\text{M}^+} = C_0 \cdot S(\lambda) \cdot n_{\text{M}^+} \cdot n_e \cdot X_{\text{M}^+} \quad (5.21)$$

Here $C_0$ and $S(\lambda)$ are the absolute and the wavelength-dependent detector’s sensitivity. $X_{\text{Ar}^+}$ and $X_{\text{M}^+}$ are the so-called emission rate coefficients [119]. By dividing the equations (5.20) and (5.21) one can calculate the ratio $\frac{n_{\text{M}^+}}{n_{\text{Ar}^+}}$ as,

$$\frac{n_{\text{M}^+}}{n_{\text{Ar}^+}} = \frac{I_{\text{M}^+}}{I_{\text{Ar}^+}} \cdot \frac{X_{\text{Ar}^+}}{X_{\text{M}^+}} \cdot \frac{S(\lambda_{\text{Ar}^+})}{S(\lambda_{\text{M}^+})} \quad (5.22)$$

The most intense emission lines for $\text{Ar}^+$ and $\text{M}^+$ species have typical wavelengths in the range between 250 and 500 nm [155]. In this range the sensitivity $S(\lambda)$ is nearly constant [120]. This leads to the expression,

$$\frac{n_{\text{M}^+}}{n_{\text{Ar}^+}} = \frac{I_{\text{M}^+}}{I_{\text{Ar}^+}} \cdot \frac{X_{\text{Ar}^+}}{X_{\text{M}^+}} \quad (5.23)$$

which can be simplified as,

$$\frac{n_{\text{M}^+}}{n_{\text{Ar}^+}} = \frac{F}{\sigma} \quad (5.24)$$

Here $F = \frac{I_{\text{M}^+}}{I_{\text{Ar}^+}}$ and $\sigma = \frac{X_{\text{M}^+}}{X_{\text{Ar}^+}}$. The substitution of equation (5.24) into equations (5.18) and (5.19) yields,

$$f_{\text{Ar}^+} = \frac{a_{\text{Ar}^+}}{a_{\text{Ar}^+} + \frac{F}{\sigma} a_{\text{M}^+}} \quad (5.25)$$

$$f_{\text{M}^+} = \frac{F}{\sigma} \frac{a_{\text{M}^+}}{a_{\text{Ar}^+} + \frac{F}{\sigma} a_{\text{M}^+}} \quad (5.26)$$

The combination of the equations (5.14), (5.15), (5.25) and (5.26) leads to the final expression for the ratio $a = \frac{R_{\text{HPPMS}}}{R_{\text{dcMS}}}$ of the HPPMS to the dcMS deposition rate,
\[ a_d = C \left[ \frac{a_{Ar}^+}{a_{Ar}^+ + a_{M}^+} + \frac{A_{Ar}^+ E^{b_{Ar}^+}}{\sigma} \frac{a_{M}^+}{a_{M}^+ + a_{Ar}^+} \frac{(A_{M}^+ E^{b_{M}^+} - 1)}{Y^{Ar^+}(E_0)} \right] \] (5.27)

where \( C \) is a proportionality constant that links the deposition rate \( R_d \) to the target erosion rate \( \Phi \). In equation (5.27) the parameters \( Y^{Ar^+}(E_0) \), \( A_{Ar}^+ \), \( b_{Ar}^+ \), \( A_{M}^+ \), and \( b_{M}^+ \) are determined by the analysis based on the TRIM computations (section 5.3.3.1). The quantity \( F = \frac{I_{M}^+}{I_{Ar}^+} \) is measured experimentally by OES. Since, the ratio \( \frac{I_{M}^+}{I_{Ar}^+} \) depends on the pulse on/off time configuration, which in turn determines the target voltage (section 5.2), \( F \) is a function of the energy of the sputtering ions. Finally, the model parameters \( a_{Ar}^+ \), \( a_{M}^+ \), \( \sigma \) and \( C \) are calculated by fitting equation (5.17) to the experimentally measured deposition rate, using the Levenberg-Marquardt algorithm [184,185]. In order to enhance the statistical accuracy of the calculated model parameters, a number of \( Ar^+ \) and \( M^+ \) emission lines were considered for the determination of the ratio \( F = \frac{I_{M}^+}{I_{Ar}^+} \). For a given species (\( Ar^+ \) or \( M^+ \)) these lines corresponded to transitions with nearly equal excitation energy, but different maximum values of electron impact excitation cross-section [187,188].

5.3.4. Results

5.4.3.1. Target characteristics and sputtering yield. In accordance to the results presented in section 5.2, the target voltage (\( V_T \)) and the peak target current (\( I_{Tp} \)) were, in general, found to increase, when the average target current (\( I_{Tav} \)) and the pulse off-time (\( t_{off} \)) were increased. In addition, the \( V_T \) and the \( I_{Tp} \) values lay on the same curves, irrespective of the used \( t_{off} \), as shown for the C, the Cr and the Cu target in Figure 5.6.
(a), (b) and (c), respectively. This feature allowed for operation at different points on
the $V_T$-$I_{tp}$ curves and thus, film growth at different deposition conditions by varying
$I_{off}$, while $I_{tav}$ was kept constant. Furthermore, the quantities $V_T$ and $I_{tp}$ could be used,
in order to describe the utilized pulse on/off time configuration. Among them $V_T$ was
mainly used, since this quantity is equal to the energy $E$ of the sputtering ions, as
mentioned in section 5.3.2. The effect of $E$ on the sputtering ($Y^{Ar^+}$) and the self-
sputtering ($Y^{Cr^+}$) yield for a Cr target, as calculated by the TRIM computations, is
demonstrated in Figure 5.7 (open squares and circles, respectively). In the same graph
the curves that result from the fit of the equation (5.15) to the calculated values are
also presented (solid and dotted lines). In addition, the value $Y^{Ar^+}(E_0)$ in equation
(5.27), i.e. the sputtering yield during dcMS, is denoted as a horizontal dashed line.

The fitting process delivered the parameter values $A_{Ar^+} = 0.028$, $b_{Ar^+} = 0.628$,
$A_{Cr^+} = 0.012$ and $b_{Cr^+} = 0.728$. These results together with those for the C and the
Cu target are summarized in Table 5.1. There, the values $Y^{Ar^+}(E_0)$ are also presented
for convenience.
Figure 5.6. Target voltage ($V_T$) - peak target current ($I_{tp}$) curves recorded for a (a) C, (b) Cr and (c) Cu target for various average target currents and pulse on/off time configurations.

Figure 5.7. Calculated (by the TRIM computations) sputtering (squares) and self-sputtering (circles) yields for a Cr target as a function of the energy of the sputtering ions. The solid and the dotted curves resulted from the fit of the equation (5.15) to the calculated data.
Table 5.1. Values of the parameters $A_{Ar^+}$, $b_{Ar^+}$, $A_{M^+}$, $b_{M^+}$ and $Y(E_0)$, as calculated by the procedure described in section 5.3.3.1.

<table>
<thead>
<tr>
<th>Target</th>
<th>$A_{Ar^+}$</th>
<th>$b_{Ar^+}$</th>
<th>$A_{M^+}$</th>
<th>$b_{M^+}$</th>
<th>$Y(E_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0003</td>
<td>1</td>
<td>0.019</td>
<td>0.42</td>
<td>0.162</td>
</tr>
<tr>
<td>Cr</td>
<td>0.028</td>
<td>0.628</td>
<td>0.014</td>
<td>0.72</td>
<td>1.001</td>
</tr>
<tr>
<td>Cu</td>
<td>0.044</td>
<td>0.646</td>
<td>0.016</td>
<td>0.77</td>
<td>1.885</td>
</tr>
</tbody>
</table>

5.4.3.2. Plasma composition. The temporal evolution of the intensity of representative Ar$^0$ and M$^0$ lines recorded from the three targets used in this work at various $V_T$ values is presented in Figure 5.8. In the case of the C target (Figure 5.8 (a)) only Ar$^0$ lines (811.53 nm [155]) are displayed since no emission from C$^0$ species was detected in the corresponding spectra. It is seen that the Ar$^0$ intensity increased continuously with the time $t$ during the pulse on-time and reached its maximum value at a time $t = 50 \mu s$, i.e. at the end of the pulse-on time, irrespective of the target voltage applied to the target. This behavior was also observed for the Cr (Figure 5.8 (b)) and the Cu (Figure 5.8 (c)) target for emission spectra recorded at the respective $V_T$ values 390 V and 470 V. At these conditions not only the intensity of the Ar$^0$ line but also the intensity of Cr$^0$ (360.53) and Cu$^0$ (324.75 nm) lines [155] increased monotonously throughout the pulse on-time. It has to be pointed out here that these target voltages corresponded in both cases to a pulse off-time of 200 µs. Further increase of voltage applied to the Cr and the Cu target to the respective values of 544 V and 629 V did not affect the shape of the Cr$^0$ and Cu$^0$ lines. However, the temporal evolution of the Ar$^0$ intensity changed. This was found to increase and reach its maximum value at $t=10$-$15 \mu s$, while a drop was observed at $t > 15 \mu s$. Similar behavior was also observed for $V_T$ values higher that 544 V and 629 V for the Cr and Cu target, respectively (results not shown in Figure 5.8).
The changes in the deposition conditions had also implications on the intensity of the Ar\(^+\) and M\(^+\) lines. This is shown in Figure 5.9, where the integrated intensity ratio $F = \frac{I_{M^+}}{I_{Ar^+}}$ is plotted as a function of the ion energy (or $V_T$) for the three targets. For the calculation of the ratio $F(E)$ in Figure 5.9 a characteristic Ar\(^+\) emission line at a wavelength of 487.98 nm [155] was used in all cases. In the case of the C target (Figure 5.9 (a)) only one C\(^+\) line at 283.67 nm [155] was detected. On the other hand, for the Cr and the Cu target (Figure 5.9 (b) and (c), respectively) three Cr\(^+\) and Cu\(^+\) lines were, respectively, used. Their wavelengths $\lambda$ [155] together with the corresponding maximum values of the electron-impact excitation cross section ($\sigma_{exc}$) [187,188] are provided in Figure 5.9 (b) and (c). It is seen that in all cases the ratio $F$ increased with increasing ion energy. In addition, for a given target the absolute values of $F$ increased when the $\sigma_{exc}$ of the used M\(^+\) line increased. This was also the case when Ar\(^+\) lines with a lower $\sigma_{exc}$ than the line at 487.98 nm were used (not shown in Figure 5.9). Finally, the measured $F$ values for the three targets could be mathematically described by exponential-like functions. The curves that correspond to these functions are also plotted as dashed lines in Fig. 5.9.
5.4.3.3. Deposition rate and model implementation. The experimentally determined ratio $a_d = \frac{R_{HPPMS,d}}{R_{dcMS,d}}$ of the HPPMS to the dcMS deposition rate, as a function of the ion energy $E$, is presented in Fig. 5.10 (open circles). It is seen that in the case of the C target (Fig. 5.10 (a)) $a_d$ increased monotonously, when $E$ was increased and adopted values greater than the unity over the entire ion energy range. A monotonous behavior was not the case for the Cr (Fig. 5.10 (b)) and the Cu (Fig. 5.10 (c)) targets. There the $\frac{R_{HPPMS,d}}{R_{dcMS,d}}$ ratio was initially found to decrease, when the ion energy increased up to a value of ~700 eV. A further increase of $E$ resulted in an increase of $a_d$. Furthermore, the $R_{HPPMS,d}$ values obtained for the Cu were higher that the $R_{dcMS,d}$ one at all deposition conditions, as shown in Fig. 5.10 (c). In contrast, values of $a_d < 1$ were measured for the Cr target (Fig. 5.10 (b)) at ion energies between ~560 eV and ~720 eV.

The curves that resulted from the fitting of the equation (5.27) to the experimental data are also presented in Fig. 5.10 (solid lines). It can be seen that the solid lines are in good agreement with the experimental $\frac{R_{HPPMS,d}}{R_{dcMS,d}}$ values. The model parameters $C, \sigma, a_{Ar^+}$ and $a_{M^+}$ calculated by the fitting process for the various Ar$^+/M^+$ line combinations, are listed in Tables 5.2 (C), 5.3 (Cr) and 5.4 (Cu). The parameter $\sigma$ was found for the Cr and the Cu target to increase, when the electron impact excitation cross-section of the $M^+$ emission line was increased. On the other hand, the values for the parameter $C$ were similar with random statistical deviations. Finally, the factors $a_{Ar^+}$ and $a_{M^+}$ exhibited differences for the various $M^+$ emission lines, as shown in Tables III and IV. However, clear trends could be observed, depending on the target material. In particular, the ratio $\frac{a_{M^+}}{a_{Ar^+}}$ was found to be equal to 0 for the C target, increased slightly to ~0.19-0.36 for the Cr target and was significantly higher and equal to ~34-47 for the Cu target. These differences had implications on the relative ion current fractions $f_{Ar^+}$ and $f_{M^+}$. By substituting the $a_{Ar^+}$ and $a_{M^+}$ values listed in Table 5.2 into equations (5.25) and (5.26), the relative
ion fractions $f^{Ar^+} = 1$ and $f^{C^+} = 0$ were calculated for the C target. The corresponding $f^{M^+}$ values for the Cr and the Cu target are plotted as a function of the ion energy in Fig. 7 (a) and (b), respectively. It is seen that $f^{Cr^+}$ spanned from 0 to ~0.8 for ion energies between ~400 eV and ~1000 eV, while $f^{Cu^+}$ adopted values between ~0.65 and ~0.75 at $E$~500 eV and saturated at $f^{Cu^+} = 0.98$ for $E$>750 eV.

**Figure 5.9.** Measured $F = \frac{I^{M^+}}{I^{Ar^+}}$ ratio (open squares) for (a) the C, (b) the Cr and (c) the Cu target. The dashed lines correspond to the fitting of the experimental data to exponential-like functions.
Figure 5.10. Experimentally determined ratio $a_d = \frac{R_d^{\text{HPPMS}}}{R_d^{\text{dcMS}}}$ of the HPPMS to dcMS deposition rate (open circles) for (a) the C, (b) the Cr and (c) the Cu target. The solid curves correspond to the fitting of the experimental data to the equation (5.27).

Table 5.2. Values obtained for the parameters $C$, $\sigma$, $a_{Ar^+}$ and $a_{M^+}$, by fitting the equation (5.27) to the experimental data presented in Figure 5.10 (a) (C target).

<table>
<thead>
<tr>
<th>$\lambda_{C^+}$ (nm)</th>
<th>$C$</th>
<th>$\sigma$</th>
<th>$a_{Ar^+}$</th>
<th>$a_{C^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>283.67</td>
<td>1.05</td>
<td>0.09</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.3. Values obtained for the parameters $C$, $\sigma$, $a_{Ar^+}$ and $a_{M^+}$, by fitting the equation (5.27) to the experimental data presented in Figure 5.10 (b) (Cr target).

<table>
<thead>
<tr>
<th>$\lambda_{C^{+}}$/ $\sigma_{exc}^{Cr^+}$ $(10^{18}$ $cm^2)$</th>
<th>$C$</th>
<th>$\sigma$</th>
<th>$a_{Ar^+}$</th>
<th>$a_{Cr^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$283.56/84$</td>
<td>0.98</td>
<td>7.33</td>
<td>0.24</td>
<td>0.087</td>
</tr>
<tr>
<td>$284.32/72$</td>
<td>0.99</td>
<td>5.28</td>
<td>0.17</td>
<td>0.034</td>
</tr>
<tr>
<td>$285.56/49$</td>
<td>1.01</td>
<td>2.75</td>
<td>0.09</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Table 5.4. Values obtained for the parameters $C$, $\sigma$, $a_{Ar^+}$ and $a_{M^+}$ by fitting the equation (5.33) to the experimental data presented in Figure 5.10 (c) (C target).

<table>
<thead>
<tr>
<th>$\lambda_{Cu^+}$ (nm)</th>
<th>$\sigma_{exc}^{Cu^+}$ ($10^{-18}$ cm$^2$)</th>
<th>$C$</th>
<th>$\sigma$</th>
<th>$a_{Ar^+}$</th>
<th>$a_{Cu^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>404.35/0.18</td>
<td></td>
<td>3.51</td>
<td>8.71</td>
<td>0.009</td>
<td>0.43</td>
</tr>
<tr>
<td>455.59/0.09</td>
<td></td>
<td>3.63</td>
<td>3.19</td>
<td>0.015</td>
<td>0.52</td>
</tr>
<tr>
<td>483.22/0.01</td>
<td></td>
<td>3.61</td>
<td>1.11</td>
<td>0.016</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Figure 5.11. Values of relative ion current fractions $f^{Ar^+}$ and $f^{M^+}$ for (a) Cr and (b) Cu target calculated by the substitution of the $a_{Ar^+}$ and $a_{M^+}$ values from Tables 5.3 and 5.4 and of the functions $F(E)$ from Figure 5.9 into the equation (5.25) and (5.26), respectively.

These differences had implications on the relative ion current fractions $f^{Ar^+}$ and $f^{M^+}$. By substituting the $a_{Ar^+}$ and $a_{M^+}$ values listed in Table 5.2 into equations (5.25) and (5.26), the relative ion fractions $f^{Ar^+} = 1$ and $f^{C^+} = 0$ were calculated for the C target. The corresponding $f^{M^+}$ values for the Cr and the Cu target are plotted as a function of the ion energy in Figure 5.11 (a) and (b), respectively. It is
seen that $f^{Cr^+}$ spanned from 0 to ~0.8 for ion energies between ~400 eV and ~1000 eV, while $f^{Cu^+}$ adopted values between ~0.65 and ~0.75 at $E$~500 eV and saturated at $f^{Cu^+} = 0.98$ for $E$>750 eV.

5.3.5. Discussion

The values $f^{C^+} = 0$ and $f^{Ar^+} = 1$ suggest that during HPPMS of C the ion target current consisted almost exclusively of Ar\(^+\) species at all deposition conditions. This was not the case for the Cr and the Cu targets as shown in Figure 5.11. There the results are indicative of a transition from an Ar\(^+\)- to an M\(^+\)-dominated ion target current, when the energy of the sputtering ions (i.e. the peak target current) was increased. These findings are in qualitative agreement with previous studies by Vlcek et al.\[179,189,190\], which showed an increase of the relative fraction of Cu\(^+\) ions in an Ar-Cu HPPMS discharge, when the peak target current was increased. Furthermore, our analysis showed that the fraction of the Cu\(^+\) ions was on average higher than the corresponding values of the Cr\(^+\) ions. In general, the composition of the ion target current is determined by the gas composition in the target’s vicinity. In sputtering processes, depletion of Ar gas takes place in front of the target, due to collisions with the sputtered species (gas rarefaction [180]). An experimental fingerprint of the gas rarefaction in HPPMS is the decay of the emission intensity of the Ar\(^0\) lines during the pulse on-time, as shown in section 5.2. This was indeed observed for the Cr and the Cu target at voltages ($V_T$) of 544 V and 629 V, respectively (Figure 5.8). Furthermore, the degree of the rarefaction depends on the target erosion rate, which is, in turn, determined by the target current and the target sputtering yield. As explained in section 5.2 the high peak target currents ($I_{Tp}$) in HPPMS result in a much higher instantaneous target erosion rate and thus, in a more pronounced rarefaction than in dcMS. The latter results in a decreased number Ar\(^+\) ions available in front of the target which together with the higher ionization of the sputtered material leads to significantly higher M\(^+\) ion target currents. In the present investigation, the $I_{Tp}$ values for the Cr and the Cu target were found to be quite similar, as shown in Figure 5.6. On the other hand, the sputtering yield for the Cu target was calculated to be higher than that for the Cr target, as demonstrated in Table 5.1. These facts speak of a higher instantaneous erosion rate and thus, a more
pronounced gas rarefaction during the HPPMS of the Cu target in comparison to Cr. Furthermore, Cr and Cu have comparable ionization potentials (6.8 eV [191] and 7.4 eV [192], respectively) and electron impact ionization cross-sections with maximum values ~5.5 x 10^{-16} \text{ cm}^2 [191] and ~3.5 x 10^{-16} \text{ cm}^2 [192], respectively. These characteristics imply that the two materials exhibit an ionization probability in the same order of magnitude. The latter combined with the more pronounced gas rarefaction for Cu is consistent with the higher relative Cu\(^+\) ion fractions in comparison to the corresponding values for Cr\(^+\) ions. In contrary to the Cu and Cr targets, the OES results did not indicate any pronounced rarefaction for the C target. This can be attributed to the lower sputtering yield for C as compared to those for Cr and Cu (Table 5.1) and the subsequent lower target erosion rate. In addition, the ionization fraction of C during HPPMS has been reported to be in the order of ~5% [193], which is significantly lower than the values reported for Cu (~70%) [37]. The low ionization of C can be attributed to its relatively high ionization potential (11.1 eV) [194] and its low electron impact ionization cross section (~ 2×10^{-16} \text{ cm}^2) [194]. The low ionization fraction and the less pronounced gas rarefaction are consistent with the fact that the lowest values of M\(^+\) relative ion current were obtained for the C target.

Finally, the previous discussion in combination with the results presented in Tables 5.2 – 5.4 and in Figure 5.11 can explain the changes in the HPPMS deposition rate, as a function of the energy of the sputtering ions (Figure 5.10). In the case of C, the relative fraction of C\(^+\) ions in the target current was negligible at all deposition conditions. Thus, the increase of the ion energy resulted in an increase of the target sputtering yield and therefore, in an increase of the deposition rate (Figure 5.10 (a)). On the other hand, in the case of Cr and Cu, the increase of the ion energy resulted in an increase of the relative ion current fraction of Cr\(^+\) and Cu\(^+\), respectively, at the expense of the Ar\(^+\) ion current fraction. This leads to a decrease of the effective target sputtering yield, due to the self-sputtering phenomenon, and is consistent with the drop of the deposition rate presented in Figures 5.10 (b) and (c). However, for ion energy values higher than ~750 eV the calculations showed that the relative fractions of the various ions in the target current did not change significantly. The latter implies that the composition of the ion flux towards the target remained constant, while the ion energy was increased, which leads to a higher target erosion rate and is in line with the increase of the deposition rate.
5.4. Enhancement of deposition rate during reactive high power pulsed magnetron sputtering of zirconium oxide films

In the preceding sections the issue of the deposition rate during non-reactive HPPMS was treated. In reactive HPPMS the deposition rate is also affected by the target coverage [30], i.e. the chemisorption of reactive gas species on the target surface. The target coverage is a general phenomenon in reactive sputtering processes and its increase results in a drop of the deposition rate in comparison to that obtained from a non-covered (e.g. metallic) target, as explained in section 2.1.5. In addition, it was mentioned in section 2.1.5 that the increase of the target coverage leads to a higher incorporation of reactive gas species into the growing film. Therefore, growth of compound films with sufficient reactive gas incorporation and rates similar to those of metallic films can be achieved at deposition conditions which correspond to a moderate target coverage (referred to as the transition sputtering zone). In reactive dcMS the transition sputtering zone is frequently unstable [30]. This feature is particularly pronounced during reactive dcMS of metal oxides [28,154,162]. On the other hand, recent studies by Davis et al. [41] and Wallin et al. [195] have shown that reactive HPPMS of several metal oxides exhibits a better stability. In addition, Wallin et al. [195] provided a theoretical description of the deposition process, which could resemble the process stabilization during reactive HPPMS of aluminum oxide. The aim of this section is to elucidate the mechanisms which are responsible for the stabilization of the deposition process in HPPMS. For this purpose the reactive HPPMS deposition of zirconium oxide is studied experimentally. This is combined with a theoretical treatment of the plasma-target interactions and the relationship between the discharge characteristics, the process stability and the deposition rate in reactive HPPMS is explained.

Zirconium oxide (ZrO$_x$) films were grown employing HPPMS and dcMS for reference, using the experimental setup which was described in section 3.1. Depositions were performed on Si (100) wafers placed at a distance of 70 mm above the center of a Zr target of 76 mm in diameter and 99.95% in purity. The target was operated at a constant average current of $I_{\text{tav}}=0.6$ A. For the HPPMS depositions the pulse frequency and duty time were varied by choosing the pulse off-times ($t_{\text{off}}$) of 450 µs and 1450 µs, while the pulse on-time was kept constant at 50 µs. In order to grow transparent ZrO$_x$ films, O$_2$ was introduced into the chamber with flows ($q_{\text{O}_2}$)
reaching up to 3 sccm, while the Ar flow was adjusted in order to maintain a constant working pressure of $8 \times 10^{-3}$ mbar.

The effect of the deposition conditions on the target coverage and the process stability was investigated by recording the target voltage ($V_T$) as a function of $q_{O_2}$, while the thickness and thus, the deposition rate were determined by means of X-ray reflectometry (XRR). In order to elucidate the relationship between the deposition rate and the target coverage, time resolved optical emission spectroscopy (OES) was employed. Emission spectra were recorded by the Andor Mechelle 5000 spectrograph (section 3.2.2) and the intensity of a characteristic Zr$^0$ emission line (351.96 nm) [155] was tracked for a total time of 70 µs from the beginning of the pulse with a time resolution of 2 µs. The shape of the time-dependent intensity curves was found to be a strong function of the pulse on/off time configuration used. In order to facilitate comparison between the results obtained at the different pulse configurations, the measured intensity was integrated over the pulse-on time. Then, the relative variation of the target coverage as a function of the O$_2$ flow was quantified by normalizing the integrated intensities to the corresponding values measured at $q_{O_2} = 0$ sccm. The target coverage is known to affect the structure, the phase composition and the optical properties of the ZrO$_x$ films [28,162]. These properties were determined, in order to identify deposition conditions at which transparent films with the crystal structure of ZrO$_2$ are grown. The structure and the phase composition were studied by X-ray diffractometry (XRD). The optical response, i.e. the wavelength dependent refractive index $n$ and extinction coefficient $k$, were determined by spectroscopic ellipsometry using the Woolam M-2000UI device (section 3.6.4).

The $V_T$-$q_{O_2}$ curves for HPPMS and dcMS are presented in Figure 5.12. In dcMS (Figure 5.12 (a)) the increase of $q_{O_2}$ from 2.2 sccm to 2.4 sccm resulted in an abrupt increase of $V_T$ from 225 V to 260 V. This is indicative of a transition from a metallic to an oxidized target [28,30,162]. In this transition area no stable $V_T$ values could be obtained and a hysteresis was observed. In contrast, in HPPMS (Figures 5.12 (b) and (c)) a stable, hysteresis-free process was observed over the entire $q_{O_2}$ range. In addition, the target voltage was higher adopting maximum values of 324 V and 364 V for the 50/450 and the 50/1450 pulse on/off time configuration, respectively. Moreover, in HPPMS target currents ranging from several Amperes at the beginning of the pulse, up to several tens of Amperes at the end of the pulse on-time, were
measured. These corresponded to average pulse currents of ~5.8 A ($t_{off} = 450$ µs) and 
~17.8 A ($t_{off} = 1450$ µs).

![Figure 5.12](image)

**Figure 5.12.** Target voltage ($V_T$) as a function of the O$_2$ flow ($q_{O2}$) recorded for (a) dcMS and the (b) 50/450 and (c) 50/1450 pulse on/off time configurations. The closed and open symbols correspond to $V_T$ values recorded for increasing and decreasing $q_{O2}$, respectively.

The changes in $V_T$ demonstrated in Figure 5.12 affected the average target power ($P_{Tav}$), since the average target current was held constant. In order to be able to compare the deposition rates obtained at the different growth conditions, the measured deposition rates were normalized to the corresponding $P_{Tav}$ values. The normalized rates are plotted as a function of $q_{O2}$ in Figure 5.13. The closed symbols correspond to non-transparent films, while the open symbols to transparent ones (i.e. films with extinction coefficient $k<10^{-2}$ in the visible spectral range). At the minimum O$_2$ flows required for the deposition of transparent films, the respective normalized rates $1.4\times10^{-3}$ nm/Ws, $3\times10^{-3}$ nm/Ws and $1.9\times10^{-3}$ nm/Ws were calculated for dcMS, 50/450 and 50/1450 HPPMS pulse configuration. In HPPMS these rates were nearly equal to the values obtained for the corresponding metallic films ($q_{O2}=0$ sccm). In contrast, in dcMS the transparent film was deposited with a rate lower by a factor of ~3, as compared to the metallic one. Finally, analysis of the properties of the transparent films revealed that they all had the crystal structure of the monoclinic ZrO$_2$ phase [196] and exhibited similar refractive indices.
Figure 5.13. Deposition rate normalized to the average power applied to the target for films by deposited by dcMS (squares), 50/450 (circles) and 50/1450 (triangles) HPPMS configurations, as a function of the O\textsubscript{2} flow. The closed and open symbols indicate non-transparent and transparent films, respectively.

The variation of the O\textsubscript{2} flow and the pulse configuration had also implications on the relative Zr\textsuperscript{0} emission intensity, as demonstrated in Figure 5.14. Similarly to Figure 5.14, the open symbols correspond to \( q_{O2} \) values at which transparent ZrO\textsubscript{x} films are obtained. It is seen that in all cases the Zr\textsuperscript{0} emission dropped, when \( q_{O2} \) was increased. This is a typical feature in reactive sputtering processes which is attributed to the increase of the target coverage [30]. Moreover, in dcMS the relative Zr\textsuperscript{0} emission intensity was \(~0.1\) at \( q_{O2}=2.5\) sccm, where the first transparent film is deposited. The corresponding values in HPPMS were \(~0.3\) for both 50/450 and 50/1450 pulse configurations. This fact implies that in HPPMS the transparent films were grown at a lower target coverage than in dcMS and explains the higher deposition rates [30]. The deposition of films at relatively low target coverage in HPPMS was facilitated by the stabilization of the transition zone. In general, the stability of the transition zone in reactive sputtering processes is determined by the competition between the formation and the sputtering of the compound on the target surface. The formation rate of the compound is proportional to the flux of reactive gas species (\( F_{O_2} \)) to the target, which is equal to [30],

\[
F_{O_2} = \frac{p_{O_2}}{\sqrt{2k_B T m}} \tag{5.28}
\]

where \( p_{O_2} \) is the O\textsubscript{2} partial pressure, \( k_B \) is the Boltzmann’s constant, \( T \) (300 K) is the gas temperature and \( m \) (5.31 \( 10^{-27} \) Kg) is the mass of the impinging species (O\textsubscript{2}). The O\textsubscript{2} partial pressure at the onset of the transition zone has a value of \(~2\times10^{-3}\) Pa,

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according to previous measurements performed by Venkataraj et al. [28]. The substitution of this value into equation (1) yielded $\dot{F}_{O_2} = 2.8 \times 10^{16}$ species cm$^{-2}$s$^{-1}$. However, this value may be further reduced, due to the gas rarefaction (section 5.2). According to Rossnagel [197] the gas density ($n_g$) in front of the target is equal to,

$$n_g = \frac{-T_0 + (T_0^2 + \beta I)^{\frac{1}{2}}}{\gamma}$$

(5.29)

where $I$ is the target current and $T_0$ is the temperature of the chamber wall. The constants $\beta$ and $\gamma$ are functions of the bulk gas density ($n_0$), the target sputtering yield, the energy and the mass of the sputtered species. Using the values which have been proposed by Rossnagel [197] for the parameters $T_0$, $\beta$ and $\gamma$ and a target current $I$ equal to the average one (0.6 A) in equation (5.29), a $\frac{n_g}{n_0}$ ratio of 0.95 was calculated for dcMS. This value corresponds to an effective reactive gas flux of $F_{O_2}^{\text{eff}} = 2.66 \times 10^{16}$ species cm$^{-2}$s$^{-1}$. In HPPMS the same $I_{av}$ was applied, but the average currents during $t_{on}$ were $\sim 5.8$ A ($t_{off} = 450 \mu$s) and $\sim 17.8$ A ($t_{off} = 1450 \mu$s) resulting in $\frac{n_g}{n_0}$ ratios of 0.75 and 0.56 for the 50/450 and the 50/1450 pulse configuration, respectively. We consider here that the gas rarefaction affects the gas density only during the pulse on-time and therefore, the effective reactive gas flux in HPPMS is given by the expression,

$$\dot{F}_{O_2}^{\text{eff}} = \frac{n_g \cdot \dot{F}_{O_2} \cdot t_{on} + \dot{F}_{O_2} \cdot t_{off}}{t_{on} + t_{off}}$$

(5.30)

which yielded the values $2.73 \times 10^{16}$ species cm$^{-2}$s$^{-1}$ and $2.76 \times 10^{16}$ species cm$^{-2}$s$^{-1}$ for the 50/450 and 50/1450 pulse configuration, respectively.

The compound sputtering rate, $\Phi_c$, can be calculated by the equation,

$$\Phi_c = \frac{I}{qA_t}Y_c$$

(5.31)

Here $I$ is the target current, $q$ is the elementary charge, $A_t$ is the area of target surface and $Y_c$ is the sputtering yield of the compound (ZrO$_2$). The compound sputtering yield
depends on the energy of the sputtering ions \( (E) \), which is equal to the target voltage.

For a target voltage of \( \sim 250 \text{ V} \) \( (\text{i.e. } E \sim 250 \text{ eV}) \) a value \( \gamma_{\text{ZrO}_2} \sim 0.07 \frac{\text{species}}{\text{impinging ion}} \) has been calculated by Severin et al. [162] At the onset of the transition zone \( V_T \) was found to be equal to 220 V, 285 V and 320 V for dcMS, 50/450 and 50/1450 pulse configuration, respectively (figure 1). It is known that for ion energies below 500 eV the sputtering yield increases linearly with \( E \) [5]. Therefore, using as reference the compound sputtering yield at \( V_T=250 \text{ V} \), the \( \gamma_{\text{ZrO}_2} \) values 0.062 \( \frac{\text{species}}{\text{impinging ion}} \) (dcMS), 0.079 \( \frac{\text{species}}{\text{impinging ion}} \) (50/450) and 0.1 \( \frac{\text{species}}{\text{impinging ion}} \) (50/1450) were calculated. By substituting the average target current \( (I_{\text{tar}}=0.6 \text{ A}) \), the target area \( (A_t \sim 8 \text{ cm}^2) \) and the sputtering yield \( (\gamma_{\text{ZrO}_2} \sim 0.062 \text{ species/impinging ion}) \) into equation (5.31) an erosion rate \( \Phi_c = 2.4 \times 10^{16} \frac{\text{species}}{\text{cm}^2 \text{s}} \) was calculated for dcMS. The same procedure yielded the values \( 3.05 \times 10^{16} \frac{\text{species}}{\text{cm}^2 \text{s}} \) and \( 3.85 \times 10^{16} \frac{\text{species}}{\text{cm}^2 \text{s}} \) for the 50/450 and 50/1450 pulse configuration, respectively.

The previous analysis enables us to calculate the ratio of the effective compound erosion rate to the effective reactive gas flux \( \left( \frac{\Phi_{\text{C}}^{\text{eff}}}{\Phi_{\text{O}}^{\text{eff}}} \right) \). This quantity is indicative of the effect of the reactive gas on the composition of the target surface and adopts the values 0.9, 1.11 and 1.41 for dcMS, 50/450 and 50/1450 pulse configuration, respectively. These values imply that in HPPMS the compound is sputtered more efficiently than in dcMS (for the same average target current) which is consistent with the stabilization of the transition zone in HPPMS [30,162]. Moreover, it is evident from the individual \( \Phi_{\text{O}}^{\text{eff}} \) and \( \Phi_{\text{C}}^{\text{eff}} \) values that in reactive HPPMS of ZrO\(_x\) the stabilization of the transition zone is promoted by the higher compound sputtering rate in HPPMS, rather than the gas rarefaction.
Figure 5.14. Relative Zr$^0$ emission intensity as a function of the O$_2$ flow for dcMS (squares) and the 50/450 (circles) and 50/1450 (triangles) HPPMS configurations. The closed and open symbols correspond to non-transparent and transparent films, respectively.

5.5. Conclusions

In section 5.2 the reasons which lead to the loss of deposition rate in HPPMS, with respect to dcMS, were unraveled. It was explained that the target voltage, $V_T$, in HPPMS is higher than that in dcMS. This results in a lower average target current, $I_{Tav}$, in HPPMS, when a constant average target power utilized. The quantities $V_T$ and $I_{Tav}$ determine the energy and the flux, respectively, of the sputtering ions and therefore, the deposition rate. The latter revealed the complexity of the process, when a constant average target power is used. In order to reduce the dimensionality of the problem, Cr films were deposited at a constant $I_{Tav}$ employing HPPMS and dcMS. It was shown that the deposition rate in HPPMS was determined by the peak target current density applied on the target. This quantity in turn, has implications on the plasma composition in the target’s vicinity and the electrical characteristics of the glow discharge. In particular, deposition rates for Cr films equal to values achieved by dcMS were obtainable by HPPMS, up to peak target current densities $I_{Tp}$ of 570 mA$\times$cm$^{-2}$. For $I_{Tp} < 360$ mA$\times$cm$^{-2}$, the plasma was dc-like. However, as $I_{Tp}$ was increased above 360 mA$\times$cm$^{-2}$, depletion of Ar species in front of the target (rarefaction) was observed, accompanied by an increase of the discharge impedance. A further increase of the $I_{Tp}$ above 570 mA$\times$cm$^{-2}$ resulted in a substantial increase in ionization which in turn led to an increase of the plasma impedance and to a decrease of the deposition rate, due to self-sputtering. Finally, for $I_{Tp} > 1900$ mA$\times$cm$^{-2}$, the
plasma impedance was again decreased which was attributed to the loss of the magnetic confinement.

In section 5.3 a theoretical description of the deposition process in non-reactive HPPMS was presented. This led to the development of a model which could describe the deposition rate as a function of the process parameters and the target material. Moreover, the deposition rate was studied experimentally for a C, a Cr and a Cu target. It was found that the model could successfully fit the experimental data. The model equations enabled also the estimation of the relative currents of \( \text{Ar}^+ \) ions and ionized sputtered species, \( M^+ \), towards the various targets. Relatively high values of relative \( M^+ \) ion current were calculated for the Cr and the Cu target. This was considered to be consistent with the high ionization probability of these materials and the pronounced gas rarefaction, which was a result of the high sputtering yield. On the other hand, the ion flux towards the C target was calculated to consist exclusively of \( \text{Ar}^+ \) ions. This was attributed to the low ionization of C and to its low sputtering yield.

Finally, in section 5.4 it was shown that reactive HPPMS of \( \text{ZrO}_x \) leads to the stabilization of the deposition process in the transition zone and suppression of the hysteresis that is commonly observed when dcMS is used. This allows for deposition of transparent films at lower target coverage and deposition rates up to two times higher than those achieved by dcMS. The stabilization of the transition mode is attributed to the higher compound erosion rate in HPPMS than in dcMS, for the same average target current.
6. The effect of the deposition parameters on the properties of transition metal compound films deposited by high power pulsed magnetron sputtering

6.1. Introduction

High power pulsed magnetron sputtering (HPPMS) has been used over the last years for the deposition of elemental and compound films. The high fraction of ionized sputtered material during HPPMS [37,183] has been utilized in order to tailor and improve the properties of the growing films, with respect to those of films deposited by conventional sputtering techniques. Alami et al. [40] showed that Ta films deposited by HPPMS exhibited an ultradense microstructure and a very smooth surface, as opposed to films grown by dc magnetron sputtering (dcMS). In addition, HPPMS allowed for tailoring of the phase composition and enhancement of the electrical conductivity of Ta films [44]. The mechanical properties of films deposited by HPPMS have also been studied. Ehiasarian et al. [181] developed a method for pre-treatment of the substrate surface by HPPMS, which enabled the deposition of CrN films [44], as well as CrN/NbN [198] and CrAlYN/CrN [199] multilayer coatings, with exceptional adhesion, high hardness, high corrosion and wear resistance. Particular effort has been put on the growth of transparent transition metal oxides by HPPMS. Davis et al. [41] studied the growth and the properties of TiO$_2$ films deposition by HPPMS and dcMS and they found that the HPPMS-grown films exhibit higher refractive index than the dcMS ones. Similar results were reposted by Konstantinidis et al. [46] who, in addition, showed that HPPMS enabled the growth of TiO$_2$ films with the rutile crystal structure at room temperature. Glocker et al. [42] deposited ZrO$_2$ and Ta$_2$O$_5$ films both by HPPMS and mid-frequency pulsed magnetron sputtering (MFPMS). In this case the MFPMS - grown films were found to exhibit the highest refractive indices. Finally, the use of HPPMS has been recently expanded to more complicated materials. Alami et al. [45] employed HPPMS for the deposition of Ti-Si-C films and showed that the films composition can be effectively controlled by varying a number of deposition parameters, such as the substrate bias.
voltage and the substrate orientation with respect to the target. It is, therefore, evident that HPPMS allows for tailoring of a variety of film properties over a vast range. In this chapter two material systems are studied in order to demonstrate the effect of the deposition parameters on the properties of transition metal compound films deposited by HPPMS. In section 6.2 the process characteristics and the film properties upon the growth of TiO$_x$ films by HPPMS from a ceramic TiO$_{1.8}$ target are studied. In section 6.3 the growth mechanisms, the microstructure and the mechanical properties of CrN films deposited by HPPMS are investigated.

6.2 Process characteristics and the film properties upon growth of TiO$_x$ films by high power pulsed magnetron sputtering from a ceramic TiO$_{1.8}$ target

6.2.1. Introduction and motivation

Titanium oxide (TiO$_2$) is one of the most extensively investigated transition metal oxides. In bulk form TiO$_2$ is known to exist in three crystalline structures [200]; two tetragonal structures, the anatase phase and the rutile phase; and an orthorhombic structure, the brookite phase. In addition, in thin film form an amorphous structure is often obtained [200]. Depending on the crystal structure, the TiO$_2$ films exhibit a variety of attractive properties. Rutile, which has the densest structure (4.24 gcm$^{-3}$) [201], is known for its transparency in the visible spectral range and its high refractive index (up to 2.75 at 550 nm) [202]. Consequently, rutile is extensively used in optical coatings [203]. Anatase, on the other hand, exhibits interesting chemical properties and is used in photocatalytic processes [204] and gas detectors [205], as well as in self-cleaning windows [206]. In order to grow TiO$_2$ films, a number of deposition techniques, such as PVD [207,208], CVD [209] and sol-gel [210], have been employed. HPPMS has also been used for the growth of TiO$_2$ films [41,46], as already mentioned in section 6.1. In these studies [41,46] the TiO$_2$ films were grown by reactive HPPMS from a metallic Ti target and compared to reactive dcMS-grown films. However, the effects of the pulse configuration upon reactive HPPMS of TiO$_2$ on the target and discharge characteristics and the films’ properties are yet to be investigated.
In the current study, TiO$_x$ ($x > 1.8$) films are grown from a ceramic TiO$_{1.8}$ target employing HPPMS at various pulse configurations in an Ar - O$_2$ ambient. The reactive sputtering of TiO$_2$ films from a compound target exhibits some interesting features, such as improved process stability and higher deposition rates, as compared to the reactive sputtering from a metallic target [211]. The effect of the pulse configuration on the target and the plasma characteristics is studied. The structure and the surface topography of the films are investigated and their optical properties are determined. Films grown by dcMS are also studied for reference.

6.2.2. Experimental procedure

TiO$_x$ films with a thickness of 50 to 70 nm were deposited on floating Si (100) substrates, placed 70 mm above the target surface, employing HPPMS as well as dcMS for reference. Depositions were carried out from a ceramic TiO$_{1.8}$ target (diameter 76 mm). High power unipolar pulses with 50 µs on-time ($t_{on}$) and off-times ($t_{off}$) ranging between 200 µs and 2450 µs were applied to the target, resulting in pulse duty cycles ranging between 20 % and 2 %. Here the pulse duty cycle is the ratio $\frac{t_{on}}{t_{on} + t_{off}}$. In all depositions, the target was operating at a constant average current of 0.3 A. The power to the target was supplied by the experimental arrangement described in section 3.1. The target current and voltage were measured using a LEM LA205 - S current transducer and a LEM CV3 - 1500 voltage transducer, respectively, while a TDS2014 digital oscilloscope was used as a monitoring device. For the depositions an Ar - O$_2$ gas mixture (99.999 %), with an Ar flow of 44 sccm, an O$_2$ flow of 1.6 sccm and a total pressure of 0.8 Pa was used.

In the HPPMS process used in this work, the target voltage $V_T$ is constant during the pulse on-time [114]. In order to study the target characteristics, the target voltage was measured as a function of the O$_2$ flow, which was varied from 0 to 3 sccm. The Ar flow was accordingly adjusted in order to keep a constant total pressure of 0.8 Pa.

The high degree of ionization of the sputtered material in HPPMS leads to changes in the target - discharge interactions, which in turn results in changes in the discharge characteristics [39]. In order to shed light on this process, TRIM computations [148] were performed. The interactions of both the gas (Ar$^+$) and the sputtered (Ti$^+$) ionized species with the target were investigated for a TiO$_{1.8}$ target. The incidence of Ar$^+$ and Ti$^+$ ions with energies equal to the target potential, $V_T$, at
the respective deposition conditions, was simulated. The computation results provided the sputtering yields $Y_{sTi}^T$ and $Y_{sO}^O$ for Ti and O target atoms, respectively.

The effect of the pulse configuration on the plasma composition was investigated employing time-resolved optical emission spectroscopy (OES). The time-resolved OES measurements were carried out by measuring the emission intensity in the spectral range from 200 to 900 nm. The emission spectra were recorded for a total time of 70 μs from the beginning of the pulse and a time resolution of 2 μs. The temporal evolution of the intensity of three wavelengths 365.32 nm, 334.90 nm, and 844.63 nm representing the species Ti⁰, Ti⁺ and O⁰ [165], respectively, were tracked.

A number of analytical techniques were employed in order to investigate the film properties for the various deposition conditions. The composition of the films was identified by means of Rutherford backscattering spectroscopy (RBS). The RBS spectra were analyzed using the XRUMP [159] software. X-Ray Reflectometry (XRR) was employed in order to determine the film thickness and, consequently, also the deposition rate. In addition, XRR was utilized to determine the film density and the roughness both at the surface and at the interface. The structural properties of the films were investigated by means of X-Ray Diffractometry (XRD) in both the Bragg-Brentano (BB) and the grazing incidence (GI) geometries. All the X-Ray measurements were carried out using the Philips X’Pert Diffractometer (section 3.4.1.5). In order to investigate the optical properties of the films, variable angle spectroscopic ellipsometry (VASE) measurements were performed using a Woolam M - 2000UI rotating compensator ellipsometer (section 3.6.4). The ellipsometric data were recorded in the range from 0.73 to 5.13 eV, using five angles of incidence, i.e. 70°, 72°, 74°, 76° and 78°, in order to enhance the accuracy of the analysis. In general, when an optical system that consists of a transparent thin film on a bare substrate is investigated by spectroscopic ellipsometry, the so - called complex pseudodielectric function $\tilde{\varepsilon}(\omega) = <\varepsilon_1(\omega)> + i <\varepsilon_2(\omega)>$ is directly obtained by the ellipsometric measurement, as explained in section 3.6.2. Here $<\varepsilon_1(\omega)>$ and $<\varepsilon_2(\omega)>$ represent the real and the imaginary parts of the complex pseudodielectric function, respectively. The optical constants of the thin film can be derived by fitting the recorded $\tilde{\varepsilon}(\omega)$ spectrum to a proper model. The $\tilde{\varepsilon}(\omega)$ spectra of the TiOₓ films were analyzed using the WVASE32 [133] software by fitting the data to a model consisting of a TiOₓ layer, with a thickness of 50-70 nm determined by the
The optical response of the TiO$_x$ layer was described using the Tauc-Lorentz dispersion model (section 3.6.3.3). The optical response of the substrate was described using a measured spectrum of a Si (100) wafer. Furthermore, a Bruggeman layer [212] that consisted of 50 % TiO$_x$ (Tauc-Lorentz layer) and 50 % voids was added as a top layer above the Tauc-Lorentz layer. The Bruggeman layer was considered in order to describe the effect of the film surface on the measured spectra. This effect was particularly significant at high photon energies (> 4 eV) where the penetration depth of the used electromagnetic radiation in the film is small. The thickness of the Bruggeman layer was calculated by the iteration process in order to obtain the best fitting for the ellipsometric spectrum and was in most cases ~ 2 nm. In order to determine the refractive index of the films in the transparent range with high precision, the experimental data were also fitted to the Cauchy model (section 3.6.3.1).

6.2.3. Results

6.2.3.1. Process characteristics. The effect of the deposition conditions on the target characteristics is illustrated in Figure 6.1. There, the target voltage ($V_T$) is plotted as a function of the O$_2$ flow ($q_{O_2}$) for dcMS and two HPPMS configurations with an on-time of 50 µs and the off-times 450 and 1950 µs (50/450, and 50/1950). It is seen that in all the three cases, $V_T$ increased and saturated as $q_{O_2}$ was increased, corresponding to a transition from a less oxidized to a more oxidized target [213]. Furthermore, saturation took place at $q_{O_2}$ ~ 1.3 sccm for dcMS and at $q_{O_2}$ ~ 1.4 sccm and $q_{O_2}$ ~ 1.6 sccm for the HPPMS configurations 50/450 and 50/1950, respectively. In addition, it is seen in Figure 6.1 that the target voltage increased, when the duty cycle was decreased, i.e. when the pulse-off time was increased. In particular, $V_T$ increased from 480 V to 650 V upon decreasing the pulse duty cycle from 20 % to 2 %, for a constant O$_2$ flow of 1.6 sccm. It was demonstrated in section 5.2 that in HPPMS, the peak target current $I_{Tp}$ varies with changing pulse configuration. This is also the case in the present work, where for the same average target current, $I_{Tp}$ increased from 2 A to 40 A when the pulse off-time was increased. Therefore, in the following, $I_{Tp}$ will be also used as a variable describing the pulse configuration used.
Figure 6.1. Target voltage ($V_T$) versus $O_2$ flow ($q_{O2}$) for dcMS and two HPPMS (50/450 and 50/1950) configurations. The target voltage for the dcMS, HPPMS 50/450 configuration and HPPMS 50/1950 configuration saturates at $O_2$ flow values of 1.3 sccm, 1.4 sccm and 1.6 sccm, respectively, as designated by the respective vertical dashed lines 1, 2 and 3.

The increase of $V_T$, upon changing the pulse configuration, leads to an increase of the mean ion energy which may affect the target sputtering yield. This was investigated by means of TRIM computations, where the sputtering ions were $Ar^+$ and $Ti^+$ ions with energies varying between 480 eV and 650 eV, i.e. $V_T$. The $Ti^+$ ion sputtering yield was investigated here because of the high abundance of the ionized sputtered material; a property inherent to HPPMS. Moreover, the effect of self-sputtering, i.e. sputtering by the target ions [44], has been well addressed in a number of studies [44, 45] showing its effect on the target-discharge interactions in the HPPMS process. The total sputtering yield $Y_s^{total} = Y_s^{O} + Y_s^{Ti}$ and the ratio $Y_s^{O} / Y_s^{Ti}$ are plotted against the energy of the $Ar^+$ ions in Figure 6.2 (a) and against the energy of the $Ti^+$ ions in Figure 6.2 (b). It is seen that $Y_s^{total}$ ranged between 1.35 and 1.54 for $Ar^+$ ions and between 1.16 and 1.44 for $Ti^+$ ions. The $Y_s^{O} / Y_s^{Ti}$ values were in the range 4 to 3.8 and 4.5 to 4.1 for $Ar^+$ and $Ti^+$, respectively. For reference, $Y_s^{total}$ was also calculated for the dcMS deposition conditions for $V_T = 420$ V and $Ar^+$ ions and found to be 1.25. The target sputtering yield by $Ti^+$ ions was not calculated in this case, since the ionization of the sputtered Ti atoms in the dcMS glow discharge is significantly lower in comparison to the Ti ionization in the HPPMS discharge [39].
Figure 6.2. Total sputtering yield, $Y_{s,\text{total}}$, and ratio of the O to Ti atoms sputtering yields, $Y_{s,\text{O}}/Y_{s,\text{Ti}}$, as a function of the incident ion energy for (a) Ar$^+$ and (b) Ti$^+$ ions.

The plasma properties were also affected by the pulse configuration as found by time-resolved optical emission spectroscopy (OES) measurements. The time-dependent intensities of the O$^0$, Ti$^0$ and Ti$^+$ emission lines were monitored for $I_{Tp} = 31$ A and are presented in Figure 6.3 (a). The O$^0$, Ti$^0$ and Ti$^+$ emission lines were numerically integrated over the on-time for a number of $I_{Tp}$ values. The results of this analysis are plotted in Figure 6.3 (b). It is seen that the integrated intensity increased as $I_{Tp}$ was increased for all the three wavelengths. However, a steeper increase was observed for the Ti$^+$ compared to the Ti$^0$ line, which in turn exhibited a steeper increase than the O$^0$ line.
The change of the pulse configuration and the O$_2$ flow were found to have implications on the deposition rate $R_d$. Figure 6.4 shows that $R_d$ increased with $I_{Tp}$, up to a value of 14 A and dropped for $I_{Tp} > 14$ A. In all cases $R_d$ was higher, by up to 40 $\%$, than the corresponding values achieved by dcMS (horizontal dashed line in Figure 6.4). Figure 6.5 shows $R_d$ values of the TiO$_x$ films that were deposited at the pulse configuration 50/950 and $I_T = 0.3$ A versus $q_{O2}$. It is seen that $R_d$ exhibited a smooth decrease upon increasing $q_{O2}$ from 0.3 nm/sec at $q_{O2} = 0$ sccm down to 0.05 nm/sec at $q_{O2} = 3$ sccm.
Figure 6.4. Deposition rate of TiO$_x$ films deposited by HPPMS as a function of the target peak current (bottom axis) and the pulse duty cycle (top axis). The horizontal dashed line corresponds to the dcMs deposition rate.

Figure 6.5. Deposition rate of TiO$_x$ as a function of O$_2$ flow for a 50/950 HPPMS configuration.

6.2.3.2. Structure, composition and surface morphology. The XRD analysis showed that all films grown by HPPMS, as well as those grown by dcMS, were amorphous. In addition, the composition of the films was found to be TiO$_{2.2}$ in all cases. The density of the films grown by HPPMS was found to vary from 3.78 g/cm$^3$ to 3.83 g/cm$^3$ upon increasing $I_{Tp}$ from 2 A to 40 A and no significant influence of $I_{Tp}$ on the density values was observed. A density of 3.71 g/cm$^3$ was obtained for dcMS grown films. On the other hand, the increase of $I_{Tp}$ had implications on the surface roughness ($\sigma_{rms}$) of the films as presented in Figure 6.6. For the dcMS film, $\sigma_{rms}$ was $\sim$ 1.35 nm, while for the HPPMS films, $\sigma_{rms}$ decreased with $I_{Tp}$ to $\sim$ 1.1 nm for $I_{Tp} = 2$ A and to $\sim$ 0.5 nm for $I_{Tp} = 14$ A. Above this $I_{Tp}$ value, no significant variation of $\sigma_{rms}$ was observed.
Figure 6.6. Surface roughness of films grown by HPPMS as a function of the target peak current. The horizontal dashed line corresponds to the surface roughness achieved for films grown by dcMS.

6.2.3.3. Optical properties. Figure 6.7 (a) shows the $\langle \varepsilon(\omega) \rangle$ spectrum of a film grown by HPPMS using the pulse configuration 50/950. The results reveal very good agreement between the experimental data (points) and the fit based on the Tauc-Lorentz model (solid lines). In Figure 6.7 (b), the calculated optical constants of the deposited TiO$_x$ films are plotted. It is seen in Figure 6.7 (b) that a band gap ($E_g$) of ~ 3.23 eV was obtained, i.e. the films were transparent in the visible spectral range. Similar $E_g$ values between 3.17 eV and 3.27 eV were found for all films, irrespective of the pulse configuration used. The fact that the grown films were transparent up to a photon energy value of 3.27 eV enabled us to fit the spectra using the Cauchy model in the spectral range 0.73 - 2.5 eV and to determine the refractive index $n$ within an error margin of $10^{-4}$. The results showed that $n$ values between 2.45 and 2.48 at a photon energy of 2.25 eV (550 nm) were obtained for the HPPMS grown films. Here too, no significant influence of $I_{Tp}$ was observed. The corresponding value achieved for the dc sputtered films was 2.38.

6.2.4. Discussion

The results in Figure 6.3 (b) showed that the emission intensity of the Ti$^0$ line and the Ti$^0$/O$^0$ intensity ratio increased by ~ 150 % and ~ 50 %, respectively, when $I_{Tp}$ was increased from 5 A to 31 A. This implies that the number of Ti atoms sputtered from the target increased with $I_{Tp}$. Moreover, the increase of $I_{Tp}$ from 5 A to 31 A corresponded to an increase of the target voltage $V_T$ from 540 V to 600 V, i.e. the energy of the sputtering ions increased. The latter had implications on the target
sputtering yield as suggested by the TRIM simulations presented in Figure 6.2, where 
\( Y_s^{total} \) increased by \(~ 1 \% \) and \( Y_s^{O}/Y_s^{Ti} \) decreased by \(~ 4 \% \) for both \( \text{Ar}^+ \) and \( \text{Ti}^+ \) ions. However, these variations are negligible compared to the changes of the OES intensities presented in Figure 6.3 (b). Therefore, the increase of the Ti fraction in the flux of the sputtered material with increasing \( I_{Tp} \), can be explained neither by an increase of the target sputtering yield nor by preferential sputtering of Ti. Hence, a different mechanism has to be invoked in order to explain the changes in the composition of the sputtered material. The composition of the sputtered material is also affected by the target’s surface stoichiometry (target coverage) [30], which in turn influences the \( V_T \) values [30]. It was seen in Figure 6.1 that the saturation area of the \( V_T - q_{O2} \) curves shifted to higher \( q_{O2} \) values with increasing \( I_{Tp} \). This means that a higher \( \text{O}_2 \) flow is required in order to reach a certain target working point, indicating an increase of the Ti fraction on the target surface. This is consistent with the increase of the Ti fraction in the sputtered material’s flux, as manifested by the OES results. The change of the target coverage can be explained as being the effect of the gas \( \text{O}_2 \) gas rarefaction, as discussed in section 5.4.

It is seen in Figure 6.4 that an increase of \( I_{Tp} \) up to a value of 14 A led to an increase of \( R_d \). Moreover, the increase of the \( I_{Tp} \) resulted in an increase of \( V_T \) which in turn led to an increase of the \( Y_s^{total} \). This increase was determined by TRIM computations and found to be \(~ 8 \% \) and \(~ 14 \% \), with respect to the value at \( I_{Tp} = 2 \text{ A} \) and for dcMS, respectively (Figure 6.2). These findings can partially explain the increase of \( R_d \). On the other hand, \( R_d \) decreased smoothly when \( \text{O}_2 \) flow was increased, as shown in the inset of Figure 6.4. The decrease of \( R_d \) is known to be a result of the increasing target coverage by \( \text{O} \) [30]. This implies that when the \( \text{O} \) fraction on the target surface decreases and/or the Ti fraction increases, \( R_d \) increases too. In the previous paragraph, it was manifested that the Ti fraction on the target’s surface increases with increasing peak current, contributing, thus, in the increase of \( R_d \) values observed in Figure 6.4. This is consistent with the increase of the deposition rate for reactively HPPMS - grown \( \text{ZrO}_x \) films, as shown in section 5.4. However, upon further increase of \( I_{Tp} \) (above 14 A) a drop of \( R_d \) was observed (Figure 6.4). The loss of deposition rate in HPPMS has been attributed to the self-sputtering phenomenon [47,48], i.e. sputtering of the target by ionized sputtered species. It has been discussed in section 5.2 that the self-sputtering is intensified when the gas rarefaction is getting more pronounced, since in that case the fraction of the ionized
sputtered species in the target’s vicinity increases. In our case this is further enhanced by the increase of the Ti ionization with increasing $I_{\text{Tp}}$, as demonstrated in Figure 6.3 (b).

Figure 6.7. (a) Real ($\epsilon_1(\omega)$) and imaginary ($\epsilon_2(\omega)$) part of the pseudodielectric function of a sample grown by HPPMS in a 50/950 pulse configuration. The points correspond to the experimental data and the solid line to their fit employing the Tauc-Lorentz model. (b) Refractive index $n$ and extinction coefficient $k$ of a film grown by HPPMS in a 50/950 pulse configuration, derived by the fit of its measured pseudodielectric function (Fig. 5 (a)) to the Tauc-Lorentz model.

Despite the fact that the target coverage changes upon changing the pulse on/off time configuration, films with similar stoichiometries were deposited. This is consistent with the observed optical properties: In all cases films with $E_g$ values above 3.1 eV were obtained. On the other hand, other film properties, such as the density, the surface roughness and the refractive index were found to be affected by the deposition conditions. This can be attributed to the change of the energetic bombardment during film growth upon increasing $I_{\text{Tp}}$. In particular, the Ti ionization increased with $I_{\text{Tp}}$ as shown in Figure 6.3 (b), which means that the flux of Ti$^+$ ions to the growing films increased as well. The increase of the ion flux leads to an increase of the energy transferred to the film per deposited atom (adatom), which in turn leads
to an increased adatom mobility and can explain the drop of the surface roughness [4] (Figure 6.6). The increase of the Ti ionization and thus, of the Ti\(^{+}\) ion flux towards the growing film is more pronounced when the HPPMS discharge is compared to the dcMS one [39]. This can explain the higher mass density values obtained for the HPPMS films as compared to those of films grown by dcMS [4]. The higher mass density is, in turn, consistent with the higher refractive indices [123] found for the films deposited by HPPMS.

6.3. Growth and microstructure of CrN films deposited by high power pulsed magnetron sputtering.

6.3.1. Introduction and motivation

The control of the thermodynamic and the kinetic conditions during film growth can be of critical importance in order to achieve the desired microstructure, as discussed in section 2.2. For example, in films deposited by evaporation, the structure is determined by the homologous temperature, \(T/T_m\), (where \(T\) is the substrate temperature in Kelvin, and \(T_m\) is the meting temperature of the deposited material, also in Kelvin) during growth and the film microstructure can be ordered in a structure zone model [75]. When films are deposited by sputtering techniques, more sophisticated structure zone models are used [77-79], which account for the effect of the energetic bombardment. The latter is an inherent characteristic of the sputtering processes. Among the various bombarding species, ions have been found to provide added means of influencing the growing film structure [214,215]. For instance, Petrov et al. [216] found that the increase of ion energy, by increasing the substrate bias voltage, densified magnetron sputtered TiN films, decreased the average grain size and increased the compressive stresses in the coatings. In addition, Hultman et al. [100] showed that the determining factor in the structure of TiN is the ion - to - atom arrival ratio, \(J_i/J_a\), rather than ion current density or deposition rate, alone.

The present section makes an attempt at understanding the effect of the intense ionic bombardment during HPPMS on the growth and the microstructure of CrN films. CrN is known for its refractory character and its exceptional mechanical properties [2,3,217]. CrN thin films are routinely used as hard coatings, and for applications in severe environments, due to their relatively high hardness and
chemical stability. In addition, CrN behaves as a semiconductor [218-220] with the single crystal (100) CrN having an optical gap of ~0.7 eV, as has been reported by Gall et al. [219]. In this study, CrN films are deposited by unipolar HPPMS using a number of pulse on/off time configurations. The effect of the resulting peak target current on the discharge characteristics is investigated. The deposition conditions under which changes in the crystalline structures take place are identified and the resulting films’ structure is determined.

6.3.2. Experimental procedure

CrN films were deposited on Si (100) substrates placed at a distance of 70 mm from a Cr Target that has a diameter of 75 mm and a thickness of 6.3 mm. An Ar/N$_2$ gas mixture was used as working gases. Measurements of the target voltage evolution as a function of increasing N$_2$ flow were performed (not shown here) in order to determine the working point for depositions. Hence, all depositions were performed at a N$_2$ flow of 30 sccm, while the total gas pressure was 0.8 Pa. High power unipolar pulses of a few hundreds of Wcm$^{-2}$ were applied to the target with a pulse on-time of 50 µs and duty times ranging between 1.8 % and 25 %, using the experimental setup described in section 3.1 Depending on the pulse configuration, the target peak current ($I_{Tp}$) ranged from 6 to 185 A, corresponding to peak target current densities in the range between 0.15 and 4.2 Acm$^{-2}$. Films of 80 to 110 nm in thickness were deposited on grounded substrates by HPPMS for a number of peak current values (but equal average target current) and by dcMS for reference using the same average target current.

The effect of the deposition parameters on the discharge properties was studied by performing plasma measurements using a Langmuir electrostatic probe. The probe was positioned at the substrates position, 7 cm from the target, and time-resolved curves of the probe current ($I$) were recorded for each applied probe voltage ($V$) with steps of 0.5 V. The data were then processed using MATLAB software tools [221]. Finally, the electron density $n_e$, electron temperature $T_e$, as well as the plasma potential $V_p$ and the floating potential $V_f$ were determined, using the equations presented in section 3.2.1. The ion flux to the substrate was also estimated by measuring the ion saturation current using a flat probe positioned at the substrate position. In order to investigate the changes in the plasma composition with changing
deposition conditions, time-resolved optical emission spectroscopy (OES) measurements were performed, using the experimental procedure described in section 6.2. The OES measurements were carried out by measuring the emission intensity corresponding to the four wavelengths 283.56 nm, 301.73 nm, 487.89 nm, and 696.53 nm, representing \( \text{Cr}^+ \), \( \text{Cr}^0 \), \( \text{Ar}^+ \) and \( \text{Ar}^0 \) species [155], respectively.

In order to examine the film properties at the various deposition conditions, X-ray measurements were performed. The film thickness and the root mean square roughness (\( \sigma_{\text{rms}} \)), as well as film density (\( \rho_m \)) were determined using X-ray reflectometry (XRR), while the crystal structure and the phase composition of the films were evaluated using X-ray diffractometry (XRD) in both Bragg-Brentano (BB) and grazing incidence (GI) geometries. Electron microscopy both in transmission (TEM) and scanning (SEM) modes was employed, in order to investigate the films microstructure and morphology. Cross-sectional samples for SEM were prepared by cutting the samples so as to obtain a brittle fracture in the CrN films. SEM measurements were carried out on a Joel JSM-7400F microscope described in section 3.4.3. Cross-sectional TEM samples were prepared using the standard mechanical thinning procedure followed by low angle Ar ion milling at incident angles of 8° to 10° using a BalTec RES101 system. The specimens were thinned from both sides with a high tension of 5 kV and a gun current of 1 mA. TEM analysis was carried out using the Philips CM 20 transmission electron microscope, described in section 3.4.2. The film microstructure was investigated by means of Fresnel fringe analysis, in order to reveal possible porous film regions. In all imaging modes the orientation of the electron beam was parallel to the <111> direction of the Si substrate.

6.3.3. Results

6.3.3.1. Plasma analysis. The electron density \( n_e \) was measured in the substrate’s vicinity for the HPPMS discharge with the pulse configuration 50/2450 (50 µs on-time and 2450 µs off-time) and was found to reach a peak value of \( 7 \times 10^{17} \, \text{cm}^{-3} \). This value is 2 orders of magnitude higher than in the dcMS discharge (\( 4 \times 10^{15} \, \text{cm}^{-3} \)). The plasma and the floating potentials measurements presented in Figure 6.8 showed that the negative floating potential had a value of \( \sim 18 \, \text{V} \) during the pulse on-time, but decreased fast after the pulse is switched off to reach a value near zero. The plasma
potential, on the other hand, was nearly constant with a value between 1 and 2 eV. The time-dependent mean electron temperature decreased from \sim 4 eV at 20 \mu s after pulse initiation to \sim 2 eV at the end of the pulse on-time, and to 0.5 eV a few tens of \mu s after the pulse was switched off, indicating a thermalization of the plasma species. The ion flux, estimated from the ion saturation current density measurements (shown in Figure 6.8), was 2 - 3 orders of magnitude higher than in dcMS. However, because of the large distance between the target and the substrate (70 mm), a large number of the ions reached the substrate tens of \mu s after the pulse was switched off. Consequently, the accelerating voltage that the ions “feel” at the substrate - plasma sheath ranged between $\Delta V = V_p - V_f \sim 1$ V for the “late” ions and $\Delta V \sim 20$ V for the “early ones”.

**Figure 6.8.** Temporal evolution of plasma ($V_p$) and floating potential ($V_f$) calculated by the Langmuir probe measurements (left axis) and time-dependent ion saturation current measured by the flat electrostatic probe (right axis) for a 50/2450 pulse configuration. The vertical dotted line indicates the end of the pulse on-time.

OES measurements performed for both the HPPMS (50/2450 pulse configurations) and the dcMS discharges revealed that the HPPMS discharge exhibited a high emission intensity of the ionized Cr and Ar species. On the other hand, very weak Ar$^+$ and Cr$^+$ emission was seen for the dcMS discharge. The emission intensities from time resolved measurements for the Cr and Ar species were integrated over the pulse time and are presented in Figure 6.9 functions of the peak target current ($I_{Tp}$). It is seen that the emission signal of Cr$^+$ has the steepest increase of all species.
6.3.3.2. Film properties. The XRR analysis revealed changes on the film roughness \( \sigma_{\text{rms}} \) and density \( \rho_m \), when \( I_{Tp} \) was increased. Figure 6.10 shows that \( \sigma_{\text{rms}} \) decreased from the dcMS value of 2.7 nm down to a value \( \sigma_{\text{rms}} \sim 0.5 \) nm at a peak current value of \( I_{Tp} \sim 30 \) A. Further increase of the peak current did not affect the film roughness. In Figure 6.11, the film density is plotted as a function of \( I_{Tp} \). An increase of \( \rho_m \) from 5.7 gcm\(^{-3}\) (dcMS) to 6.05 gcm\(^{-3}\) can be observed for the HPPMS film grown at \( I_{Tp} \sim 20 \) A. At higher \( I_{Tp} \), no change of \( \rho_m \) was measured.
Figure 6.11. Mass density ($\rho_m$) of HPPMS - grown films as a function of the peak target current. The horizontal dashed line indicated the $\rho_m$ value for dcMS-grown films, while the horizontal dotted line corresponds to the density of the bulk CrN.

The SEM cross-sectional micrographs shown in Figure 6.12 display the film microstructure as a function $I_{Tp}$. It is seen that the dcMS film (Figure 6.12 (a)) exhibited a porous structure with columnar growth. When HPPMS was used, a distinct change in the microstructure was seen. At a low $I_{Tp}$ of 44 A (Figure 6.12 (b)), the film still exhibited a columnar structure, but the columns were smaller and the intercolumnar space was denser compared to the dcMS film. As $I_{Tp}$ was increased to 74 A, the grains became more equiaxed and the grain size decreased (Figure 6.12 (c)). The last micrograph in Figure 6.11 corresponds to a film deposited at $I_{Tp} = 180$ A. It shows a featureless structure that is best described as a nanocrystalline structure. In order to illustrate the structural transition, the observed microstructures were sketched next to the SEM micrographs. The observations made using SEM on the microstructure of the CrN films were further confirmed by TEM, as seen in Figure 6.13. There the dcMS CrN film (Figure 6.13 (a)) exhibited clearly the columnar grain growth with an underdense and porous microstructure, as revealed by the Fresnel fringes. The corresponding selected area electron diffraction pattern (SAED) is shown in the inset, which reveals the polycrystalline nature of the film. In contrast, the HPPMS CrN films (Figure 6.13 (b) and (c)) exhibited a fully dense microstructure without pores or voids as is evident from the Fresnel contrast imaging, where the Fresnel fringes were not visible. In addition, the SAED in Figure 6.13 (b) and (c) show a degradation of the film crystallinity, when $I_{Tp}$ was increased.
Figure 6.12. Cross-sectional SEM micrographs of CrN films grown by (a) dcMS and HPPMS at (b) $I_{TP} = 44$ Å, (c) $I_{TP} = 74$ Å and (d) $I_{TP} = 180$ Å. On the right-hand side schematic illustrations of the microstructures observed in the corresponding SEM are also provided.
Figure 6.13. Cross-sectional TEM micrographs of CrN films grown by (a) dcMS and HPPMS at (b) $I_{tp} = 44$ A, (c) $I_{tp} = 180$. On the right-top corner of each micrograph selected area electron diffraction patterns are also presented.

The degradation of the film crystallinity, when HPPMS was employed, was also confirmed by the XRD analysis. This is evident by the Bragg-Brentanno and grazing incidence XRD patterns presented in Figure 6.14 and 6.15, respectively. It is seen that much broader peaks were detected for the HPPMS - grown films (Figure 6.14 and 6.15 (b) - (e)) in comparison to the dcMS one (Figure 6.14 and 6.15 (a)). These peaks were assigned to the (111) and (200) reflections of the CrN phase [164]. The angular
position of the reflections in unstrained bulk CrN is designated by vertical solid lines. Moreover, it is seen in Figure 6.15 that the film grown using dcMS showed a strong (111) reflection and a much weaker (200) one. In the HPPMS films, the (200) reflection was dominant at $I_{tp} = 44$ A and was the only observed peak as $I_{tp}$ increased to 74 A and above.

![Figure 6.14. Bragg-Brentano XRD patterns recorded for CrN films deposited by (a) dcMS and HPPMS at (b) $I_{tp} = 44$ A, (c) $I_{tp} = 74$ A and (d) $I_{tp} = 120$ A (e) $I_{tp} = 180$ A.](image)

![Figure 6.15. Grazing incidence XRD patterns recorded for CrN films deposited by (a) dcMS and HPPMS at (b) $I_{tp} = 44$ A, (c) $I_{tp} = 74$ A and (d) $I_{tp} = 120$ A (e) $I_{tp} = 180$ A.](image)

6.3.4. Discussion

The plasma analyses results presented in section 6.3.3.1 revealed that an increased electron density and an increased ionization fraction were achieved during the HPPMS operation. In addition, by varying the pulse on/off time configuration and
thus, the peak target current ($I_{TP}$) different bombarding conditions during the film growth could be provided. Similarly to the results presented in section 6.2 for the TiO$_x$ films, the enhanced ionization in HPPMS had implications on the film properties and led to smoother and denser films, in comparison to the dcMS ones, as demonstrated in Figures 6.10 and 6.1q. However, no further improvement of the film properties was observed for $I_{TP} > 30$ A. More pronounced was the effect of the intense ion irradiation on the film microstructure. In particular, the dcMS - grown films exhibited a typical zone I/T structure (section 2.2), with competitive columnar growth and intercolumnar porosity. These features are common for dcMS grown films [222]. The HPPMS film structure, on the other hand, evolved from a dense columnar structure indicating zone II growth in the structure zone model scale at $I_{TP} \sim 44$ A to a structure typical for zone III growth with nanocrystalline and fully dense grains at $I_{TP} \sim 74$ A. This gradual change of the film microstructure can be explained to be the effect of the low energy/high flux ion bombardment during HPPMS which results in an interruption of the grain growth and re-nucleation [4,72], as discussed in section 2.2.

6.4 Conclusions

In section 6.2 TiO$_x$ films were deposited employing reactive HPPMS at various pulse on/off time configurations at a constant average target current. The effect of the pulse on/off configuration on the target and discharge characteristics and the films properties was investigated. Films grown by dcMS were also studied for reference. The increase of the pulse off-time, while the on-time was kept constant, resulted in an increase of the peak target current and the target voltage, which in turn led to an increase of the Ti fraction on the target surface. This was attributed to the O$_2$ gas rarefaction with increasing peak target current. In addition, the increase of the target voltage resulted in higher sputtering yield. Both the change of surface composition of the target and the increased sputtering yield resulted in a higher deposition rate for the films grown by HPPMS. The corresponding rates were higher by up to 40% than the rates achieved by dcMS. The change of the target coverage did not influence the sample stoichiometry, since films with similar composition and visible transparency were obtained at all deposition conditions. Furthermore, the HPPMS films showed lower surface roughness (up to 0.4 nm) compared to dcMS films (1.35 nm), exhibited
higher densities (up to 3.83 g cm\(^{-3}\) vs 3.71 g cm\(^{-3}\) for dcMS) and higher refractive indices (up to 2.48 vs 2.38 at 550 nm for dcMS). The enhancement of the film properties was already achieved at moderate peak target current values, where the deposition rates are significantly higher than the corresponding dcMS rates.

In section 6.3 CrN films were deposited reactively by HPPMS and dcMS. Plasma analysis revealed that the electron density in the substrate’s vicinity during HPPMS was \(\sim 2\) orders of magnitude higher than in dcMS, resulting in a \(2 - 3\) orders of magnitude higher ion current towards the growing film. Furthermore, the ionization and thus, the energetic bombardment during HPPMS could be increased by increasing the peak current applied to the target. The increased ionization in HPPMS allowed for deposition of smoother and denser films than those deposited by dcMS. The density was further increased and surface roughness was decreased when \(I_{Tp}\) was increased up to a value of \(\sim 20\) A and \(\sim 30\) A, respectively, while no improvement of these properties was observed at higher \(I_{Tp}\) values. More pronounced was the effect of HPPMS on the microstructure of the CrN films. The dcMS grown films exhibited a polycrystalline, columnar structure. The increase of \(I_{Tp}\) during HPPMS deposition resulted in a gradual transition to ultra dense nanocrystalline films.
7. Outlook

Although dc magnetron sputtering is a well established deposition technique and despite the existence of a great amount of relevant literature, the analysis presented in chapter 4 revealed that there are still issues which are unclear or largely not addressed. In particular, in chapter 4 it was manifested that N species, which are generated from dissociation and backscattering of N$_2^+$ ions upon impingement on the target’s surface, act as a source of energetic bombardment that affect the growth and the properties of reactively sputtered transition metal nitride films. In order to further understand and control the effect of these species, the experimental determination of their energy, relative flux and spatial distribution is necessary. This can be facilitated by using sophisticated plasma diagnostic tools, such as energy resolved mass spectroscopy, and could allow for a systematic tailoring of the film properties.

In chapter 5 the issue of deposition rate in a novel sputtering technique, the high power pulsed magnetron sputtering (HPPMS), was addressed. First, in section 5.2 the effect of the used pulse parameters, such as the pulse frequency and the pulse duty cycle, on the deposition rate of Cr films was studied. There, an important phenomenon, the gas rarefaction, was manifested. This is the depletion of Ar atoms in front of the target, due to collisions with sputtered species and it was shown to affect the density of both neutral and charged species in the target’s vicinity. This in turn, determines the target sputtering rate and thus, the deposition rate. The experimental quantification of the rarefaction effect would provide additional information for the mechanisms which determine the deposition rate in HPPMS. This could be achieved by measuring the partial pressures of all species in the target’s vicinity and is suggested as a further step. The understanding gained in section 5.2 enabled the theoretical description of the process in HPPMS and led to the development of a model that could explain and predict the deposition rate as a function of the process parameters and the target material, as presented in section 5.3. There, the relative currents of the Ar$^+$ ions and the ionized sputtered species towards the target were shown to be of crucial importance. These quantities were estimated from optical emission spectroscopy (OES) measurements. The light emitted form the plasma depends, in turn, on the interactions of the neutral and ionized plasma species with the electrons. In order to further increase the accuracy of the OES - based analysis, the
experimental determination of plasma parameters, such as the electron density, the electron temperature and the electron energy distribution function, by means of electrostatic probe measurements, is suggested. Finally, the deposition rate of ZrO$_x$ films grown reactively by HPPMS was studied in section 5.4. There, the process was found to be stable the entire O$_2$ flow range used for the deposition, when HPPMS was employed. This allowed for growth of transparent films in the transition sputtering mode with deposition rates up to $\sim 2$ times higher than those achieved by dc magnetron sputtering (dcMS). In the latter case transparent films could be deposited only in the oxidic mode, due to the inherent instability of the transition area. The process stabilization during HPPMS was suggested to be the effect of the low target coverage, due to the high target erosion rate during the pulse on-time. The experimental determination of the target coverage throughout the pulse duration could provide important information about the dynamics of the plasma-target interactions and further support the validity of the suggested mechanism. This analysis could be facilitated by a combination of time resolved optical emission spectroscopy and time- and energy-resolved mass spectroscopy. Moreover, it is known that during the reactive sputtering of transition metal oxides negative oxygen ions, which are generated on the oxidized target’s surface and accelerated towards the anode (substrate), due to the negative target potential, crucially affect the properties of the growing films [154]. The process stabilization in HPPMS provides additional means for the control of the target coverage and the energetic bombardment by O$^-$ ions, in comparison to dcMS. This appears to be a promising potential of HPPMS, which should be further investigated. Finally, the process stability and the deposition rate during the reactive HPPMS of other transition metal oxides, as well as nitrides should be investigated. This will allow for conclusions about the universality of the mechanisms that determine the deposition process in reactive HPPMS.

In chapter 6 two material systems were studied, in order to explore and demonstrate the effect of HPPMS on the film properties. In section 6.1 the effect of the pulse parameters on the properties of TiO$_x$ films grown reactively from a ceramic TiO$_{1.8}$ target was investigated. It was shown that HPPMS-grown films exhibited the higher refractive indices, higher mass densities and smoother surfaces, as compared to the dcMS ones. Moreover, both HPPMS and dcMS grown films were amorphous, i.e. the use of HPPMS did not result in changes of the film structure and phase composition. Since the structure of the TiO$_x$ is of utmost importance for a variety of
applications, as mentioned in section 6.1, the reason for this behavior should be unraveled. Here the effect of the energetic bombardment by O\(^-\) and positively charged ions seems to be important, while deposition from a metallic target could also be quite helpful. In section 6.2 the microstructure of CrN films deposited by HPPMS and dcMS was studied. The dcMS-grown films were found to be polycrystalline and exhibited columnar structure typical for this deposition technique with intercolumnar porosity. The use of HPPMS led gradually to the formation of nanocrystalline and ultra-dense films. This was attributed to the more intense energetic bombardment during the HPPMS deposition process. Here the quantification of the energy and the flux of the energetic species, e.g. by means of energy resolved mass spectroscopy, is suggested. This together with the investigation of other nitride systems would enable the development of a universal structure model for the growth of transition metal nitrides by HPPMS.
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[38] This technique is also referred to as High Power Impulse Magnetron Sputtering (HiPIMS).
[115] www.chm.bris.ac.uk.s


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Presentations in scientific conferences


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1. *Stress formation in thin films*, Essen University, Essen, Germany May 2005

2. *Modeling and enhancement of the deposition rate in high power pulsed magnetron sputtering*, Materials Chemistry department, RWTH Aachen University, Aachen, Germany June 2007.

3. *Process characteristics and film properties upon growth of transition metal oxides by high power pulsed magnetron sputtering*, Duisburg-Essen University, Duisburg, Germany June 2007.

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