Growth and characterization of HfON thin films with the crystal structures of HfO$_2$

Bo Lü

Diploma work performed with
The Plasma and Coatings Physics Division
2011-07-07

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Abstract

HfO₂ is a popular replacement for SiO₂ in modern CMOS technology. It is used as the gate dielectric layer isolating the transistor channel from the gate. For this application, certain material property demands need to be met, most importantly, a high static dielectric constant is desirable as this positively influences the effectiveness and reliability of the device. Previous theoretical calculations have found that this property varies with the crystal structure of HfO₂; specifically, the tetragonal structure possesses the highest dielectric constant (~70 from theoretical calculations) out of all possible stable structures at atmospheric pressure, with the cubic phase a far second (~29, also calculated). Following the results from previous experimental work on the phase formation of sputtered HfO₂, this study investigates the possibility of producing thin films of HfO₂ with the cubic or tetragonal structure by the addition of nitrogen to a reactive sputtering process at various deposition temperatures. Also, a new physical vapor deposition method known as High Power Impulse Magneton Sputtering (HiPIMS) is employed for its reported deposition stability in the transition zone of metal-oxide compounds and increased deposition rate. Structural characterization of the produced films shows that films deposited at room temperature with a low N content (~6 at%) are mainly composed of amorphous HfO₂ with mixed crystallization into c-HfO₂ and c-HfO₃, while pure HfO₂ is found to be composed of amorphous HfO₂ with signs of crystallization into m-HfO₂. At 400 °C deposition temperature, the crystalline quality is enhanced and the structure of N incorporated HfO₂ is found to be c-HfO₂ only, due to further ordering of atoms in the crystal lattice. Optical and dielectric characterization revealed films with low N incorporation (~6 at%) to be insulating while these became conductive for higher N contents. For the insulating films, a trend of increasing static dielectric constant with increasing N incorporation is found.

Keywords
hafnium dioxide, thin films, gate dielectric, nitrogen incorporation, dielectric constant, crystal structure, HiPIMS, magnetron sputtering.
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Acronyms

CMOS – Complementary Metal-oxide-semiconductor
dcMS – Direct-current magnetron sputtering
DFT – Density functional theory
EDX – Energy dispersive x-ray (analysis)
ERDA – Elastic recoil detection analysis
FCC – Face-centered cubic
GIXRD – Grazing incidence XRD
HiPIMS – High power impulsed magnetron sputtering
HR-XRD – High Resolution XRD
IRSE – Infrared spectroscopic ellipsometry
PVD – Physical vapor deposition
scmm – Standard cubic centimeter
SEM – Scanning electron microscope
UHV – Ultra-high vacuum
VASE – Variable angle spectroscopic ellipsometry
XRD – X-ray diffraction
XRR – X-ray reflectivity
ABSTRACT

HfO$_2$ is a popular replacement for SiO$_2$ in modern CMOS technology. It is used as the gate dielectric layer isolating the transistor channel from the gate. For this application, certain material property demands need to be met, most importantly, a high static dielectric constant is desirable as this positively influences the effectiveness and reliability of the device. Previous theoretical calculations have found that this property varies with the crystal structure of HfO$_2$, specifically, the tetragonal structure possesses the highest dielectric constant (~70 from theoretical calculations) out of all possible stable structures at atmospheric pressure, with the cubic phase a far second (~29, also calculated). Following the results from previous experimental work on the phase formation of sputtered HfO$_2$, this study investigates the possibility of producing thin films of HfO$_2$ with the cubic or tetragonal structure by the addition of nitrogen to a reactive sputtering process at various deposition temperatures. Also, a new physical vapor deposition method known as High Power Impulse Magnetron Sputtering (HiPIMS) is employed for its reported deposition stability in the transition zone of metal-oxide compounds and increased deposition rate. Structural characterization of the produced films shows that films deposited at room temperature with a low N content (~6 at%) are mainly composed of amorphous HfO$_2$ with mixed crystallization into t-HfO$_2$ and c-HfO$_2$, while pure HfO$_2$ is found to be composed of amorphous HfO$_2$ with signs of crystallization into m-HfO$_2$. At 400° C deposition temperature, the crystalline quality is enhanced and the structure of N incorporated HfO$_2$ is found to be c-HfO$_2$ only, due to further ordering of atoms in the crystal lattice. Optical and dielectric characterization revealed films with low N incorporation (< 6 at%) to be insulating while these became conductive for higher N contents. For the insulating films, a trend of increasing static dielectric constant with increasing N incorporation is found.
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* * * * *

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1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

In today’s society, it is difficult to imagine life without a myriad of electronic appliances accompanying us in our everyday routines. The mobile phone, the personal computer and even the dishwasher all contain some form of microprocessor, microcontroller or other digital logic circuits. In turn, these microelectronic components, or integrated circuits, are built on arrays of transistors collected onto a chip, i.e. a computer chip. The widespread use of such computer chips was made possible by the invention of complementary metal-oxide-semiconductor (CMOS) transistors. CMOS based circuits are able to operate with sufficiently high noise immunity and low static power consumption to make mass production and long term operation economically viable.

It is commonly known that digital electronics devices are based on manipulating ones and zeroes, i.e. they use a binary code to transmit information. This task is physically performed by coupled transistors in various configurations, known simply as logic. The schematic cross-section of a single CMOS transistor is shown in Figure 1.1a). Generally, these consist of a metallic gate electrode attached to an insulating gate oxide, of which the latter acts to separate the gate from a semiconductor substrate; hence the ‘MOS’ in CMOS. The substrate is most commonly made of Si, which can be either p-doped (electron deficient) or n-doped (electron rich). In a p-doped substrate, two n⁺ doped regions are created, known as the source and drain. The transistor as a whole is then known as an n-type or npn transistor and sometimes also NMOS transistor. Conversely, an n-doped substrate with p-doped source and drain regions is known as a p-type, pnp or PMOS transistor. CMOS circuits use both n-type and p-type transistors to accomplish signal processing, hence the ‘C’ in CMOS signifies this complementary action. The function of each transistor is to either permit or prohibit a current passing from source to drain. This is controlled by applying a voltage to the gate electrode, which in turn causes the gate oxide to polarize and attract charges to its top and bottom surfaces. In the p-Si substrate, if the applied

![Figure 1.1](image-url)

**Figure 1.1**

a) The schematic of an npn CMOS-transistor. b) The gate oxide area enlarged. Figure adapted from reference [1].
gate voltage $V_G$ is positive, the attracted charges are electrons that populate the valence band of p-Si in the vicinity of the oxide-semiconductor interface, creating a **depletion zone**. Further increasing $V_G$ attracts yet more electrons to the interface and expands the depletion zone until a certain threshold voltage $V_T$ is reached, whereupon some layers of the depletion zone at the interface become inverted from non-conductive p-Si to conductive n-Si. An **inversion zone** or **channel** is now present through which current may pass between source and drain, and the transistor is said to be in the ‘on’ state. For $V_G \gg V_T$, the depletion zone no longer increases in size; instead, the inversion of surface layers becomes stronger, i.e. the channel conductivity increases. To summarize, the ‘on’ state is achieved by applying a gate voltage $V_G$ larger than a threshold voltage $V_T$. In the ideal case, the latter is given by

$$V_T = -\frac{Q_d}{C_{ox}} + \phi_s$$  \hspace{1cm} (1.1)$$

The first term in Equation (1.1) is the capacitive voltage drop across the oxide, with $Q_d$ representing the accumulated charges that form the depletion zone. Since these charges are electrons for NMOS ($Q_d = -Q_p$, from Figure 1.1b)), this term becomes positive, giving a positive $V_T$. The second term is the additional potential needed to invert the surface layers. Equation (1.1) assumes that the Fermi levels of the metal and semiconductor are aligned prior to applying $V_G$, i.e. there is no band bending at equilibrium; the so called ‘flat-band’ condition. In a real case, this is hindered in part by work function differences between the metal and semiconductor as well as the existence of unintentional charges within the gate oxide (defects, trapped charges, mobile ionic charges etc.). Therefore, additional terms are needed in Equation (1.1) to account for these, resulting in

$$V_T = \Phi_{ms} - \frac{Q_{ox}}{C_{ox}} - \frac{Q_d}{C_{ox}} + \phi_s$$  \hspace{1cm} (1.2)$$

where the first term is the work function difference, the second term collectively accounts for the additional charges in the oxide and the remaining two terms are from Equation (1.1). From this, the current flowing between drain and source in the fully on state, called the saturation drive current, can be calculated as

$$I_d(sat.) \approx ZC_{ox}V_d(sat.) = \bar{v}_s$$  \hspace{1cm} (1.3)$$

where $Z$ is the width of the channel, $V_d(sat.) = (V_G - V_T)$ is the saturation drain voltage and $\bar{v}_s$ is the saturated charge carrier velocity in the channel. Equation (1.3) is a simplified version of the saturation drive current which applies only to short channel transistors, which is the case for most devices produced today. Traditionally, $I_d(sat.) \propto V_d(sat.)^2$ and the carrier velocity cannot be summarized by a single variable as it varies with position in the channel. From the above description, it can be seen that the gate oxide plays multiple roles, i.e. not only does it serve as an insulator between the gate and the channel, but its capacitance also governs depletion zone formation, the threshold voltage level and the operating current level. The oxide capacitance is found though

$$C = \frac{\kappa \varepsilon_0 A_{ox}}{t_{ox}}$$  \hspace{1cm} (1.4)$$

where $\kappa$ is the dielectric constant of the oxide material and $A_{ox}$ and $t_{ox}$ are as given in Figure 1.1b). A high capacitance lowers $V_T$ and increases $I_d(sat.)$, which sums the desired
Introduction

electrical characteristics for most devices. Structural properties of the gate oxide must also be taken into account, such as thermodynamic stability with the underlying substrate, interface roughness and crystalline purity, as evidenced by $Q_{ox}$ in Equation (1.2). Traditionally, $\text{SiO}_2$ has been the most common gate oxide material, since it is easy to manufacture by oxidizing the Si substrate, and satisfies the structural property demands. However, due to technological developments, it has been deemed inadequate for reasons that shall be explained presently.

A major trend in the development of IC devices is the scaling of transistors, which entails the proportional reduction of all dimensions of a transistor by a factor $1/k$. The most obvious benefit is the ability to put more transistors on every chip, or to put the same amount of these on a smaller chip; in any case there is a boost in device performance. Less obvious are the device characteristics improvements such as reduced operating voltage and power dissipation by $1/k$ and $1/k^2$ respectively. The scaling of transistors was first proposed in the late 1960’s, most notably by Gordon E. Moore, who predicted that the number of transistors per unit area would double every 2-3 years; a prediction now known as Moore’s Law. [2] The industry has successfully followed Moore’s law through the 1980’s and 1990’s, moving through the stages of medium (MSI), large (LSI), very large (VLSI) and finally ultra large (ULSI) scale integration with more than a million transistors fitting onto a single chip. Further scaling of transistors in the 21st century is overseen by an international committee known as the International Technology Roadmap for Semiconductors (ITRS), who produce annual reports on new technologies and predicted developments. According to these report, transistor scaling is now divided into technology nodes specified by the gate length at each node, which is scaled by $1/k \approx 0.7$ for consecutive nodes. This, of course, begs the question, ‘how far can we scale the transistor?’ Starting from the end of the last millennium, it was realized that further scaling would be hindered by the reduced thickness of the $\text{SiO}_2$ gate oxide. With $t_{ox} < 1.5$ nm, the probability for electrons to quantum mechanically tunnel (by the direct tunneling mechanism) through the gate oxide is increased to such a degree that it constitutes a leakage current. Due to this, a higher drain current is needed to differentiate between on and off states, which increases operation costs as well as the deterioration rate of the transistor. Heat dissipation of larger currents is also an issue, and in the worst case, the device becomes inoperable. [3] Since the key property of the gate oxide for device operation is its capacitance, the solution lies in increasing the oxide thickness to reduce the tunneling probability while preserving the capacitance. From Equation (1.4), it is realized that the latter can be achieved by increasing $\kappa$, which requires changing the oxide material or at the very least the composition of $\text{SiO}_2$. [4] Initially, the nitridation of $\text{SiO}_2$ was successfully employed to give a slightly higher $\kappa$ value than $\kappa_{\text{SiO}_2} = 3.9$, along with added benefits such as higher resistance to boron penetration from the gate. [5] However, the permittivity increase from SiON was too small to sustain continued transistor scaling, and a better alternative material was needed. Transition metal oxides (TMOs) are often used as the dielectric material in electrical capacitors. These are known to have high dielectric constants, but little was known about their thermodynamic stability with Si. Through the past decade, much effort has been put in selecting the best suited TMO to replace $\text{SiO}_2$/SiON, and the suitable candidates became collectively classified as high-$k$ materials. [6], [1] Further sifting among these eventually revealed the top candidate to be Hf-based dielectrics, which includes the pure oxide, the oxynitride and combinations with other TMOs as stacks or by doping. Historically, $\text{HfO}_2$ has been used as the dielectric material in thin film capacitors and resistors, and in later years, it was also a common dielectric for DRAM capacitors. [7] [8] According to ITRS reports from 2005 and later, Hf-based dielectrics have been implemented in production line products since 2008. From the latest ITRS report, the technology is said to be in a state of continuous improvement, expected to be sustainable through further transistor scaling as well as being compatible with new transistor structures such as FinFET and SOI.
Continuous improvement requires more research, and currently, efforts are focused on further improving the material properties of HfO$_2$. From the device research side, efforts are concentrated partly on the manufacture process, as different deposition techniques are tested in an attempt to improve production speed and quality. Currently, atomic layer deposition (ALD) and chemical vapor deposition (CVD) are favored for producing films with atomic level control of film composition and thickness, but physical methods such as pulsed laser deposition and magnetron sputtering are also being explored due to their higher production yields. [4] Researchers are also concerned with the electrical characterization of produced devices, seeking to improve device efficiency and reliability. [1]

From the materials research side, experimentalists and theoreticians work together to explain the underlying physics behind material properties such as crystal phase formation, dielectric response, various material defects and their consequences as well as interfering effects with surrounding materials, specifically Si and different metals used in the transistor gate. Previous first principle density functional theory (DFT) calculations have shown that the three common phases of HfO$_2$, monoclinic, cubic and tetragonal, have dielectric constants of ~16-18, ~29 and ~70, respectively. [9] The monoclinic phase forms naturally at room temperature due to its thermodynamic stability, but the dielectric properties of tetragonal and cubic HfO$_2$ are more valuable in gate dielectric applications. In recent years, it has been shown that the addition, or doping, of selected elements in HfO$_2$ coupled with high temperature post deposition annealing (PDA) can produce these crystal structures and allow them to remain stable at room temperature. For example, doping of Y, or Si in the metal sub-lattice has been shown to stabilize the cubic and tetragonal structures respectively. [10, 11, 12] An alternative route was taken by Sarakinos et al., in which sub-stoichiometric HfO$_2$ as well as N-incorporated HfO$_2$ was studied. [13] It was found by both experimental and theoretical techniques that both the presence of O-vacancies and incorporation of N in the O sub-lattice allowed for preferred growth of cubic or tetragonal phase HfO$_2$. Since the produced films showed good crystalline quality, there was no need for PDA; a strong benefit with regards to transistor production procedures. However, a definitive crystal structure could not be discerned as the employed techniques did not allow for conclusive investigations. The theoretical approach involved DFT calculations on the relative energies of formation for m-, c- and t-HfO$_2$ phases for the two cases and showed that preferred phase formation only occurred above certain concentrations of O-vacancies and N-incorporation. Further investigations of HfO$_2$ samples produced in this way are needed; specifically their optical and electrical properties are of high interest and the current study seeks to provide these.

1.2 **AIM AND RESEARCH STRATEGY**

The aim of this project is to use the results from Reference [13] as a starting point in order to elucidate the effect of the non-metal sub-lattice configuration on the optical an dielectric properties of synthesized HfON thin films. In addition, experiments are performed to compliment the structural analysis of Reference [13] by using more advanced equipment. The thin films are grown by High Power Impulse Magnetron Sputtering (HiPIMS) in an Ar-O$_2$-N$_2$ atmosphere, and the non-metal sub-lattice is controlled by the composition of the gas atmosphere. The use of HiPIMS is motivated by (i) its ability to create a stable deposition process as compared to conventional direct current Magnetron Sputtering (dcMS), (ii) its ability to synthesize denser, smoother films and (iii) its ability to produce highly ionized particle fluxes in the process plasma, which is relevant for microelectronics fabrication. HfO$_2$ samples are also prepared as reference samples, in which the O-vacancy content is controlled and their effects on the films are studied. Compositional analysis is performed to determine the sub-lattice configuration. This is followed by structural and optical properties analysis to establish the relation between the structure, the composition and finally the optical/dielectric response.
1.3 OUTLINE, DELIMITATIONS AND ABBREVIATIONS

Chapter 2 proceeds by shortly reviewing the basic theory behind the materials and methods used during the project. It is meant to give a deeper understanding of the “whys” of this project, such that the remainder of the thesis will be more easily absorbed by the reader. Once this is accomplished, Chapter 3 gives a detailed account of the experimental setup for both the film deposition process, as well as for each of the investigative instruments, in chronological order of use. This chapter aims to provide the reader with the “hows” of the project. In Chapter 4, material characterization results are presented and discussed. These are divided into the different material properties, since results from several analytical methods must be compared and cross-checked in order to derive a conclusion. These conclusions are then drawn in Chapter 5. Finally, with the findings of this thesis in mind, we take a look at future possibilities for this project in Chapter 6.

Note that, in order to limit this thesis to an acceptable length, the characterization techniques are only briefly explained in Chapter 3, and the reader is referred to the references provided in the corresponding section of each respective technique.

Presented below is a list of the written out forms of acronyms used in this work, in alphabetical order:

- CMOS – Complementary Metal-oxide-semiconductor
- dcMS – Direct-current magnetron sputtering
- DFT – Density functional theory
- EDX – Energy dispersive x-ray (analysis)
- ERDA – Elastic recoil detection analysis
- FCC – Face-centered cubic
- GIXRD – Grazing incidence XRD
- HiPIMS – High power impulsed magnetron sputtering
- HR-XRD – High Resolution XRD
- IRSE – Infrared spectroscopic ellipsometry
- PVD – Physical vapor deposition
- sccm – Standard cubic centimeter
- SEM – Scanning electron microscope
- UHV – Ultra-high vacuum
- VASE – Variable angle spectroscopic ellipsometry
- XRD – X-ray diffractometry
- XRR – X-ray reflectivitometry
2 THEORY AND MATERIALS

2.1 THE DIELECTRIC CONSTANT

As the determination of the dielectric constant is a fundamental part of this study, it is worth spending a moment to go through the basic material science behind this quantity. Most equations presented here are derived in references [14] and [15] except where otherwise stated, and the reader is referred to these references for any needed clarifications.

2.1.1 DEFINITION OF \( \kappa \) AND ITS RELATION TO VARIOUS POLARIZATION MECHANISM

The ‘dielectric constant’ \( \kappa \) or ‘relative permittivity’ \( \varepsilon_r \) of a material can be considered to be its ability to permit an electric field, or E-field, \( E \) to pass through it, hence the additional name permittivity. The relative part refers to a material’s \( \kappa \) relative to that of vacuum, \( \varepsilon_0 \), as \( \kappa = \varepsilon / \varepsilon_0 \).

When an E-field is applied across a dielectric material, the atoms or molecules within become polarized such that the average dipole moment \( p_{\text{induced}} \) per particle is turned to be in the direction of the field. This shuffle induces an opposing E-field which acts to cancel out a measurable portion of the applied E-field, and causes a charge build-up, \( +Q_p \) and \( -Q_p \), on opposite surfaces of the dielectric material, as shown in Figure 2.1. On the atomic level, the magnitude of \( p_{\text{induced}} \) is given by the relation

\[
p_{\text{induced}} = \alpha_e E_{\text{loc}}
\]

where \( \alpha_e \) is the electronic polarizability, and \( E_{\text{loc}} \) is the local E-field around an atom. \( \alpha_e \) is a property found in all atoms and describes the displacement of electrons around an atomic core. We shall shortly see that there are other ‘polarizability factors’ stemming from different types of polarization. It must be stressed that \( E_{\text{loc}} \) is not the same as the average field crossing the material, since each atom is also affected by the field caused by its neighboring atoms. Ergo, \( E_{\text{loc}} \) depends on the chemical and structural composition of the material. The ‘Lorentz field’ is an approximation of \( E_{\text{loc}} \) for the simplest case of materials with a cubic crystal structure,

\[
E_{\text{loc}} = E + \frac{1}{3\varepsilon_0} P
\]

where \( P \) is the magnitude of the total polarization in the material and \( \varepsilon_0 \) is the permittivity of
... vacuum. A detailed derivation of this equation can be found in reference [15]. Next, we find $P$ as

$$ P = Np_{\text{induced}} $$  

(2.3)

where $N$ is the number of dipole moments per unit volume. In the case depicted in Figure 2.1, $P$ can also be calculated as

$$ P = \frac{p_{\text{Total}}}{\text{Volume}} \frac{Q_p d}{A} = \frac{Q_p}{A} $$  

(2.4)

where $Q_p / A$ is also known as the surface polarization charge density $\sigma_p$. Finally, $P$ is also related to the applied $E$-field through the familiar relation

$$ P = \chi_e \varepsilon_0 E $$  

(2.5)

where the electric susceptibility $\chi_e = \kappa - 1$. By combining Equations (2.1) - (2.3) with (2.5), we come to the following expression

$$ \frac{\kappa - 1}{\kappa + 2} = \frac{N \alpha_e}{3 \varepsilon_0} $$  

(2.6)

which is known as the ‘Clausius-Mossotti equation’. We have now related the dielectric constant of a material, a macroscopic property, to its microscopic cause.

Electronic polarizability is one of four polarization mechanisms found in dielectric materials; the others are ionic, dipolar and interfacial or space charge polarization. Out of these, only the electronic and ionic values of $p_{\text{induced}}$ can be represented sufficiently with the Lorentz field approximation and a corresponding polarizability factor. For ionic materials, the polarization stems from a displacement of the ionic cores of the material in response to an applied $E$-field. In such materials, $p_{\text{induced}} = \alpha_i E_{\text{loc}}$, and the ‘total polarization’ under both electronic and ionic mechanisms can be calculated by simply adding their respective contributions

$$ p_{\text{Total}} = p_e + p_i = (\alpha_e + \alpha_i) E_{\text{loc}} $$  

(2.7)

$\alpha_i$ can be related to the dielectric constant in the same way as $\alpha_e$, through a slightly modified Clausius-Mossotti equation

$$ \frac{\kappa - 1}{\kappa + 2} = \frac{N_i \alpha_i}{3 \varepsilon_0} $$  

(2.8)

where $N_i$ is the number of ion pairs per unit volume. Again, the two contributions can be added to yield the dielectric constant under both electronic and ionic polarizations

$$ \frac{\kappa - 1}{\kappa + 2} = \frac{1}{3 \varepsilon_0} (N_e \alpha_e + N_i \alpha_i) $$  

(2.9)

In the dipolar polarization mechanism, molecules with permanent dipole moments, such as $\text{H}_2\text{O}$, are caused to align with an applied $E$-field, but their thermal energy disrupts the alignment by stimulating mutual collisions. If the average thermal energy $E_{\text{thermal}}$ per molecule is much larger...
than the average potential energy $E_{\text{dip}}$ per dipole in the E-field, there will be no alignment and no net polarization. For the general case, the average induced dipole moment $p_{\text{induced}}$ of a dipolar polarized material can be calculated as

$$p_{\text{induced}} = \frac{1}{3} p_0^2 E_{\text{loc}}$$

where $p_0$ is the magnitude of polarization in the direction of the field. The derivation of this can be found in reference [14]. From the previous expression, we may define a dipolar polarizability $\alpha_d$ as

$$\alpha_d = \frac{1}{3} \frac{p_0^2}{k_B T}$$

Due to the random distribution of dipole moments local to each molecule, calculation of the local E-field in dipolar polarization is non-trivial. The application of a Lorentz field approximation is not sufficient, which in turn rules out use of the Clausius-Mossotti equation to relate $\kappa$ and $\alpha_d$.

Interfacial polarization occurs when there is a buildup of space charge at an interface in the dielectric material, such as grain boundaries, crystal defects or the outer surface. These charges may be composed of any type of mobile carrier, e.g. electrons, holes or ions either of the dielectric material or from impurities. When an external E-field is applied, these charges gain kinetic energy from the field and diffuse through the material; their accumulation in any part of the material biases the average dipole moment, which in turn affects the dielectric constant of the material. However, $E_{\text{loc}}$ is not well defined at the interfaces, and since the excess dipole moments are localized to these, they are not representative of an average polarization per molecule in the bulk material. These limitations prohibit the use of a polarizability factor and the Clausius-Mossotti equation to calculate the dielectric constant.

### 2.1.2 Frequency dependence of the complex dielectric function

So far, we have only considered the dielectric constant dependence on material properties; the applied E-field has been implicitly taken to be static. Strictly speaking, the dielectric constant should then be referred to as the ‘static dielectric constant’. If an AC E-field is applied, e.g. electromagnetic radiation, the response time of dipole alignment must be taken into account. Generally, this response will tend to lag behind the E-field oscillations; how much so will depend on the frequency of the latter and the physical nature of each polarization mechanism. At high frequencies, the high inertia of molecular dipoles prohibits them from following the rapid changes of an applied field, while the surrounding electron gas can do so easily. Thus at high frequencies, the main contribution to polarization as well as the dielectric constant is electronic polarization.

A simple schematic overview of the different polarization mechanisms and their active frequency ranges is given in Figure 2.2 as a dielectric dispersion graph. The grey area marks the frequency region that can be measured by performing spectroscopic ellipsometry.

At lower frequencies (below GHz), two main factors govern the dipole alignment time of a material: thermal randomization, e.g. lattice vibrations and phonons, and molecular interaction with neighbors. If $\tau$ is taken to be the average time between molecular collisions, the so called ‘relaxation time’, we can write the time dependence of $p_{\text{induced}}$ as

$$\frac{dp_{\text{induced}}}{dt} = - \frac{p - \alpha_d(0) E}{\tau}$$

where $p$ is the momentary induced dipole moment and $\alpha_d(0)$ is the frequency dependent dipolar...
polarizability factor at angular frequency $\omega = 0$. The leading negative sign indicates that the derivative is of depolarization. If the applied field is taken as $E = E_0 \exp(i\omega t)$ and entered into Equation (2.12), we can integrate over $t$ to find the frequency dependence of $p_{\text{induced}}$ as

$$p_{\text{induced}}(\omega) = \alpha_d(\omega) E_0 \exp(i\omega t)$$

where $\alpha_d(\omega)$ is given as

$$\alpha_d(\omega) = \frac{\alpha_d(0)}{1 + i\omega \tau}$$

Finally, using the result from (2.13) and Equations (2.3) and (2.5), we find an expression for the frequency dependent dielectric function

$$\varepsilon(\omega) = 1 + \frac{N\alpha_d(\omega)}{\varepsilon_0} = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

where the final equation is called the ‘complex dielectric function’ with $\varepsilon'$ and $\varepsilon''$ as its real and imaginary parts respectively. These two have physical meaning, as $\varepsilon'$ represents the dielectric constant we would use for calculating capacitance, and $\varepsilon''$ represents the energy loss of polarization due to molecular collisions. Regard the $\varepsilon''$ curve in Figure 2.2, the four peaks in the dielectric dispersion represent approximate frequency ranges in which distinct ‘dielectric resonance frequencies’ for the various polarization mechanisms cause resonance and absorption of light. It should be pointed out that the peaks in Figure 2.2 provide only a quantitative description of the physical mechanisms of light absorption by matter. The reason is that in each frequency regime, the contribution of each polarization mechanism is in general complex and may well manifest itself as distinct multiple peaks.

Last but not least, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are not independent of each other. They are related through a set of relations called the Kramers-Kronig relations,

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} \text{p.v.} \int_0^\infty \frac{\omega' \varepsilon''(\omega')}{\omega^2 - \omega'^2} d\omega'$$

$$\varepsilon''(\omega) = -\frac{2\omega}{\pi} \text{p.v.} \int_0^\infty \frac{\varepsilon'(\omega') - 1}{\omega^2 - \omega'^2} d\omega'$$

Figure 2.2
A schematic diagram of the frequency dependence of the real and imaginary dielectric function components, also known as the dielectric dispersion. Illustrated are also the four polarization mechanisms present in dielectric materials, as well as the frequency range commonly studied by spectroscopic ellipsometry. Figure adapted from references [4] and [14].
Their derivation can be found in many textbooks such as references [16] and [17]. With these, it is possible to measure only the absorption, or energy loss part of \( \varepsilon(\omega) \) (as in IR absorption spectroscopy) and calculate \( \varepsilon'(\omega) \) to find the full dielectric dispersion.

### 2.2 HFO\(_2\) AND HFON

Group IV-B transition metal oxides include TiO\(_2\), ZrO\(_2\) and HfO\(_2\), all of which have been suggested as candidates for high-\( k \) gate dielectric applications. These materials are characterized by their strong ionic-covalent bonds, giving rise to high degrees of (ionic) polarizability and thereby also high dielectric constants. Specifically, the lighter the metal ion, the more prone to polarization a material is, why TiO\(_2\), in any of its phases, has the highest dielectric constant out of the three. [4] However, this is not the only consideration taken into account for high-\( k \) dielectrics; for instance, it has been shown that with high polarizability comes low dielectric breakdown resistance, as the atoms are more loosely bound within the crystal structure. This is a decisive factor for gate dielectric applications, and pure TiO\(_2\)* has since been ruled out as a candidate that HfO\(_2\) and ZrO\(_2\) are isomorphic, with lattice constants very close to each other. [19, 20, 21] This similarity is due to lanthanide contraction in the Hf atom, giving it a smaller atomic radius than would be expected. [22] Many of their material properties lie close to each other, such as their dielectric constants, band gap energy and breakdown threshold voltages. Most importantly, they have been proven to be thermodynamically stable in contact with Si, a strong requirement in today’s microelectronics devices. [4, 23] Table 2.1 gives a summary of the key material properties of group IV-B metal oxides in regards to gate dielectric applications. From this summary, it can be seen that HfO\(_2\) has the most rounded set of features, why much effort has

<table>
<thead>
<tr>
<th>MATERIAL PROPERTY</th>
<th>HFO(_2)</th>
<th>ZRO(_2)</th>
<th>TIO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal Structure</strong></td>
<td>Monoclinic ( \sim )1022</td>
<td>Monoclinic ( \sim )1022</td>
<td>Tetragonal:</td>
</tr>
<tr>
<td>(transition temperature in °C)</td>
<td>Tetragonal ( \sim )1022-2422</td>
<td>Tetragonal ( \sim )1022-2422</td>
<td>Anatase ( \sim )600</td>
</tr>
<tr>
<td></td>
<td>Cubic ( \sim ) &gt;2422</td>
<td>Cubic ( \sim ) &gt;2422</td>
<td>Rutile ( \sim )700</td>
</tr>
<tr>
<td>Band gap energy ( E_g ) (eV)</td>
<td>5.5 – 6.0</td>
<td>5.0 – 7.0</td>
<td>3.0 – 3.5</td>
</tr>
<tr>
<td>Dielectric constant ( \kappa )</td>
<td>22 – 25*</td>
<td>22 – 24*</td>
<td>80 – 100*</td>
</tr>
<tr>
<td>Dielectric breakdown voltage density ( E_{bd} ) (MV/cm)</td>
<td>3.9 – 6.7</td>
<td>3.3 – 5.7</td>
<td>1.4 – 2.5</td>
</tr>
<tr>
<td>Gibbs free energy for Si+Mo( _2)→M+SiO( _2) at 1000 K</td>
<td>47,648</td>
<td>42,326</td>
<td>7,527</td>
</tr>
</tbody>
</table>
| \( \Delta G^\circ_{1000} \) (kcal/mol) | *Values are reported for amorphous materials.

*Studies on the mixtures of TiO\(_2\) and HfO\(_2\) have been performed for gate dielectric applications, which report materials with the orthorhombic crystal structure of HfTiO\(_4\) and having dielectric constants of \( \sim \)50. [18]
been put into understanding the correlation between its processing and structural evolution as a thin film. The next section is devoted to explaining the basic properties of HfO₂, going from bulk to thin film. Following this, the effects of various degrees of nitrogen incorporation are discussed and finally, a more detailed discussion on the material property demands on high-\( k \) gate dielectrics is given.

### 2.2.1 Growth and Structural Properties of HfO₂

Bulk HfO₂ exhibits up to six different crystal structures, depending on temperature and pressure. For normal pressures, at temperatures below ~1022-1900 K, we find the monoclinic \( P2_1/c \) crystal structure with each metal atom coordinated to seven O atoms (MO₇ coordination). Between this temperature and ~2422-2640 K, the \( P4_{nmc} \) tetragonal structure is found, with the metal sub-lattice in an elongated FCC structure and the O atoms at slightly distorted positions within. Above 2640 K, the cubic phase is found with a CaF₂ structure (Fm3m) in which the metal sub-lattice is now a perfect FCC unit cell with the O atoms placed symmetrically within. [13, 24, 25] The Hf-O phase diagram and these three crystal structures are illustrated in Figure 2.3. DFT calculations predict a separate Pa₃ cubic structure at even higher temperatures, where the only difference from Fm3m is a distorted O sub-lattice similar to that in the tetragonal structure, resulting in a slightly larger lattice parameter. [20, 24] However, experimental data on this phase is scarce, and the potential area of use, hard coatings, is a bit far from our applications as a gate oxide. If instead the temperature is fixed, and pressure is added to the monoclinic phase, an expected transformation from \( P2_1/c \) to the orthorhombic phase Pbca occurs at around 3 GPa, with a further transformation to a different orthorhombic phase, Pnma, at 12-22 GPa. [20, 24] Experimental values place these pressure limits a bit higher, at 10 GPa for the first transformation and 32 GPa for the second, noting that “traces” of Pbca and Pnma are found at pressures lower than their respective limits. [21]

In the transistor fabrication process, HfO₂ is usually deposited in the amorphous phase, due to the low process temperature (< 300° C) and hence low surface mobility of deposited particles. Crystallization into the monoclinic phase can be achieved by high temperature annealing above ~700° C. It is not common to anneal at the higher temperatures required to form the tetragonal and cubic phases, as the melting temperature of other materials in the device may lie below these temperatures. Likewise, it is not common to apply high pressures due to the different structural integrities in the device, why the orthorhombic phases are rarely found in gate dielectric applications. But even among the temperature dependent phases alone, monoclinic HfO₂ was found to have the lowest average dielectric constant. First principles calculations by Zhao et al. have shown the tetragonal and cubic phases to possess average dielectric constants of ~70 and 29 respectively, of which the former nearly rivals that of TiO₂. [9] From this, it is clear that if one can control the relative stability among crystal phases during film growth to favor the high-temperature polymorphs, the average dielectric constant of the film can be increased. Several experiments proved this to be achievable through cation doping with various transition metals. [8, 10, 11, 12] A summary of dopants and an explanation of the physical principles behind their stabilizing effects are given by Lee et al. in Reference [29]. Dopants with significantly smaller atomic radii than Hf create shortened dopant-O bonds; a configuration favored by the tetragonal phase since it naturally has four shortened M-O bonds in its unit cell (see Figure 2.3d). In contrast, dopants with larger atomic radii than Hf create elongated dopant-O bonds. The strain energies due to this size mismatch should be higher in the tetragonal and monoclinic structures, so the cubic structure is favored instead. Altering the crystal structure of a material introduces

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* There are reported cases, such as reference [26], in which the orthorhombic phase of HfO₂ was produced at normal pressure with ALD at 500° C. However, this was not the goal in this reference.
vacant lattice sites. In particular, it has been found that vacancies in the non-metal sub-lattice, i.e. O-vacancies, have their own effect on the relative stability among HfO₂ phases, similar to cation doping. For the following discussion, it is necessary to consider the coordination number of constituent atoms in HfO₂. For O-atoms, the coordination number is the number of metal atoms bound to each O-atom, while this is reversed for the M-atom coordination numbers. In m-HfO₂, O atoms can be either threefold or fourfold coordinated, while in c- and t-HfO₂, these are all fourfold coordinated. Consequently, Hf atoms are sevenfold coordinated in m-HfO₂, while they are eightfold coordinated in c- and t-HfO₂. It is known that neutral O-vacancies (V̄O⁰) may be generated during film growth or through doping processes, and are nearly equally distributed at both threefold and fourfold O-lattice sites, with reported energies of formation of 9.36 eV and 9.34 eV for the threefold and fourfold sites respectively. [28] These can then be singly (V̄O¹⁺) or doubly ionized (V̄O²⁺) by thermal processes, doping with specific elements or in the application of gate dielectrics, by charge exchange interactions with Si. The 2+ charged vacancies have been found to be more stable at threefold O-lattice sites rather than fourfold lattice sites. Hf atoms prefer to be sevenfold coordinated, and it is due to the resulting bond structure of such an atomic coordination that the monoclinic crystal structure is inherent stability. In Reference [28], the outward relaxation of Hf atoms neighboring a V̄O⁰ is 0.5-1.0% of the Hf-O bond length, while this is 10 times larger for V̄O¹⁺ and V̄O²⁺. Due to this, Hf atoms in c- and t-HfO₂ become sevenfold coordinated around each charged O-vacancy, thereby causing a relative stability increase of these crystal structures. [29] This change in coordination number does not occur for V̄O⁰, but they nevertheless give a small stabilization effect due to their influence on the metal sub-lattice.
The relation between number of vacancies and relative energy of formation is calculated by Sarakinos et al. for stoichiometric Hf\textsubscript{16}O\textsubscript{32} cells, in which six O-vacancies, i.e. Hf\textsubscript{16}O\textsubscript{26}, marked the beginning of the stability switch. [13] Table 2.2 gives a summary of the calculated lattice parameters and dielectric constant of the three temperature dependent HfO\textsubscript{2} phases, as well as the energies of the cubic and tetragonal phases relative to the monoclinic for neutral and 2\textsuperscript{+} charged O-vacancies.

<table>
<thead>
<tr>
<th></th>
<th>Sarakinos et al. [13]</th>
<th>Zhao and Vanderbilt [9]</th>
<th>Lee et al. [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-HfO\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.056</td>
<td>5.248</td>
<td>5.05</td>
</tr>
<tr>
<td>κ</td>
<td>-</td>
<td>~29</td>
<td>-</td>
</tr>
<tr>
<td>ΔE V\textsubscript{O}\textsuperscript{0}</td>
<td>-</td>
<td>-</td>
<td>7.75\textsuperscript{*}</td>
</tr>
<tr>
<td>ΔE V\textsubscript{O}\textsuperscript{2+}</td>
<td>-</td>
<td>-</td>
<td>4.42\textsuperscript{*}</td>
</tr>
<tr>
<td>t-HfO\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.060</td>
<td>5.298</td>
<td>5.06</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.243</td>
<td>5.373</td>
<td>5.20</td>
</tr>
<tr>
<td>κ</td>
<td>-</td>
<td>~70</td>
<td>-</td>
</tr>
<tr>
<td>ΔE V\textsubscript{O}\textsuperscript{0}</td>
<td>-</td>
<td>-</td>
<td>5.16\textsuperscript{†}</td>
</tr>
<tr>
<td>ΔE V\textsubscript{O}\textsuperscript{2+}</td>
<td>-</td>
<td>-</td>
<td>3.30\textsuperscript{†}</td>
</tr>
<tr>
<td>m-HfO\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.272</td>
<td>5.291</td>
<td>5.12</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.102</td>
<td>5.405</td>
<td>5.20</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.246</td>
<td>5.366</td>
<td>5.28</td>
</tr>
<tr>
<td>β (o)</td>
<td>96.29</td>
<td>97.72</td>
<td>99.7</td>
</tr>
<tr>
<td>κ</td>
<td>-</td>
<td>~16-18</td>
<td>-</td>
</tr>
</tbody>
</table>

* ΔE = 8.09 for stoichiometric cubic composition. † ΔE = 5.47 for stoichiometric tetragonal composition.

The relation between number of vacancies and relative energy of formation is calculated by Sarakinos et al. for stoichiometric Hf\textsubscript{16}O\textsubscript{32} cells, in which six O-vacancies, i.e. Hf\textsubscript{16}O\textsubscript{26}, marked the beginning of the stability switch. [13] Table 2.2 gives a summary of the calculated lattice parameters and dielectric constant of the three temperature dependent HfO\textsubscript{2} phases, as well as the energies of the cubic and tetragonal phases relative to the monoclinic for neutral and charged O-vacancies.

### 2.2.2 Electrical characteristics of HfO\textsubscript{2} high-κ gate dielectrics

Ideally, the gate dielectric should be completely insulating, but this is not the case in real devices. Quantum mechanical tunneling of electrons into the gate dielectric is a phenomenon that occurs if the gate dielectric’s energy barrier to surrounding materials is thin enough. For physically thick insulators, the probability for direct tunneling through the entire insulating layer is close to zero, but the probability for electron tunneling into the conduction band of the insulator is large enough for this to be a measureable quantity. The latter mechanism is known as Fowler-Nordheim tunneling, and its probability varies with the electric field across the gate dielectric. When the band structure of the gate dielectric is modeled as a vertical box, a voltage drop across the gate dielectric will cause the box to deform into a rhombic shape, as in Figure 2.4a). Electrons in the Si conduction band now sense a narrower, triangular energy barrier, and can tunnel through into the conduction band of the insulator. As the material is insulating, these electrons quickly relax into the valence band of the gate dielectric with an associated emission of phonons.
From there, the electrons can only reach the gate by moving successively along defects, which should be few in a well-designed gate dielectric. This type of conduction in an insulator happens when the defects create electron trap energy levels within the band gap of the insulator, thereby allowing electrons to reach the conduction band again by Poole-Frenkel emission. However, as the gate oxide becomes thinner with transistor scaling, electron tunneling no longer proceeds by the Fowler-Nordheim process. Electrons may tunnel through the entire gate dielectric without having to go via the conduction band by a process known as direct tunneling, shown in Figure 2.4b. In references [6, 30], the direct tunneling current density \( J_{DT} \) is approximated by

\[
J_{DT} = \frac{A}{t_{ox}} \exp\left(-\frac{t_{ox}}{\hbar} \sqrt{8m_{eff} q \left( \Phi_b - \frac{V_{ox}}{2} \right)} \right)
\]

(2.18)

where \( A \) is a constant, \( m_{eff} \) is the effective electron mass in the dielectric, and \( \Phi_b \) is the energy barrier at the dielectric-to-gate interface as shown in Figure 2.5. Equation (2.18) is valid for electron tunneling from the gate to the Si-channel; in the reverse case, \( J_{DT} \) is also dependent on the work function of the gate, such that \( \Phi_b \) should be replaced with \( \chi - (\Phi_m - \Phi_b) \). This illustrates the main problem with scaling \( t_{ox} \). When SiO\(_2\) is used as the gate dielectric, increasing \( t_{ox} \) is not practical as this also reduced its capacitance according to Equation (1.4). By using high-\( k \) materials, \( t_{ox} \) can be increased in Equation (2.28) without this loss of capacitance since \( C \) is amplified by the high \( \kappa \) value. In the literature, the thickness of a high-\( k \) dielectric layer is often compared to the capacitively equivalent thickness \( t_{eq} \) of a SiO\(_2\) layer through

\[
t_{ox} = \frac{\kappa_{high-k}}{\kappa_{SiO_2}} t_{eq} \iff EOT = \frac{\kappa_{SiO_2}}{\kappa_{high-k}} t_{ox}
\]

(2.19)

where \( EOT \) stands for equivalent oxide thickness. However, as the right side of Figure 2.6 shows, high-\( k \) dielectric gates are usually composed of several layers, either intentionally or unintentionally. The \( EOT \) is then calculated as

\[
EOT = \kappa_{SiO_2} \sum_i \frac{t_i}{\kappa_i}
\]

(2.20)

and \( t_{ox} = \sum t_i \). From Equations (2.18) and (2.20), one can find the quantity \( \kappa \sqrt{m_{eff} \Phi_b} \), which is used as a figure of merit (FOM) for the effectiveness of a high-\( k \) dielectric at a certain \( EOT \).
When $\Phi_b$ is plotted against $\kappa$, an optimal value of $\kappa$ can be found, where both higher and lower values will increase $J_{DT}$. [30] With interlayers though, the effective dielectric constant is composed of contributions from all the layers in the gate dielectric, with a value generally lower than that of the high-$\kappa$ material alone. This and the increased layer thickness are both detrimental to the total capacitance, why this figure of merit should be considered with precaution.

Understanding the nature of unintentional interlayer formation in Hf-based gate dielectrics is a crucial part of device design. An ultrathin layer of SiO$_2$ is present on Si surfaces whenever they are exposed to air, but additional SiO$_2$ formation may also stem from Si oxidation during processing. In a study on the effects of O-vacancies in HfO$_2$, Guha and Narayan report on SiO$_2$ formation due to diffusion of oxygen through these O-vacancies during annealing in oxygen atmospheres. [31] An interlayer may also form between the dielectric layer and the gate, depending on the gate material. Historically, boron-doped polycrystalline Si (poly-Si) has been preferred, since the band structure of poly-Si can be tailored with respect to doping concentration to reduce $V_G$. [5, 6] For HfO$_2$, this should be a good solution considering the thermodynamic stability between HfO$_2$ and Si. However, the doping process requires the high temperature (>1000°C) activation of dopants, which can cause the small boron atoms to diffuse into the dielectric layer. Incorporation of boron in HfO$_2$ adversely affects the band alignment to Si by reducing the energy
barrier preventing electron tunneling. The solution to this can be found either by applying an HfON diffusion barrier, which will increase the EOT, or by using a metal gate. The choice of material is then a question of thermodynamic stability and band alignment with HfO₂ and material cost. For instance for an npn MOS, Al is cheap and creates a high barrier with HfO₂, but will reduce nearly any oxide, forming a layer of Al₂O₃ at the interface. In this case, various conductive metal nitrides, such as TaN, have been employed successfully. [6, 32]

As mentioned in the previous section, commercial HfO₂ gate dielectrics are commonly amorphous, since low temperature depositions facilitate mass production, but this choice is also based on electrical properties considerations. Polycrystalline materials are anisotropic, i.e. there is almost always a preferred orientation of grains, which gives the dielectric constant a spacial dependence (hence the need for a dielectric tensor). This effect is stronger when the grain size is in the order of device sizes. Further, grain boundaries are regarded as a form of defect as O-vacancies, both charged and neutral, can accumulate at these and form percolation paths for Fowler-Nordheim electron tunneling. [4, 6, 33] The number of O-vacancies accumulated at such boundaries will depend on their charge, as electrostatic repulsion will limit accumulation of charged vacancies. However, electrons from surrounding Si may neutralize many of these, and a large number of neutral vacancies agglomerate instead. Considering facts from the previous section, this should hinder the use of polycrystalline cubic or tetragonal HfO₂ films. Fortunately, the Si electron sources can be isolated by creating an intentional interface layer of amorphous SiO₂ or HfSiO; the increase in $EOT$ being balanced by the heightened $κ$ of cubic/tetragonal HfO₂. Another solution would be to create a single crystalline dielectric layer void of grains and hence grain boundaries, but the currently known processes of achieving this are either too time consuming or costly for industrial use.

Through the last two paragraphs, O-vacancies have been repeatedly mentioned as the cause of various phenomena in HfO₂. Indeed, O-vacancies have been studied thoroughly as they may also exist as defects in stoichiometric HfO₂. Neutral vacancies act as electron donors with energy levels situated ~3.8 eV above the valence band edge, causing defect states to appear in the band gap. [4, 31, 33] At the dielectric-to-gate interface, if the gate’s Fermi level lies below this energy level, electrons may tunnel from the oxide into the gate, causing a positive charge gradient and associated voltage drop across the dielectric. In order to counteract this effect, $V_G$ must be increased and device performance is degraded. Once again, the solution is to create a wide band gap interlayer at the interface, the choice of material weighed against the $EOT$.

The reliability of HfO₂ gate dielectrics has been gauged through high voltage time-dependent dielectric breakdown (TDDDB) tests, in which the dielectric breakdown mechanism has been divided into a soft and hard breakdown. [5, 4, 6] A popular model that explains this mechanism begins with Fowler-Nordheim tunneling of electrons into the gate dielectric, where they gain energy form the gate voltage $V_G$ and can force their way through the insulator. These so called ‘hot’ electrons may cause impact ionization, creating electron-hole pairs that separate and accumulate at opposite sides of the insulator. This extra charge buildup in turn causes local band deformations; specifically, the conduction band is further lowered on the Si side in Figure 2.5a). This allows yet more electrons to tunnel into the gate dielectric, resulting in a positive feedback effect that eventually causes a conduction path to form though the gate dielectric. At that point, a hard breakdown has occurred. According to industry standards, the minimum device lifetime must be at least ten years, during which time the device is under full normal operation. From this model we see that an unnecessarily high $V_G$ is deleterious to the gate oxide, why projections of nominal $V_G$ for HfO₂ gate dielectrics have been made. For an HfO₂ gate dielectrics with $t_{ox} = 10$ nm and $A = 1600 \, \text{μm}^2$, a nominal $V_G$ has been found to be -2 V. For the same thickness but with $A = 0.1 \, \text{cm}^2$, $V_G$ is projected to -1.75 V. [4]
2.2.3 HfON, the Effects of Nitridation

Nitridation of HfO$_2$ gate dielectrics can be achieved in several ways, for example during deposition or by PDA in an N-based atmosphere. Within a crystalline gate dielectric, atomic N can either substitute for O-atoms/vacancies in the non-metal sub-lattice, forming Hf-N bonds, or incorporate themselves as interstitials, forming O-N bonds. The latter bond type may also be formed between O-ion interstitials and substituting N-atoms. First principles studies have shown that within the crystal lattice, N-atoms are likely to couple to O-vacancies. [34] This coupling can eliminate trap states in the gate dielectric’s band gap, since the excess electrons of neutral O-vacancies are bound by neighboring N-atoms, effectively reducing the vacancies to charged ones. [35] In effect, the trap-assisted electron leakage current is reduced as well as O-vacancy diffusion. Interstitial O-ion diffusion is also reduced in the gate dielectric, as these are captured by N-atoms and form less mobile NO$^-$ molecules, thereby reducing unwanted formation of SiO$_2$ at the Hf/Si interface. Specifically for this purpose, a technique is used in which the Si substrate surface is nitried prior to HfO$_2$ deposition. [4] In addition to capturing interstitial O, the surface layer acts to reduce the number of available Si-atoms for O to bond with, as Si-N bonds are more stable than Si-O bonds.

A side effect of nitridation is the decrease in band gap energy. In HfO$_2$, the valence band edge consists of O2p states while the conduction band edge is formed by Hf5d states. With N in the non-metal sub-lattice, N2p states overlap the O2p states at the valence band edge, extending into the band gap with increasing N concentration and reducing the band gap energy. [35, 36, 37] If a majority of N atoms are at interstitial sites, gap states will also appear within the band gap close to the valence band edge which causes a severe reduction in band gap energy. To eliminate such gap states, it is suggested by the authors of reference [35] that PDA in vacuum may break the O-N bonds of interstitial N-atoms and cause these to form more stable Hf-N bonds. However, later studies attribute the reduction in band gap energy specifically to the formation of Hf-N bonds. [36, 37].

DFT calculations have shown that N atoms are fourfold coordinated for x < 9 for the composition (HfO$_2$)$_{10-x}$(Hf$_x$N$_x$), where x = 9 corresponds to Hf$_2$ON$_2$, in which N atoms are reduced to threefold coordination due to stretching of Hf-N bonds. [37] It has also been reported that N-incorporated HfO$_2$ exists in the crystal structure of m-HfO$_2$ for N concentrations below ~9.3 at.%, while it may exist in one of several pseudo-cubic (precisely rhombohedral) structures for increasing N concentrations above 9.3 at.%. [38] These structures, suggested by the authors of reference [38], are modeled after the crystal structures of ZrON at varying N concentrations, since Hf and Zr have the same outer electron configuration and are similar in size due to Lanthanide contraction. With these, they show that the dielectric constant of HfON varies non-linearly with N incorporation, changing its slope approximately together with each structure change. For example, the dielectric constant reaches a local maximum of $\kappa_{HfON}$ ~ 25 at ~9 at.% N incorporation, corresponding to where the monoclinic phase disappears. Together with XPS and REELS measurements, the authors were able to conclude that N concentrations in the range from 7.6 to 16.7 at.% showed the best figures of merit for application as a gate dielectric. In the ab initio analysis of Reference [13] was also reported the effect of N incorporation on the energy of formation of the m-, c- and t-HfO$_2$ crystal structures. It was shown that for Hf$_{16}$O$_{32-3x}$N$_x$, a composition with x ≥ 6 energetically favors the c/t-HfO$_2$ crystal structures.
3 METHODS, EXPERIMENTAL ARRANGEMENTS AND CONDITIONS

3.1 FILM DEPOSITION BY MAGNETRON SPUTTERING

Magnetron sputtering is a physical vapor deposition (PVD) technique used for the synthesis of thin films. An introduction to magnetron sputtering can be found in Reference [39]. This thin film deposition technique is very popular in the industry due to its simplicity and speed; typical areas of use include decorative coating of various objects, thermal barriers on turbine blades and hard coatings on cutting tools. The process utilizes an ionized inert gas, or plasma, to bombard a piece of chosen material, called the target, effectively transferring small quantities of this material into the vapor phase. This is known as ‘sputtering’, and is illustrated in Figure 3.1. The target vapor is then allowed to deposit onto a substrate, where the thin film is eventually formed. Ionization of the inert gas is realized by applying a negative voltage to the target (mounted atop a magnetron cathode) while keeping the substrate and chamber walls grounded (collectively making up the anode). This creates an electric field through the inert gas which attracts the few intrinsically existing gas ions towards the target. Target particles get sputtered due to the high energy bombardment of these ions and gain kinetic energy through momentum transfer. Secondary electrons are also emitted from the target surface, which ionize more inert gas by electron impact.

![Figure 3.1](image)

A depiction of the magnetron sputtering process. Ar\(^+\) ions are created in the plasma and accelerated towards the target along the electric field direction. These high energy particles knock out target atoms, which travel through the plasma and deposit onto the substrate. The emission of secondary electrons is also shown. Notice that the target shielding is grounded. This makes up the main anode to the magnetron cathode, and it is the potential difference between these that accelerates the Ar\(^+\) ions.
ionization, leading to increased sputtering and secondary electron emission. This process then avalanches, and when enough of the inert gas has been ionized to create a ‘quasi-neutral ionized gas’, i.e. a plasma, an equilibrium is reached and further gas ionization happens only to maintain the plasma. In a basic sputtering process, the ion density in the plasma, and hence the number of particles available for sputtering, can be increased by increasing the target voltage and total pressure in the chamber. Naturally, this becomes inefficient at some point, as power and process gas consumption are necessarily limited by economic considerations. In addition, high pressures increase the gas phase scattering and cause significant reduction in the film growth rate. Furthermore, the target voltage affects free electrons in the plasma by accelerating these negative particles towards the substrate, which causes unwanted substrate heating. Therefore, ‘magnetron sputtering’ was invented. By placing magnets beneath the target (usually permanent magnets, but there are cases where electromagnets are required [39]), magnetic fields are introduced that trap electrons close to the target surface, thereby increasing the process gas ionization rate directly above the target. In effect, the plasma becomes confined to where it is most useful, allowing for smaller amounts of process gas, i.e. lower total pressures, to be used. This may increase the deposition rate, as a lower pressure in the chamber results in less scattering of sputtered particles. Also, due to the magnetic enhancement of the ionization rate, lower target voltages can be used in magnetron sputtering, thus lowering the acceleration energy of free electrons and, concurrently, reducing the substrate heating form electron bombardment.

Additional process gases may be introduced into the chamber, which are allowed to react with the target material to form a compound that deposits on the substrate. This is known as reactive sputtering, and is the topic of the next section. Also, there are several modifications of magnetron sputtering such as radio-frequency (rfMS). High power impulse (HiPIMS) and, most commonly, direct current (dcMS) magnetron sputtering. In dcMS, the cathode voltage is held constant, as opposed to rfMS, where the cathode voltage is pulsed at radio-frequencies (hence the name). The latter is used to sputter insulating target materials by making them conductive though dielectric breakdown. It can also be used in some reactive sputtering processes to alleviate target charging effects due to compound formation on the target surface. Generally, most of the sputtered target material is in the form of neutral atoms or molecules, relying on the kinetic energy gain from being sputtered and line-of-sight travel to reach the substrate. This is why it is common to use a low total pressure in the chamber during deposition, so as to reduce the scattering of sputtered material due to collisions in the plasma. However, if a substantial fraction of sputtered material is ionized, these ions may be collimated and guided to the substrate by applying a negative voltage, or bias, to this substrate. There exists a relation between the target power density (target voltage and induced target current per unit area) and the ionized fraction of target material, higher target power yields a higher ionized fraction, but the target cannot withstand exceedingly high power densities. Without extensive cooling, which becomes physically unfeasible at a certain stage, the target will melt. A relatively new development is the HiPIMS technique, which applies such high power densities in pulses with short on times and long off times. This allows the target to cool between pulses, as well as creating high ionized fractions of the target material. A more detailed description of HiPIMS is given in Chapter 3.1.2.

3.1.1 REACTIVE SPUTTERING

In reactive sputtering, additional process gases are introduced into the chamber during deposition, such as O₂, N₂ or even complex molecular vapors such as butane, with the purpose of producing compounds of the target material; for the given example gases, these would be oxides, nitrides and carbides. Sputtering of the target material is still mainly performed by the noble gas, but depending on the partial pressure of additional gases, these may contribute to the target sputtering. However, these gases are more likely to react with the target, forming a layer of com-
pound on its surface. This is known as target poisoning, and has a nonlinear relation to the flow rate of reactive gases, as illustrated in Figure 3.2a) through so called ‘process curves’. In particular, when increasing the flow rate of a single reactive gas, the target is initially slowly poisoned along the grey curve, as gas is also consumed at other available surfaces in the chamber, such as the walls. This slow target coverage continues up to a certain point $P_1$, after which an intense spreading of compound material occurs on the target surface. The target coverage is now at point $P_2$, and for further increasing reactive gas flows, target coverage will once again increase along the grey curve until the target is fully poisoned. If the reactive gas flow is decreased from this fully poisoned state, compound target coverage will follow the grey curve to point $P_3$, where the compound formation rate is abruptly halted and most of the remaining compound material is sputtered away, resulting in the target coverage at point $P_4$. The compound fraction of the target surface will now follow the grey curve as the reactive gas flow reaches zero. The S-shape of the curve in Figure 3.2a) is known as hysteresis, and the area marked in light grey is known as the ‘transition zone’. This hysteresis behavior in the transition zone complicates the reactive sputtering process, and is not only present in target poisoning, but also in the target erosion and

**Figure 3.2**

a) Illustration on the behavior of target coverage as a function of the reactive gas flow. b) The target erosion rate and substrate deposition rate as functions of the reactive gas flow. In both figures, the hysteresis area, or transition zone, is marked in light grey. Figures adapted from reference [40].

**Figure 3.3**

Reactive sputtering reactions. a) A schematic overview of a simple reactive sputtering system with two reactive gases. The distribution of process gases is also illustrated as $Q_{\text{tot}}$, $Q_c$, $Q_p$, and $Q_t$, along with the ion current density $J$. b) Illustration of the distribution of material, where black arrows indicate compound and grey arrows indicate pure target material. $\theta_c$ and $\theta_t$ signify the compound covered fractions of the collecting area and target respectively, while $A_c$ and $A_t$ are their respective total areas. $F_c$ and $F_m$ denote the flux of compound and pure target material respectively. Figures adapted from reference [40].
substrate deposition rates, as is shown in Figure 3.2b). Deposited from the fully poisoned target state results in stoichiometric films, but as can be seen in the figures, the deposition rate is significantly lower when compound target coverage is high. It is therefore desirable to deposit films from a ‘working point’ close to the transition zone border, in this case close to point P3 coming from the right. This requires a reliable feedback system to prevent the target surface composition jumping from P3 to P4, which is not always realizable. Of course, for the inverse case when substoichiometric films are desired, the optimum working point would be close to P1 coming from the left, and the feedback system would prevent a jump from P1 to P2. Specifically for this work, it is also desirable to deposit films with compositions that lie within the transition zone as well.

In the review paper by Berg and Nyberg, an overview of the various experimental parameters that affect hysteresis is presented. [40] The reactive sputtering process is treated with a mathematical model, of which the key inherent variables were presented in Figure 3.3. The derivation of this model is extensive, and the reader is referred to the relevant reference. Most notably, it is found by this model that a high pumping speed as well as a short target-to-substrate distance, or equivalently small size of the collecting area, reduces the hysteresis effect, indicating that by using a small chamber with a large pump, it is possible to eliminate this effect entirely. In contrast, the target ion current is found to have a different effect on process curves. Increasing the target power amplifies the ion current density and subsequently the sputter erosion rate. At first, this would seem a good way to keep target poisoning in check while the reactive gas flow is increased. However, it is found that varying the ion current density does not affect the shape of process curves, but has only a magnifying or demagnifying effect on these. The type of target used can also affect deposition characteristics. By minimizing its size, the hysteresis region width is reduced. The target material influences hysteresis through a property known as its sputtering yield: if the sputtering yield of elemental target material is close to that of its compound, the hysteresis effect is less pronounced. Finally, the hysteresis effect is also affected by the particular reactive gas used. For example, it is known that O2 is a more reactive gas than N2, i.e. there is a more pronounced hysteresis effect in oxide depositions. In Reference [41], Severin et al. show, with both modeling and sample synthesis, that by adding N2 at a low, constant flow rate to an oxide deposition process, the hysteresis region width can be reduced and the transition zone stabilized. It is explained that this is due to the coexistence of both nitride and oxide compounds on the target surface. Since nitrides generally have a higher sputtering yield than the oxides, the effective sputtering yield in an oxynitride deposition process is increased, thus reducing the hysteresis effect and also increasing the deposition rate. The high sputtering yield of nitrides stems from their relatively low heat of formation with metals as compared to that of oxides. This means that N-incorporation in oxynitride films will be lower than expected, as M-N bonds are easily broken and replaced by M-O bonds.

3.1.2 HiPIMS

The HiPIMS technique has received a great deal of interest in academic research in recent years, due to its reported benefits over conventional dcMS. Most prominently, a high degree of target particle ionization is found in HiPIMS plasmas, which allow these to be collimated and directionally accelerated (to a higher degree than dcMS plasmas) towards the substrate by applying a substrate bias voltage. [42, 43] This low energy, high flux of ions makes the deposited films denser and more uniform*, which has proven useful for coating the insides of vias on ICs;

---

* Ion bombardment on the growing film may suppress the evolution of porous, columnar microstructures by forcing new grains to grow with a crystal orientation different from underlying ones, an effect known as ‘repeated nucleation’. Such ions may also impart energy locally on the substrate surface, effectively increasing the adatom mobility there. These effects frequently result in the creation of dense, nanostructured materials.
generally a hard task as these are often deeper than they are wide. The HiPIMS power source supplies high DC voltages (400 to 2000 V, compared to ~300 V in dcMS) to the target in pulses with short ‘on’ times and long ‘off’ times; the setup is illustrated in Figure 3.4. In this way, the target is kept at tolerable temperatures while high power densities are achieved on its surface. This in turn leads to higher densities of the magnetically confined plasma and consequently a higher electron density in this. Since the main ionization mechanism in high density plasmas is electron impact ionization (as opposed to Penning ionization in low density plasmas, see reference [39]), the increased electron density effectively produces a larger amount of ionized particles. The observed results are the aforementioned ability to manipulate target material and densification of deposited films. Naturally, the fraction of ionized target particles is also dependent on the target element, specifically that element’s ionization potential, mass and ionization rate. However, the deposition rate of HiPIMS is generally lower than that of dcMS. Reports suggest that this is due to portions of the positive target ions being attracted back to the cathode after being sputtered, since most ionization occurs close to the target in the confined plasma. Also, studies of the voltage characteristics in process plasmas show that though the target voltage mainly drops across the so called plasma sheath, some portion penetrates into the bulk plasma, creating an area with a potential gradient, known as the plasma pre-sheath. If a target atom is ionized

![Figure 3.4](image)

The HiPIMS target power setup. A DC power supply is connected to the vacuum chamber via a pulse power controller. Within this controller, a capacitor bank is charged by the power supply, releasing the energy in pulses using high-speed switches. Figure adapted from reference [43].

![Figure 3.5](image)

Illustrative comparisons of process curves between dcMS and HiPIMS. a) Compound target coverage and b) deposition rate. Figures adapted from reference [44].

*The plasma sheath is a region of plasma that forms close to any surface it is in contact with. It is characterized by a deficiency of electrons and is consequently positively charged.*
within this area, it must gain enough kinetic energy to overcome this potential in order to reach the substrate. Otherwise, it will be attracted back to the target and contribute to self-sputtering. Finally, it is reported that there are several benefits to be gained by using HiPIMS in reactive sputtering processes. Work on alumina (Al$_2$O$_3$) thin film synthesis, comparing reactive transition from metal to compound mode less abrupt (i.e. a wider ‘process window’ is attained) HiPIMS with reactive dcMS, has shown that HiPIMS can eliminate the hysteresis effect, make the and increase the maximum deposition rate of stoichiometric compound material*, as was illustrated in Figure 3.5. [44] It has been suggested that these effects are due to the pulsing nature of the target erosion. During the pulse ‘on’ time, neutral gas particles in the vicinity of the target become rarefied due to the high instantaneous erosion rate, i.e. the gas particles are pushed away by sputtered target material. Further, since there is no target voltage applied during the pulse off time, there is an absence of plasma for this duration, leading to a lesser degree of activation (excitation/ionization) of the reactive gas. These facts combined mean that higher flows of reactive gas are needed to push the compound target coverage into the poisoned mode, i.e. the compound target coverage is displaced towards higher reactive gas flow rates, as was shown in Figure 3.5a). [43, 44]

### 3.1.3 DEPOSITION EQUIPMENT ARRANGEMENTS

A UHV chamber with a regular base pressure in the order of 10$^{-8}$ Torr (after baking) was used. This system is outfitted with a turbomolecular pump with a pumping speed of 450 l/s, backed by a diaphragm pump to eliminate the risk of back-streaming lubrication oils. A total of three pressure gauges are available in the system: a capacitance manometer for the pressure range 0 – 1000 Torr with 10 Torr resolution, a second capacitance manometer for the pressure range 0 – 10 Torr with 10$^{-5}$ Torr resolution used during deposition for process pressure monitoring, and finally a cold cathode gauge for base pressure gauging in the high to ultra-high vacuum range (7.5x10$^{-11}$ – 3.75x10$^{-3}$ Torr).

The Hf target was mounted onto a sputtering cathode below and on-axis to the substrate holder. A differentially pumped radiative heater is mounted above the substrate holder to provide accurate substrate heating. Calibration of the heater was performed once, prior to the elevated substrate temperature depositions. The entire substrate holder/heater structure is vertically mobile, and was lowered to a working distance (target-substrate distance) of 80 mm during depositions. For Al capping layer depositions, an Al target was mounted on a 45° off-axis cathode while the substrate holder was lowered to the same position as for Hf; the actual working distance was not critical for depositing the capping layer. The magnetrons were powered by a direct current power supply (Advance Energy Pinnacle) with automatic voltage on/off ramping. This was coupled to a MELEC SPIK 1000A pulse power controller, with pulse characteristics set by an external pulse generator. Power and pulse characteristics were monitored manually with an oscilloscope.

The available process gases consisted of high purity (99.9997% purity) Ar, O$_2$ and N$_2$ from individual gas lines. These were introduced into the chamber via different mass flow controllers (MFCs) with flow rates controlled by a digital multi-gas MFC pressure controller unit. Since this unit was calibrated for N$_2$, necessary adjustment factors for other gases were previously calculated. For both Ar and N$_2$, the maximum flow of their MFCs was 100 sccm, with an accuracy of ~1 sccm. Since the O$_2$ flow rate was the most important variable for the different deposition sets, a more accurate MFC was used on the O$_2$ gas line. This MFC had a maximum flow rate of 10 sccm, with an accuracy of ~0.1 sccm.

* The HiPIMS power supply was configured to obtain the same pure metal deposition rate as with dcMS. The compound deposition rate of both dcMS and HiPIMS could then be easily compared to this common value.
3.1.4 SUBSTRATE PREPARATION

The substrates used for these experiments were single crystal Si(004)-wafers grown by the Czochralski method, cut to a thickness of 525 ± 20 µm. According to the manufacturer, these were p-doped with boron to give a resistivity value of 10-20 Ω cm.

Prior to deposition, the 4 in. wafers were cut down to size (18x18 mm squares) by diamond tip scribing along high symmetry crystal planes, followed by manual breaking. This was then followed by a two-step cleaning process in which the substrates were first immersed in acetone and sonicated for 5 minutes, followed by immersion in isopropanol and a final 5 minutes of sonication. The acetone removes mostly dust from the cutting procedure, but can also work on some organic contaminants, though these are carefully avoided by following appropriate clean room conventions. Isopropanol then removes the acetone, to prevent residue formation of the latter which has a high rate of evaporation. The substrates were allowed to remain in isopropanol, to avoid dry stains, until time came for introduction into the deposition chamber, upon which these were air-dried with pure nitrogen gas. For the depositions at elevated temperatures, the substrates were also baked in UHV for approximately 60 min at the same temperature as the deposition. All substrates were introduced into the chamber via a load lock and transfer tube system, with separate vacuum pumping for each; the transfer tube is continuously kept at UHV and vented only during maintenance.

3.1.5 DEPOSITION CONDITIONS

First, process characterization was carried out to determine the desired working points by increasing the O₂ flow rate, ΦO₂, while monitoring the target voltage; results are presented in chapter 4.1. The rest of project can be divided into several research stages, each with complementary sets of HfON and HfO₂ samples. The characterization results from these sets were cross-examined with each other within each stage to see the difference between the effects of N-incorporation and O-vacancy content on the non-metal sub-lattice configuration of the synthesized films. Table 3.1 gives an overview of these sample sets. Note that ΦN₂ was the same for all HfON samples while multiple ΦO₂ values were chosen for both HfON and HfO₂. For all depositions, the total working pressure was kept constant at 7.6 mTorr by adjusting only the Ar flow rate during deposition. Pre-chosen N₂ and O₂ flow rates were retained for the whole duration of each sample deposition. Similarly, the target power was kept constant at 100 W by adjusting the target voltage during the deposition process. The unipolar HiPIMS pulse had a frequency of 1 kHz, with an ‘on’ time of 50 µs.

In sample set 1, nine HfON films were synthesized for equally spaced ΦO₂ ranging from 0 sccm (pure HfN) to 3.2 sccm, with the substrate at room temperature. In this way, the O/N ratio is varied, and the effect of this ratio on the non-metal sub-lattice configuration of HfON thin films may be studied. The deposition of each film in sample set 1 was terminated after exactly five minutes, allowing the deposition rate to be calculated by measuring the thickness of each film and dividing by this deposition time. A similar procedure was performed for sample set 2, where 8 HfO₂ films were deposited for ΦO₂ values chosen from the initial process characterization results to cover key working points. These values ranged from 0 sccm (pure Hf) to 3 sccm, and the individual depositions lasted for exactly five minutes each. In this case, ΦO₂ affects the O-vacancy content of the synthesized films, and now it is the effect of this content on the non-metal sub-lattice configuration that is under scrutiny. Deposition rate calculations were carried out in the same manner as they were in sample set 1. Since the Hf compound films in these two sample sets are revealed, i.e. in direct contact with the atmosphere, they were also suitable for measurement by spectroscopic ellipsometry.
Sample sets 3 and 4 were comprised of HfON and HfO$_2$ samples deposited without substrate heating, for times calculated to produce an equal thickness (250 nm) for all films. The number of samples in set 3 as well as their respective Φ$_{O_2}$ was chosen identically to sample set 1. For set 4, the range of Φ$_{O_2}$ was truncated as the stoichiometric composition was believed to be reached already at Φ$_{O_2}$ = 2.0 sccm. Consequently, sample set 4 consisted of only 6 samples. Directly after the film deposition, all samples in these two sample sets were covered with a pure Al capping layer to preserve the as-deposited composition. This was done by dcMS from a separate magnetron cathode mounted in the same chamber; the depositions took five minutes each. This allowed for accurate structural and compositional characterization of these samples.

The remaining two sample sets were deposited with substrate heating to enhance crystallization in the synthesized films. A smaller subset of Φ$_{O_2}$ was chosen, 0.8 sccm and 2.0 sccm, for both HfON and HfO$_2$ samples, making a total of four samples in each set, two HfON and two HfO$_2$. Samples in set 5 were synthesized with a substrate temperature of 400° C, while samples in set 6 were subjected to a substrate temperature of 700° C. The same deposition times were used for these samples as those used for their room temperature counterparts. In the same way as samples in sets 3 and 4, the samples in sets 5 and 6 were covered with a pure Al capping layer, and analyzed by structural and compositional characterization techniques.

### Table 3.1
Deposition sets, together with their specific deposition settings and purposes

<table>
<thead>
<tr>
<th>SAMPLE SET NUMBER</th>
<th>O$<em>2$ FLOW RATE Φ$</em>{O_2}$ (SCCM)</th>
<th>N$<em>2$ FLOW RATE Φ$</em>{N_2}$ (SCCM)</th>
<th>DEPOSITION TIME (MIN)</th>
<th>SUBSTRATE TEMPERATURE (° C)</th>
<th>SAMPLE PURPOSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0 – 3.2</td>
<td>1.5</td>
<td>5</td>
<td>Room temperature</td>
<td>Process characterization and ellipsometry</td>
</tr>
<tr>
<td>2</td>
<td>0.0 – 3.0</td>
<td>0.0</td>
<td>5</td>
<td>Room temperature</td>
<td>Process characterization and ellipsometry</td>
</tr>
<tr>
<td>3</td>
<td>0.0 – 3.2</td>
<td>1.5</td>
<td>Calculated†</td>
<td>Room temperature</td>
<td>XRD, ERDA</td>
</tr>
<tr>
<td>4</td>
<td>0.0 – 2</td>
<td>0.0</td>
<td>Calculated†</td>
<td>Room temperature</td>
<td>XRD, ERDA</td>
</tr>
<tr>
<td>5</td>
<td>0.8 and 2.0*</td>
<td>0.0 and 1.5</td>
<td>Calculated†</td>
<td>400</td>
<td>Crystallinity improvement test, XRD, ERDA</td>
</tr>
<tr>
<td>6</td>
<td>0.8 and 2.0*</td>
<td>0.0 and 1.5</td>
<td>Calculated†</td>
<td>700</td>
<td>Crystallinity improvement test, XRD, ERDA</td>
</tr>
</tbody>
</table>

* Samples composed of two HfON samples synthesized with 0.8 and 2.0 sccm Φ$_{O_2}$ as well as two HfO$_2$ samples synthesized with 0.8 and 2.0 sccm Φ$_{O_2}$.
† Deposition times varied between samples due to different growth rates at different O$_2$ flow rates.

Crystalline materials are characterized by the orderly periodic arrangement of atoms in a lattice, and as such may coherently scatter, or diffract, light provided that the wavelength of this
light is similar to the distance between the atoms of such a lattice. The region of wavelengths satisfying this criterion lies in the X-ray region; thus, X-rays can be used to find the atomic structure of a crystalline material with X-ray diffractometry (XRD). Specifically, diffraction from the various atomic planes collectively produces a diffraction pattern, which contains much information about the material, including structural strain, grain size and preferred grain orientation (also known as texturing) in addition to the atomic structure. Further, XRD may be performed in both reflection and transmission mode, but the former is by far more common, and the only mode of XRD used in this project. However, finding most these material properties requires modified versions of the basic measuring equipment (the diffractometer), and often advanced result analysis procedures as well. For the current study, XRD analysis was performed for atomic structure determination only, with Grazing incidence X-ray diffractometry (GIXRD) and high-resolution X-ray diffractometry (HR-XRD). Also, a closely related X-ray technique which does not rely on diffraction, X-ray reflectometry (XRR), was used to determine film thicknesses. These three techniques, along with basic XRD theory, are briefly explained in this chapter. For a comprehensive description of X-ray diffractometry in general, see Reference [45].

The most common X-ray diffractometer employs the Bragg-Brentano parafocusing geometry, named after its founders. In this configuration, reflections from atomic planes can be focused one at a time by varying the angle between the incident beam and the sample surface. This focusing condition is only satisfied when the X-ray source and detector are symmetric around the sample, i.e. when the sample surface makes equal angles with the incident and diffracted beams. This necessarily means that only atomic planes parallel to the sample surface are measured, but since the grains in a polycrystalline material have different orientations, different atomic planes are able to be measured with varying intensities. A simple but often presented equation is Bragg’s Law, which states the necessary conditions for diffraction to occur for a specific set of wavelength of light \( \lambda \), beam angle of incidence \( \theta \) and atomic plane spacing \( d_{hkl} \):

\[
n\lambda = 2d_{hkl} \sin(\theta)
\]  

(3.1)

A visualization of Bragg’s law is illustrated in Figure 3.6a). Equation (3.1) can also be expressed in reciprocal space, in terms of the wavevectors \( k_{Q} \) and \( k \) of the incident and diffracted X-rays respectively and the reciprocal lattice vectors \( G_{hkl} \) of the atomic planes,

\[
\vec{k} - \vec{k}_Q = \vec{G}_{hkl}
\]  

(3.2)

As the diffractometer scans over different \( 2\theta \) angles, a scattering vector \( Q \) can be visualized growing/contracting in reciprocal space, as shown in Figure 3.6b). Whenever \( Q \) is pointing at a reciprocal lattice point, or equivalently when \( Q = G_{hkl} \), the diffracted intensity is maximized; this is known as the Laue condition. It is evident from the figure that in the parafocusing geometry, \( Q \) is always parallel to the sample surface normal \( n_s \), which is not the case in other diffractometer configurations such as GIXRD.

The experimental setup is illustrated in Figure 3.7. The X-ray source and detector are situated on opposite sides of the sample at distances \( r_g^* \), the radius of the diffractometer circle (this is a constant). Commonly, X-rays are produced from the core electron transitions of a chosen element, for instance the K shell transitions of Cu. This radiation is then filtered through a thin foil

\* The subscript of \( r_g \) stands for ‘goniometer’, which is the name of the mechanical structure holding the sample and detector arm. The goniometer also contains the motors that allow these components to move.
of a proper material in order to obtain a monochromatic beam. In the case of Cu radiation, the filter is made of Ni which absorbs Cu$K_\beta$ radiation, leaving a beam of monochromatized Cu$K_\alpha$.

The resulting beam is divergent, and the degree of divergence can be limited by placing a narrow slit in the beam path. This helps to reduce the amount of air-scattered X-rays picked up by the detector. During measurements, the sample is rotated at a constant speed, making an angle $\theta$ between the sample surface and the incident beam. The detector arm, consisting of the receiving slit, monochromator and X-ray detector, moves radially around the sample at twice the sample rotation speed, always making an angle of $2\theta$ with the incident beam. This way, a small portion of the total diffracted radiation can be selected by an appropriately placed narrow receiving slit, which lets the focused radiation reflect off a monochromator to enter the X-ray detector as a parallel collimated beam. In Figure 3.7, the symmetry condition for focused diffraction is fulfilled if the detector arm moves along the diffractometer circle, while the radius of the focusing circle is adjusted to keep the receiving slit at the intersection of the diffractometer and focusing circles. The X-ray source is then always at the other intersection of these two circles, and the sample is always on the circumference of the focusing circle. A simple relationship exists between the diffractometer and focusing circles:

$$r_f = \frac{r_g}{2\sin(\theta)}$$ (3.3)
The Bragg-Brentano diffractometer configuration has a major drawback when it comes to thin film analysis. If a single crystalline substrate is used, this configuration may produce high intensity substrate peaks in the diffraction pattern, depending on the substrate material and measured range of angles. In the worst case, the position of such peaks may coincide with those of the thin film and overlap these, making data analysis difficult. For this reason, the grazing incidence method is especially useful for thin film analysis, since the small angle between the incident X-ray beam and the sample surface provides a large, shallow interaction volume, as seen in Figure 3.8. In effect, diffraction patterns are dominated by features from surface layers, while those from the substrate are reduced or even eliminated. For this method, the incidence angle $\theta$ must be fixed at a chosen angle $\omega$ throughout the entire measurement, while the detector scans over a range of $2\theta$ values. Due to this deviation from the symmetric configuration of the source and detector, the focusing condition is unfulfilled. To remedy this, special optics has been developed. A parallel plate collimator acts to limit the degree of divergence in the detected beam, while further parallelization is achieved with a monochromator before the beam is permitted into the detector. As a result, the detected intensity is reduced by the optics. In general, the measured intensity from GIXRD and Bragg-Brentano XRD may differ several orders of magnitude. Another important aspect of this diffractometer configuration is that the scattering vector $\mathbf{Q}$ is no longer required to be parallel to $\mathbf{n}_S$. As the detector scans over $2\theta$, $\mathbf{Q}$ changes both direction and magnitude, such that atomic planes not parallel to the sample surface can also be measured.

Phase determination is achieved by comparing measured diffraction patterns with standardized powder diffraction files (PDFs). Pressed powder samples are considered to be isotropic, i.e. there are no preferred grain orientations in these, so that all orientations are represented equally. Measurement of such a sample yields a diffraction pattern containing all possible Bragg reflections in the range of measured $2\theta$, with peak intensities determined by the atomic scattering factors (see reference [45]). In this project, sample sets 3 through 6 were measured by GIXRD. The equipment used was a Philips X’Pert-MRD PW1830 materials research diffractometer was used with Ni-filtered Cu$K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å) and the optics shown in Figure 3.8. For all measurements, the beam angle of incidence $\omega$ was chosen to $1^\circ$, while the detector scanned over a $2\theta$ range of $25^\circ – 65^\circ$ (relative to the sample surface). Measurement results were compared to JCPDS-ICDD powder diffraction files (PDFs) for phase determination. The principle PDFs used were for the monoclinic, tetragonal and cubic phase and can be found in References [46], [47] and [48] respectively.

The PW1830 is also capable of using high-resolution optics, which are needed for the precise measurement of small differences in d-spacings (likewise $2\theta$ angles). The idea is to limit the dispersion of Cu$K_{\alpha 1}$ by monochromatizing the source radiation as much as possible without exterminating the beam all together, as well as parallel collimating both the source and detector beams to increase angular resolution in $\omega$ and $2\theta$. This entails the use of monochromators in both the source and detector beam paths. On the source side, the monochromator works by permitting only a thin slice of parallel collimated Cu$K_{\alpha 1}$ radiation to reach the sample (see Figure 3.9), while the monochromator on the detector side, known as the analyzer, works as an atomic level parallel beam collimator. This extreme monochromation further reduces the measured intensity as compared to GIXRD, and puts requirements on the sample itself to be of good crystal line quality (HR-XRD is usually used for determining the stress-induced relaxation in epitaxially grown thin films). In general, this is not the case for the magnetron sputtered thin films; these are usually polycrystalline with varying grain sizes. A special monochromator can then be used, known as a hybrid mirror, in the source beam while a triple-axis analyzer is used in the detector beam (see Figure 3.10). The hybrid mirror is not as stringent as typical monochromators in the limiting of Cu$K_{\alpha 1}$, resulting in higher diffraction intensities. Closer studies of deposition set 5 were performed with HR-XRD optics, with grazing incidence geometry.
Methods, experimental arrangements and conditions

Figure 3.8
The GIXRD instrument setup, in which the sample size has been exaggerated to show the large interaction volume at the surface of the sample. Also illustrated are the beam optics used in this project and their respective angular resolutions. The function of the parallel plate collimator is to prevent the short-dashed lines from entering the detector, while permitting the dot-dashed lines to pass through.

Figure 3.9
The wavelength dispersion of Cu$K_\alpha$ radiation, with its characteristic peaks $K_{\alpha 1}$, $K_{\alpha 2}$ and $K_{\beta}$. $\Delta \lambda$ signifies the wavelength selection of an arbitrary monochromator.

Figure 3.10
A schematic illustration of the HR-XRD setup used in this project.
If the Bragg-Brentano geometry is used with extremely low incidence angles, total reflection of the incident beam may occur. This is due to the refractive index of X-rays being able to take values below unity. In the literature, the complex refractive index for X-rays is often given by (compare with that of visible light, \( n = N + iK \))

\[
\hat{n} = 1 - \delta - i\beta
\]  

(3.4)

where \( \delta \) and \( \beta \) are the real and imaginary parts of the dielectric susceptibility and are given by a material’s atomic density and suitable atomic form factors. It is commonly known that total reflection of visible light occurs when the light beam transits from one material to another from below a certain critical angle, which is dependent on the refractive indices of the two materials. When this occurs, the incident beam deviates towards the normal of the interface between the two materials, which is why this is more precisely called total internal reflection. X-rays, on the other hand, behave in the opposite manner. An X-ray beam transits that from one material to another from below a critical angle will instead deviate towards the sample surface, and the phenomenon is known as total external reflection (TER). It can be shown that the critical angle \( \alpha_c \) for TER can be calculated by

\[
\alpha_c = \sqrt{2\delta}
\]  

(3.5)

where delta is dependent on the electron density in the sample; the higher the electron density, the higher the critical angle. For most materials, \( \alpha_c \) has a value below 0.5° for CuK\( \alpha \) radiation. The effect of total external reflection of X-rays is exploited by the XRR technique, which can determine the density, chemical composition* and thickness of thin film samples. For the present study, only the thicknesses of thin films are determined by XRR. As this technique does not rely on diffraction, XRR can also be used for amorphous materials. If the reflected intensity \( I \) of an

\footnote{With XRR, the X-ray refractive index of a material can be found, in which the term \( \beta \) is dependent on the linear absorption coefficient \( \mu \). This absorption coefficient relates a material’s ability to absorb X-rays to its chemical composition. However, this method is generally not very accurate for composition analysis and other techniques such as ERDA, XPS or EDX are often preferred instead.}

Figure 3.11

\( \text{a)} \) A schematic illustration of the reflected and refracted beams measured with XRR. \( \text{b)} \) A fictional example of experimental data obtained by XRR. Curve fitting in the Win GIXA software begins by manually aligning the \( 2\alpha_c \) point of the experimental and generated curves, after which the model is fit to the remaining experimental data by computation. Figures adapted from Reference [45].
XRR measurement is plotted against the measuring angle $2\theta$, intensity oscillations can be found, which are known as Kiessig fringes. The measuring angles corresponding to these fringes are angles at which the phase difference $\Delta$ between a reflected and refracted beam is a multiple of the incident beam wavelength, as shown in Figure 3.11. This phase difference is related to the film thickness $t$ via the equation

$$\Delta = 2t\sqrt{\theta^2 - \alpha_c^2} \quad (3.6)$$

where $\theta$ is the incident beam angle. However, many other factors affect the experimental data, such as surface roughness, background radiation and reflected beam divergence. Modern XRR data analysis uses computer generated models and curve fitting to account for these factors. In this way, the thickness of a thin film may be determined with Å precision. An upper limit for measurable thicknesses is set by the ability of the software to discern individual Keissig fringes from the experimental data, as these fringes grow denser with increasing film thickness. The actual value of this limit depends on the aforementioned factors affecting the experimental data, but 100 nm is often said to be the highest measurable film thickness for CuK$_\alpha$ radiation. With this in mind, sample sets 1 and 2 were analyzed with XRR for thickness determination. The measurements were performed on a Philips X'Pert-MRD PW3040, with CuK$_\alpha$ radiation. Curve fitting was performed with the software program WinGIXA from Philips.

### 3.2.2 SPECTROSCOPIC ELLIPSOMETRY

With ellipsometry, the polarization state of light after reflection from (or in some cases transmission through) a dielectric material can be measured, which can be seen as a direct mapping of the dielectric tensor in an anisotropic material since the E-field of the incident light is polarized differently depending on its path through the material. In most experimental configurations, this is achieved by irradiating a sample with linearly polarized light which, after reflection at sample interfaces, generally becomes elliptically polarized. Quantitatively, this is represented by the complex ratio $\rho$ between the perpendicular ($r_s$) and parallel ($r_p$) components of the reflected light, which can be further parameterized by the ellipsometry parameters $\Psi$ and $\Delta$. Thus, the ratio $\rho$ is presented as a complex number in exponential form

$$\rho = \frac{r_p}{r_s} = \tan \Psi \exp(i\Delta) \quad (3.7)$$

where $\tan \Psi$ and $\Delta$ expresses the amplitude and phase of the complex number respectively. Depending on the physical aspects of a measured sample, if may be possible to find the dielectric function by direct inversion of the ellipsometry parameters $\Psi$ and $\Delta$. For a simple bulk material, an isotropic two-phase (air/material) model can be used [16, 49],

$$\varepsilon = \varepsilon' + i\varepsilon'' = \sin^2(\phi) \left[ 1 + \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right] \tan^2(\phi) \quad (3.8)$$

where $\phi$ is the angle of incidence. This gives an exact solution to the dielectric function of the bulk material (for the measured frequency range). For thin film samples, this is not as straightforward. A model needs to be created which takes into account all the different layers in a sample, from the substrate to the film through any eventual intermixed layers of these, as well as their various material properties. For each layer, a function is defined to model their individual contributions to the total dielectric function of the sample, the so called pseudo dielectric function. In the case of intermixed layers, an effective medium approximation (EMA) can be
used which averages a set of dielectric functions, one for each constituent material. [16] If vacuum or air (collectively known simply as ‘void’) is chosen as one of these constituent materials, the EMA can also be used to model surface roughness. The dielectric function is related to the refractive index \( n(\omega) \) and extinction coefficient \( k(\omega) \) through

\[
\varepsilon'(\omega) = n^2(\omega) - k^2(\omega) \\
\varepsilon''(\omega) = 2n(\omega)k(\omega)
\]

These frequency dependent optical parameters and knowledge of the angle of incidence enable us to use the Fresnel equations in calculating model \( r_{s,\text{calc}}(\omega) \) and \( r_{p,\text{calc}}(\omega) \) values, which in turn yield \( \rho_{\text{calc}}(\omega) \). Now we can compare \( \rho_{\text{calc}}(\omega) \) to the experimental values \( \rho_{\text{exp}}(\omega) \), and through a curve fitting procedure find the model parameters giving the best match; the final model parameters then represent the thin film material properties. An example of such a model and the dielectric function of a thin-film top-layer are given in Figure 3.12.

In this project, spectroscopic ellipsometry in the ultraviolet to near-IR frequency (UV-IR) region was performed with a Variable Angle Spectroscopic Ellipsometer (VASE) from J. A Woollam Co for all samples in set 1 to inspect their refractive indices. With these, it was possible to tell whether a specific film was conductive or insulating. The experimental measurement data was analyzed by computer modeling in a software program called CompleteEASE; this was provided by the ellipsometer manufacturer. Model dielectric functions for the Si-substrate and native oxide were selected among standard, predefined functions. For the UV-IR measurements, the refractive indices of the N incorporated HfO\(_2\) films were modeled by the Cauchy model

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

where the variables \( A, B \) and \( C \) were adjusted to match the refractive index in the experimental data. Following these measurements, two samples each from sample sets 1 and 2 with deposition O\(_2\) flow rates of 0.8 and 2.4 sccm, were chosen for further measurements at lower frequencies. In the ionic polarization regime, the dielectric resonance frequencies of \( \varepsilon' \) as well as the transitional effects of \( \varepsilon'' \) coincide with the lattice vibration or phonon frequencies. By using radiation in the infrared and THz region, these can be measured by infrared spectroscopic ellipsometry (IRSE). Such measurements were performed with an Infrared VASE (IR-VASE) from J. A Woollam Co, capable of accurately measuring down to a frequency of ~400 cm\(^{-1}\); below this, the signal-to-noise ratio of the experimental data compromises curve fitting accuracy. Measurements at even lower frequencies were performed at the University of Nebraska in Lincoln, NE, USA, where the equipment allowed for IRSE measurements using light in the wavelength range of 14 to 100 mm. The four samples that were locally measured by IRSE were also chosen for these measurements. For all IRSE data analysis, the same functions used to account for the substrate and its native oxide in the UV-IR data analysis were once again employed, while the thin film was modeled by the following function

\[
\varepsilon(\omega) = \varepsilon(\infty) \times \prod_{n} \frac{\omega_{\text{LO},n}^2 - \omega^2 - i\gamma_{\text{LO},n}\omega}{\omega_{\text{TO},n}^2 - \omega^2 - i\gamma_{\text{TO},n}\omega}
\]

where \( \varepsilon(\infty) \) is the dielectric constant at high frequencies and \( \omega_{\text{LO},n} \) and \( \omega_{\text{TO},n} \) are the \( n^{\text{th}} \) LO and TO phonon frequencies with their respective broadening parameters \( \gamma_{\text{LO},n} \) and \( \gamma_{\text{TO},n} \). In this case, the value of \( \varepsilon(\infty) \) is taken at a reasonable distance from the highest phonon frequency to account for the offset in the dielectric function due to dielectric resonances at higher frequencies. Equation (3.11) is well suited for modelling HfO\(_2\), as it takes into account the anharmonic
coupling effects of multiple-phonon modes often found in metal oxides. To ensure the physical validity of the modeled optical and dielectrical values, the following constrains were used in accordance with reference [49]. Equation (3.11) is well suited for modelling HfO$_2$, as it takes into account the anharmonic

$$\sum_n \gamma_{LO,n} - \gamma_{TO,n} > 0$$  \hfill (3.12)

When these conditions are met, the extinction coefficient $k$ has a positive value. If $k$ is negative, $\varepsilon$ loses its physical meaning.

In the study of gate dielectrics, one is interested in finding the static dielectric constant $\varepsilon(0)$, corresponding to the dielectric response of a material to a DC electric field. Unfortunately, there are no measurement techniques that can physically measure down to zero frequency, as this would imply measurements employing light with an infinitely long wavelength. However, it can be seen that if $\gamma_{LO,n}, \gamma_{TO,n} \ll \omega_{LO,n}, \omega_{TO,n}$ in Equation (3.11), the static dielectric constant can be directly related to the transverse and longitudinal optical phonon frequencies and the high-frequency dielectric constant through the following equation [15, 49]

$$\varepsilon(0) = \varepsilon(\infty) \times \prod_n \frac{\omega_{LO,n}^2}{\omega_{TO,n}^2}$$  \hfill (3.13)

This relation is known as the Lydanne-Sachs-Teller equation.

### 3.2.3 Heavy Ion Elastic Recoil Detection Analysis

ERDA is a nuclear technique used for compositional analysis of thin films. The information obtainable with this technique depends on the experimental conditions and also the film thickness, but can for instance be an elemental concentration depth profile or a concentration ratio of elements present in the sample. [50] The principle of ERDA is to irradiate a target sample with a high-energy ion beam from an angle $\alpha$, upon which target particles are knock out, or ‘recoiled’, in the forward direction at specific exiting angles depending on the particle species. The energy distributions of these recoiled particles are detected by a suitable ion detector from under a certain angle $\phi$ (see Figure 3.13). The ion beam typically consists of heavy ions (such as Au$^+$, I$^+$ or Cl$^+$) with energies in the order of 1 MeV/amu. With such a beam, it is possible to measure both

#### Figure 3.12

- **a)** An example model of an arbitrary thin film on a Si substrate, with a native oxide at the interface.
- **b)** The dielectric response from the pseudodielectric function of the thin film layer around its resonant frequency.
heavier (e.g. transition metals) and lighter elements (e.g. N, O, C), making ERDA a very comprehensive compositional analysis tool.

In the ideal case, only two processes shape the measured experimental data: the transfer of energy from primary (i.e. from the ion beam) to recoiled target particles during collisions, and the energy loss of these particles while they travel through the sample. The first process determines the energy of recoiled atoms, while the second determines the deviation from this energy with depth in the sample. Collisions between primary and target particles can be described by the Coulomb repulsion between two interacting nuclei. From the laws of energy and momentum conservation, the energy fraction transferred in such a collision is given by the kinematic factor for recoiling,

\[ K_r = \frac{4M_1M_2 \cos^2 \phi}{(M_1 + M_2)^2} \]  

(3.14)

in terms where \( M_1 \) and \( M_2 \) are the masses of the primary and recoil particles respectively and \( \phi \) is the recoil angle. With this equation, it can be shown that the energy of recoil is at a maximum when \( M_1 = M_2 \). Another important property of particle collisions is the probability with which it takes place, and also the probability that the recoiled particle gains momentum in the direction of the detector. These probabilities are proportional to the areal density (atoms/cm\(^2\)) of the specific particle species in the sample, and the proportionality constant is given by the Rutherford differential cross section,

\[ \frac{d\sigma}{d\Omega} = \left( \frac{Z_1Z_2e^2}{2E_i} \right)^2 \frac{(1 + M_1/M_2)^2}{\cos^3 \phi} \]  

(3.15)

where \( Z_1 \) and \( Z_2 \) are the atomic numbers of the primary and recoiled particles, \( e \) is the electron charge and \( E_i \) is the kinetic energy of the recoiled particle. This equation is very common in textbooks, and may be presented in several forms; here, it is presented in form given in reference [50]. The energy loss of particles moving within the sample results mainly from interactions with electrons, which causes excitation and ionization of the sample atoms, while the energy loss due to interaction with the sample nuclei constitutes only about 1% of the total energy loss. This total energy loss can be parameterized by an energy loss factor \( S \), given by

\[ S = \frac{K_r e_{\text{in}}}{\sin \alpha} + \frac{e_{\text{out}}}{\sin(\phi - \alpha)} \]  

(3.16)
where $e_{in}$ and $e_{out}$ are the stopping powers of the primary particle on the inward path and of the recoiled particle on the outward path respectively. Stopping powers are treated as a material property, but depend on both the type and energy of the primary particle as well as the properties of the sample material. However, the energy loss factor and stopping powers have the same numerical values and units; the difference is that $S$ describes what happens to a particle. It has been found that the spectral energy width of a certain measured element can be determined by $S$. For thin film analysis, this means that $S$ relates the energy of the recoiled particles as they enter the detector to the depth of origin.

The experimental setup used in conventional ERDA was illustrated in Figure 3.13. For ion detection, there exist a few different types of detectors. The most advanced types measure the time-of-flight of particles traveling through the detector, while the most common detectors are gas ionization chambers. Such detectors are filled with a gas, usually some kind of alkane, which becomes partially ionized upon collision with the detected particles. An electric field applied between an anode and a cathode in the chamber, which attracts the produced gas ions and electrons to respective sides where they are picked up by electrodes, thereby inducing a measurable electric signal. Gas ionization chambers are preferred in heavy ion ERDA since they are more resilient to radiation damage from heavy particles; a common problem with semiconductor-based ion detectors, which are often used for the detection of lighter elements. The gas detector can be easily modified to perform both elemental determination and energy measurement of incident particles simultaneously, as well as providing directional information. This last feature permits large solid angles for ERDA, which in turn results in high detection sensitivity that helps to reduce the sample exposure time to the ion beam. Indeed, gas ionization detectors can provide relative energy resolutions of better than 1%. The specific type of gas ionization chamber used for ERDA measurements in this project is commonly known as a Bragg-ionization chamber; the axial design of such chambers provides better energy resolution. This chamber was filled with isobutane gas and used a full energy detection circuit and a fast timing circuit to obtain a $Z$ dependent signal to separate ion species. The measurements were performed at the Helmholtz Zentrum Dresden-Rossendorf (HZDR) research center in Dresden, Germany; a facility that operates a 4.375 MV tandem accelerator which, when used with Cl$^{7+}$ ions, produces a 35 MeV ion beam readily capable of recoiling Hf atoms. The tandem accelerator has two stages of acceleration, one of Cl$^-$ and one of Cl$^{7+}$, such that the resulting energy of the ions in the beam is calculated by $4.375 \text{MV} \times (7 + 1 e) = 35 \text{MeV}$. The beam angle of incidence $\alpha$ was set to 15°, while the detector angle $\phi$ was set to 31°. The beam analyzes an area of about 1.5 mm $\times$ 1.5 mm on the sample surface. There was also a solid state detector installed at the 38° detection angle for specific detection of hydrogen. To screen out other recoiled and scattered particles, a Mylar (C$_{10}$H$_{8}$O$_{4}$, density 1.395 g/cm$^3$ [50]) stopper foil was used to cover the entrance to this detector.
4 RESULTS AND DISCUSSION

4.1 PROCESS CHARACTERIZATION

The results from process characterization are presented in Figure 4.1. In Figure 4.1a) and b), the values of target voltage applied in order to maintain a constant average target power of 100 W has been plotted against the O₂ flow rate, Φ₀₂. In both deposition atmospheres, the target voltage begins to increase at the dashed lines; these dashed lines mark the onset of compound target coverage. As can be seen, the target voltage gradually reaches a plateau at around 3 sccm Φ₀₂, indicating that the target is in the poisoned mode. The effect of target voltage and Φ₀₂ on the film growth rate is illustrated in Figure 4.1c) and d), where the film growth rates are plotted against Φ₀₂. It is shown that the growth rate is increased at Φ₀₂ = 1.0 sccm in both deposition atmospheres, but drops steeply as Φ₀₂ is slightly increased. Above 1.6 sccm Φ₀₂, the growth rate continues to drop, but the rate of decrease is reduced. These results are in accord with the literature review presented in Chapters 3.1.1 and 3.1.2, and comparable to other results from reactive HiPIMS deposition of metal oxides. [44, 52] Judging from slope of the target voltage curves, it can be seen that the combined use of HiPIMS and N₂ addition makes the transition from metallic

![Figure 4.1](image)

Process characterization curves for the two deposition atmospheres Ar-O₂ and Ar-O₂-N₂. The dotted lines indicate the onset of target poisoning in the two deposition atmospheres respectively. a) and b) show the target voltage vs. Φ₀₂ while c) and d) show the calculated growth rate vs. Φ₀₂ for the two deposition atmospheres respectively.
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to poisoned target mode much smoother than by using HiPIMS alone. Further, the target voltage at high $\Phi_{O_2}$ in the Ar-O$_2$-N$_2$ case is lower than that of the Ar-O$_2$. The increase in deposition rate around the dashed lines can be attributed to the deposition of both metal and reactive gas particles on the substrates. This can also be due to the increased target voltage, as higher target voltage levels result in higher target erosion rates. As $\Phi_{O_2}$ increases, the compound covered fraction of the target grows, and the deposition rate is reduced since the sputtering yield of compound materials is in general lower than that of pure metallic materials.

4.2 CHEMICAL COMPOSITION ANALYSIS

The results from the ERDA measurements are presented in Figure 4.2. In all cases, less than 2 at% hydrogen was detected in the thin film samples (not shown in the figure). For most of the samples, a certain degree of intermixing was found between the film and the Al capping layer, while no such intermixing was detectable between the film and substrate. The compositions presented in Figure 4.2 are accurate to within 0.5 at%; this error margin accounts for both measurement statistics as well as uncertainties in the data analysis.

The sample with $\Phi_{O_2} = 0.4$ sccm in Figure 4.2a) shows the largest degree of N incorporation, with a film composition of Hf$_{37}$O$_{47}$N$_{16}$. Considering no Hf-vacancies and assuming that all N and O atoms are situated at non-metal lattice sites, a film with this composition may contain at least 8% O-vacancies. For $\Phi_{O_2} = 0.8$ sccm, the composition shifts to higher O content at the expense of Hf.

![Figure 4.2](image)

Figure 4.2

Compositional data from ERDA measurements on N incorporated and pure HfO$_2$ thin films, deposited at 17°C and 400°C.
of N content, resulting in a film with the composition Hf$_{36.5}$O$_{59}$N$_{4.5}$. With the same conditions in mind, a film with this composition may also contain at least 8% O-vacancies. At Φ$_{O2}$ = 2.0 sccm, the film composition can be considered that of stoichiometric HfO$_2$. The lack of detectable N incorporation in the last sample is due to the higher reactivity of O, which replaces N atoms during the film growth. The energy of formation for Hf atoms in HfO$_2$ is ΔH$^f_{\text{HfO}_2}$ = -11.63 eV/metal atom, much more thermodynamically favorable than for Hf atoms in HfN, ΔH$^f_{\text{HfN}}$ = -3.82 eV/metal atom. For the samples deposited in an Ar-O$_2$ atmosphere shown in Figure 4.2b), Φ$_{O2}$ = 0.4 sccm produces films with the composition Hf$_{51}$O$_{49}$, which suggests a possible 33% O-vacancy content. The sample at Φ$_{O2}$ = 0.8 sccm shows the composition of stoichiometric HfO$_2$, while the sample at Φ$_{O2}$ = 2.0 sccm shows a slightly higher content of Hf.

Samples deposited at elevated substrate temperatures show similar compositions to their room temperature substrate counterparts. Figure 4.2c) shows that for Φ$_{O2}$ = 0.8 sccm, films obtain the composition Hf$_{34.6}$O$_{59}$N$_{6.4}$, which may contain at least 3% O-vacancies with the same considerations as mentioned earlier. The film at higher Φ$_{O2}$ in Figure 4.2c) shows no signs of N incorporation, and approximately retains the composition of stoichiometric HfO$_2$. Lastly, Figure 4.2d) shows the composition of HfO$_2$ films deposited without N$_2$ at elevated substrate temperatures. The low Φ$_{O2}$ sample shows a composition of Hf$_{42}$O$_{38}$, suggesting a possible 20% content of O-vacancies. At Φ$_{O2}$ = 2.0 sccm, the film approaches the ideal HfO$_2$ stoichiometry, with a slightly higher content of Hf.

### 4.3 CRYSTAL STRUCTURE ANALYSIS

Figure 4.3 shows the XRD patterns recorded from samples within the sets 3 (Figure 4.3a)) and 4 (Figure 4.3b)), which were synthesized at room temperature by varying Φ$_{O2}$. In almost every diffraction pattern, a small peak can be seen at 20 = $\approx$ 38°. This peak corresponds to the (111) reflection of the Al capping layer. Also, the exceedingly sharp peak seen in some of the HfO$_2$ diffraction patterns at 20 = $\approx$ 33° belongs to the Si substrate, which exhibits a forbidden peak, (200), at 20 = 32.95° (calculated by Bragg’s law and the interplanar spacing $d_{200}$). In the diffraction pattern at Φ$_{O2}$ = 0.4 sccm of Figure 4.3a), two strong peaks are visible around 20 = $\approx$ 30° and 50°. These peaks are diminished for increasing Φ$_{O2}$, and disappear entirely for the sample with Φ$_{O2}$ = 1.2 sccm. In this sample, a different peak emerges at 20 = $\approx$ 28°, which corresponds to the strongest characteristic peak of P2$_1$/c monoclinic HfO$_2$, m-HfO$_2$(-111), at 20 = 28.36°. [46] For further increasing values of Φ$_{O2}$, the m-HfO$_2$(-111) peak becomes more pronounced, while traces of other peaks belonging to the monoclinic crystal structure can be seen at higher 20 angles. Throughout the diffraction patterns in Figure 4.3a), an amorphous feature is visible between 25° and 40°. This feature is attributed to the thin film, as the various HfO$_2$ crystal structures all exhibit diffraction peaks in that angular region. A similar amorphous feature can be found in the diffraction patterns in Figure 4.3b), and is in fact the defining characteristic of most of the patterns save for the one at Φ$_{O2}$ = 0.4 sccm. The diffraction pattern of this particular sample shows strong peaks from crystalline pure Hf in the hexagonal crystal structure, and is evidence that phase separation into pure Hf and HfO$_2$ occurs in films deposited at this Φ$_{O2}$ value. Indeed, no HfO$_2$ phase can accommodate 33% of O-vacancies and remain stable. According to Reference [22] and the phase diagram presented in Chapter 2.2.1, the HfO$_2$/HfO$_2$ + α-Hf phase boundary is found somewhere between 63.5 and 66 at% O; an accurate limit has not been determined thus far. A simple calculation can show that the sample may be composed of up to ~26% pure Hf, while the remainder is in oxide form (not accounting for any cation or anion vacancies). At Φ$_{O2}$ = 0.8 sccm, the amorphous feature appears to be centered around 20 = $\approx$ 34°, while for higher Φ$_{O2}$, this seems to be shifted to a slightly lower 20 angle. Finally for the diffraction pattern at Φ$_{O2}$ = 2.0 sccm in Figure 4.3b), a small crystalline peak at 20 = $\approx$ 28° is visible, corresponding to the m-HfO$_2$(-111) diffraction plane.
The amorphous nature of the samples grown in Ar-O$_2$ resembles that of HfO$_2$ thin films prepared by reactive dcMS [53, 54, 55] or rfMS [56] at room temperature. It is attributed to the low substrate surface mobility of the film forming atoms. This means that such atoms are incorporated into the growing film wherever they land, and are unable to maneuver themselves to any energetically more favorable sites, typically the lattice sites of a crystalline lattice. This explanation can account for the amorphous features in both Figure 4.3a) and b). Note that the formed microstructure does not need to be truly amorphous; the films may also be nanocrystalline. In any case, both the absence of crystalline structure and the small grain size of a nanocrystalline material will prevent the samples from being adequately studied by XRD.\(^*\) However, these results are in stark contrast with previous work on HfO$_2$ films prepared by reactive HiPIMS, also at room temperature, which show films of high crystalline quality in both Ar-O$_2$-N$_2$ and Ar-O$_2$ atmospheres. [13] It is known that the flux of ionized particles is higher in HiPIMS than dcMS. Without substrate bias, these ions may be accelerated across the plasma sheath surrounding the substrate and bombard the substrate/film surface, thereby imparting some kinetic energy to surface-dwelling particles. Effectively, this increases adatom mobility and allows these to reposition

\(^*\) The microstructure of the films may be further investigated by transmission electron microscopy to reveal whether the films are truly amorphous or nanocrystalline. In the latter case, electron diffraction may also determine the crystal structure within such nano-sized grains.
themselves to more energetically favorable positions on the substrate/film surface. Unfortunately, the energy gained by acceleration across the plasma sheath is small, and may be insufficient to affect the crystallinity of the synthesized films. Furthermore, the flux, or amount, of ionized particles impinging on the substrate is dependent on the deposition characteristics, such as the target to substrate distance, the total working pressure and the peak current density on the target. A longer distance generally increases the probability for particle collisions within the plasma. This is also true for higher total working pressures, but one must keep in mind that a higher pressure helps to enhance the plasma density. Finally, the peak current density, measured as the peak current over the target surface area, is the main influence on the plasma density. As the effect of these deposition characteristics are hard to quantify, the only defensible statement that can be made is that differences in these characteristics may have played a substantial role in separating the structural properties observed in films prepared in this study as opposed to those prepared in reference [13].

The two peaks found in the N incorporated HfO₂ sample diffraction patterns with ΦO₂ ≤ 0.8 sccm at ~30° and ~50° may correspond to one of several high symmetry HfO₂ crystal structures. This assumption is backed by the DFT calculations of Reference [13], which predicted the definitive stabilization of c/t-HfO₂ over m-HfO₂ when O-vacancy/N incorporation levels exceeded a certain limit. The Fm3m cubic (c-HfO₂) has its strongest characteristic peaks at θ = 30.362° and 50.635° for the (111) and (022) diffraction planes respectively. [48] The P4₃nmc tetragonal HfO₂ crystal structure exhibits its strongest peak at 30.092°, closely spaced twin peaks at the angles 34.201° and 35.127°, 49.632° and 50.394° and finally 58.496° and 59.744°. [47] Since the peak at ~30° is most prominent in the diffraction patterns, this peak is used to deduce that these samples are composed mainly of t-HfO₂, as it can be seen that the peak centroid is closer to the t-HfO₂ reflection at 30.092°. However, the slightly asymmetric shape of this peak and also the one at 50° suggests that there may be a mixture of both c- and t-HfO₂ in the samples. In comparison, the peak around 30° seems to broaden and shift towards lower angles from ΦO₂ = 0.4 sccm (θ = 30.04°) to ΦO₂ = 0.8 sccm (θ = 29.88°). The broadening is due to competitive formation of the monoclinic phase (not visible yet at ΦO₂ = 0.8 sccm), which will tend to increase atomic disorder in the film and hinder grain growth; smaller grains cause diffraction peaks to broaden and lose intensity. The shift is associated with changes in the lattice spacings induced by changes in composition. Finally, these compositions indicate that the rhombohedral crystal structures of HfO₂N₄ and HfO₁₃N₂ are also possible candidates, but due to the lacking crystalline quality of the samples in sets 3 and 4, it is impossible to pinpoint their exact crystal structures by studying the diffraction patterns presented in Figure 4.3.

Figure 4.4 shows comparisons between samples deposited at the same O₂ flow rates, but at different substrate temperatures. It is clear that the crystalline quality is drastically improved by applying 400° C to the substrates, as the high temperature (HT) diffraction patterns contain sharper peaks with higher intensities. Also, the amorphous feature seen in the RT diffraction patterns is not present in the HT cases, proving that the amorphous feature stems from the thin film, and not the substrate. In Figure 4.4a), the monoclinic crystal structure is clearly evident in both the RT and HT samples, exhibiting a strong peak at θ = 28° in both diffraction patterns. Notice that the previously mentioned peaks that possibly correspond to c-HfO₂ are also present in the HT diffraction pattern, as indicated by the arrows, meaning that the two crystal structures coexist in that particular sample (albeit with a higher percentage of m-HfO₂). This may also be the case for the RT sample, but it is difficult to tell from the diffraction pattern since any low intensity peaks may be buried within the amorphous feature. In relation to the DFT calculations of Reference [13], samples grown at this ΦO₂ possess a level of O-vacancy/N incorporation that should be too low for any significant c/t-HfO₂ formation. It is suggested that a high temperature during growth may affect film crystallization in a way that the defect limit is reduced for the
Results and Discussion

formation of higher symmetry crystal structures over m-HfO$_2$. In contrast, the HT diffraction pattern in Figure 4.4b) shows only peaks belonging to m-HfO$_2$, but with improved crystalline quality as compared to the RT diffraction pattern. Figure 4.4c) shows the RT and HT diffraction patterns of HfON with $\Phi_{O_2} = 0.8$ sccm. The HT diffraction pattern still shows the two peaks at $2\theta \approx 30^\circ$ and $50^\circ$, but now a third peak is also visible at $2\theta \approx 35^\circ$, and the entire diffraction pattern corresponds better with c-HfO$_2$ than t-HfO$_2$. The previous assumption regarding a decreased defect limit with increased growth temperature is also in agreement with this difference between RT and HT sample diffraction patterns. If the defect limit is lowered, t-HfO$_2$ formation will be more prominent at a low temperature and high defect content, while c-HfO$_2$ is more probable at

Figure 4.4
A comparison of the XRD patterns of HfON and HfO$_2$ samples synthesized with different substrate temperatures. The dashed lines indicate the position of the single diffraction peak from the Al capping layer. The intensity scale is matched for all diffraction patterns. a) HfON with $\Phi_{O_2} = 2.0$ sccm. The arrow indicates the presence of a c-HfO$_2$ peak in an otherwise m-HfO$_2$ diffraction pattern. b) HfO$_2$ with $\Phi_{O_2} = 2.0$ sccm. c) HfON with $\Phi_{O_2} = 0.8$ sccm. d) HfO$_2$ with $\Phi_{O_2} = 0.8$ sccm.
higher temperatures due to the transformation order (with increasing temperature) of m-t-c. In Figure 4.4d), the HT diffraction pattern shows mainly peaks belonging to m-HfO₂, but with a preferred orientation in the (111) direction, as evidenced by the intense peak at 20 = 31°. The strongest peak h-Hf is also visible at ~37°, suggesting that this film has phase separated into up to ~13% pure Hf and 87% stoichiometric HfO₂, calculated again without considering any cation or anion vacancies.

Previous work on the effect of N incorporation in HfO₂ suggests that the strongest influence on crystal structure does not come from the N substitution itself, but instead from the effect of N on O-vacancies. [34, 37, 38] Nevertheless, the DFT calculations from Reference [13] suggest that N alone is sufficient to stabilize c/t-HfO₂ formation during film growth. In Reference [38], the lengths of all anion bonds in HfON are calculated as functions of varying at% of N content. From this graph, the average anion bond length for 6 at% N (roughly corresponding to the composition Hf₃₄.₆O₅₉N₆.₄) is ~2.18 Å, which is slightly larger than that of pure HfO₂ at 2.15 Å (from the same graph). This elongation of the average anion bond length is roughly of the same magnitude as that caused by neutral O-vacancies (0.1-0.2 Å according to Reference [28]), and should therefore be enough to have an effect on crystal structure formation.

For low concentrations of N (< 20-40 at%) in HfO₂, the N atoms are predominantly fourfold coordinated (to Hf atoms), while O atoms are distributed between threefold and fourfold coordination due to the structural relaxation that occurs around O-vacancies, leaving Hf atoms to be sixfold or sevenfold coordinated. As mentioned in Chapter 2.2.1, these structural relaxations happen by Hf atoms being displaced outwards from an O-vacancy while O atoms are displaced towards the center of the vacancy. Further, it was mentioned that charged O-vacancies have a significantly larger effect on the crystal structure of HfO₂ than neutral O-vacancies. As discussed in Section 2.2.3, N atoms are likely to couple to O-vacancies in HfO₂ and modify the charge state of the crystal structure of HfO₂ films. This is observed as the stabilization of the cubic crystal neutral O-vacancies to positively charged ones. Thus, N incorporation should significantly affect structure over the monoclinic for the sample with low O content in Figure 4.4c), and the presence of the cubic structure even in the sample with higher O content in Figure 4.4a). This is not the case observed for the HfO₂ samples in Figure 4.4b) and d), which instead show a difference in preferred crystallite orientation with varying O content. For low O contents, the presence of pure Hf strains the m-HfO₂ lattice, giving the preferred orientation shown in Figure 4.4d). This effect has been previously reported for both HfO₂ [56] and HfON [59] thin films with low O contents.

Samples were also produced at a higher substrate temperature (700° C), but this temperature proved to be too high, and the films exhibited undesired effects, as can be seen in Figure 4.5. For low O₂, the N incorporated films exhibited bad adhesion to the substrate, which suggests the formation of some undetermined phase of HfON or HfSiON that possesses lattice parameters incompatible with those of cubic Si. This assumption is probable, as the pure HfO₂ film showed formation of HfSiN. For higher O₂, the N incorporated films showed a more even distribution of coexistent m-HfO₂ and c-HfO₂, while the pure HfO₂ sample showed only m-HfO₂ diffraction peaks, with a minor improvement in crystalline quality (sharper diffraction peaks with higher intensities).

From the HT diffraction pattern in Figure 4.4c), we may consider the crystal structure to be cubic HfO₂. This can be determined by successively eliminating probable candidates. First, considering the P4₂/mmc tetragonal structure, there are no indications of a double peak at 20 ≈ 35°. A similar argument is used in reverse by Tomida, Kita and Toriumi in Reference [12], where the authors determine Si-doped HfO₂ to have the tetragonal structure. In the HRXRD diffraction pattern presented in this reference, the double peak at 20 ≈ 35° is clearly evident, as well as a double
Results and Discussion

Figure 4.5
XRD diffraction patterns from both N incorporated and pure HfO$_2$ thin film samples, deposited with a substrate temperature of 700$^\circ$ C.

Figure 4.6
Comparison of peak broadenings in the c-HfO$_2$ diffraction pattern as calculated from an ideal case and from experimental data. For the ideal calculation, a lattice constant of 5.095 Å used for c-HfO$_2$, with CuK$_{\alpha1}$ = 1.54056 Å and CuK$_{\alpha2}$ = 1.54441 Å. The difference in the y-scales are due to the fact that the ideal broadening is calculated from the CuK$_{\alpha}$ emission line separation only, while the experimental broadenings are affected by other film properties such as grain size and instrumental broadening.

peak at 20 $\approx 60^\circ$, which was also not found when samples in this study were measured at higher 20 angles. HRXRD measurements performed for the N incorporated samples in the present study produced diffraction patterns of low quality due to the polycrystalline nature of the films, and are not presented here. Nevertheless, in comparing the diffraction pattern of Reference [12] to the HT diffraction pattern in Figure 4.4c), the latter has similar quality to the former with respect to angular resolution, i.e. the measured range of angles versus the average width of constituent peaks. The HT diffraction pattern in Figure 4.4c) is considered sufficient to reveal any split peaks with an angular separation of $\sim$1$^\circ$. By fitting the peak at $\sim$35$^\circ$ with a Gaussian function, the peak centroid is determined to 35.34$^\circ$ ± 0.007$^\circ$ with a FWHM of 0.511$^\circ$. The peak at 20 $\approx 50^\circ$ in

* Compare to the tabulated values 35.202$^\circ$ (c-HfO$_2$(002)), 34.201$^\circ$ (t-HfO$_2$(002)), 35.127$^\circ$ (t-HfO$_2$(200)). [47, 48]
the HT pattern in Figure 4.4c) appears broader than the two lower angle HfO₂ peaks, which is suggestive of peak overlapping. With a similar peak fitting procedure, the peak centroid is found to be located at 50.64° ± 0.005° with a FWHM of 0.947°. For sake of completeness, the peak at 20 ≈ 60° was also analyzed, with a resulting peak centroid at 60.22° ± 0.01° and FWHM of 1.015°. It is a known artifact of X-ray diffractometry with CuKα radiation that the separation between CuK₁α and CuK₂α emission lines grows with increasing scattering angles, resulting in a broadening of high angle peaks in the diffraction pattern as was depicted in Figure 4.6. Note that the experimental curve data is also affected by other types of broadenings such as grain size broadening and instrumental broadening. This sets the calculated and experimental y-scales apart. With this in mind as well as the lacking evidence of overlapping peaks at the 35° and 60° positions, one may conclude that the tetragonal crystal structure is not present in the film in any significant amount. Next, we consider the orthorhombic crystal structure. Of the two possible orthorhombic structures, Pbca and Pnmc, only the former is a valid candidate, as the Pnmc structure exhibits intense peaks at 2θ ≈ 32°, which is obviously not the present case. [57] Similar to the tetragonal structure, the Pbca HfO₂ diffraction pattern also exhibits multiple peaks at 2θ ≈ 35°, and by the same argument used before, this structure may also be disregarded. [58]

Next, we consider the possible HfON crystal structures. These have been reported to exist in the following compositions: Hf₂ON₂, Hf₂O₈N₄ and Hf₂O₁₁N₂, which all possess a cubic or cubic-like structure. [38] From ERDA, the sample under discussion has the composition Hf₃₄.⁶O₅₉N₆.⁴ which is then closest to Hf₂O₁₁N₂. According to diffraction patterns calculated by Ino et al. (Reference [38]), the crystal structure of this material is rhombohedral, showing multiple low intensity peaks in the 2θ region between 10° and 25°. Additional measurements (not presented here) in this angular region showed no signs of any such peaks, so the HfON crystal structures can also be excluded.

4.4 OPTICAL AND DIELECTRIC PROPERTIES

The experimental data and the curves originating from fitting the dispersion model to these data in the UV-NIR wavelength range are presented in Figure 4.7. As can be seen, the Cauchy model fits the experimental data very accurately, and is able to provide confident values for the

![Figure 4.7](image)

Experimental Ψ (full circles) and Δ (open circles) spectra along with best fit model generated Ψ (whole-drawn lines) and Δ (dashed lines) spectra from two samples with contrasting N incorporation.

* Compare to the tabulated values 50.635° (c-HfO₂(022)), 49.632° (t-HfO₂(202)), 50.394° (t-HfO₂(220)). [47, 48]
optical constants of the films. The general trends of the refractive index $n$ and extinction coefficient $k$ with radiation wavelength for different $O_2$ flow rates $\Phi_{O_2}$ are graphed in Figure 4.8a). For samples with $\Phi_{O_2} \geq 0.8$ sccm, both the refractive index $n$ and extinction coefficients $k$ behave similarly for all samples, being generally flat from the ultraviolet down through visible wavelengths and increasing towards some absorption feature outside of the measured wavelength region below 250 nm. The sample with $\Phi_{O_2} = 0.4$ sccm is seen to deviate strongly from this trend due to the inability of the Cauchy model to fit the experimental data accurately, indicating that this sample is conductive. Considering the high N and O-vacancy content of this sample, a hafnium nitride phase may be present in the sample or, similarly to the HfO$_2$ sample produced at the same $\Phi_{O_2}$, pure Hf may be present since both of these materials are conductive. It was also mentioned in Chapter 2.2 that O-vacancies introduce trap states within the band gap that may create electron leakage paths, while N incorporation tends to reduce the band gap by creating energy levels just above the valence band; these effects can also influence the conductivity of the sample. In Figure 4.8b), the $n$ and $k$ at 550 nm for different $\Phi_{O_2}$ are given to facilitate comparisons. This shows that $n$ is highest for high levels of N incorporation, at ~2.14, and drops to ~0 for the sample at $\Phi_{O_2} = 3.2$ sccm. On the other hand, $k$ apparently varies from 3.8E-4 to 9.4E-4 from $\Phi_{O_2} = 0.8$ sccm to $\Phi_{O_2} = 3.2$ sccm, with a dip to $k = 0$ for $\Phi_{O_2} = 2.0$ sccm. These values are consistent with previous experimental work on N-incorporated HfO$_2$ and indicate that the thin films are transparent to visible light and thus insulating. [36, 59]
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Figure 4.9 Experimental IRSE $\Psi$ (full circles) and $\Delta$ (open circles) spectra along with best fit model generated $\Psi$ (whole-drawn lines) and $\Delta$ (dashed lines) spectra from samples of decreasing order of N incorporation from a) to c). The model determined LO and TO phonon resonance frequencies are marked by vertical dashed lines.

Figure 4.9a)-c) show the IRSE experimental data collected from samples with decreasing N/O ratio, deposited at room temperature. Also shown are the generated best-fit dispersion model curves. Throughout all the spectra, the small dip features visible at ~1200 cm$^{-1}$ are associated with the absorption band of Si-O stretching vibration mode, which for stoichiometric SiO$_2$ is located at 1075 cm$^{-1}$. [60, 61] SiO$_2$ or a sub-oxide of this may exist as a thin (< 2 nm) interfacial layer between the HfO$_2$ films and their Si substrates, either from exposure of the substrates to the atmosphere prior to deposition, or from reactions between the film oxygen and the substrate. The model revealed these vibration modes to lay at 1073 ± 4.78 cm$^{-1}$, 1087.5 ± 3.04 cm$^{-1}$ and 1072.6 ± 3.94 cm$^{-1}$ for the samples in Figure 4.9a), b) and c) respectively. The larger deviation from 1075 cm$^{-1}$ for the sample in Figure 4.9b) suggests that interfacial layer in this sample is in the form of a sub-oxide of Si.

The dielectric function parameters extracted from the dispersion model are presented in Table 4.1. Error bars given in parenthesis represent the confidence of the model relative to the fitted range of frequencies (250 - 2250 cm$^{-1}$). Indeed, the values of these parameters depend as much on the accuracy of the model as the span of experimental data used for fitting. Bundesmann et al. performed similar IRSE measurements for amorphous Al-doped HfO$_2$ grown by metal-organic chemical vapor deposition, in which a 90% confidence limit (i.e. the error bar should be less than 10% of the parameter value) was used. [62] It can be seen that for most of the parameters in Table 4.1, this confidence limit is achieved. The only exceptions are the broaden-
ings of $\omega_{\text{TO},1}$, whose error bars are at most 13% of the parameter value. This is likely due to the high noise level in the experimental data at frequencies below ~600 cm$^{-1}$, which makes accurate fitting of the TO mode difficult. Specifically since the measurements did not cover frequencies below 250 cm$^{-1}$, the position of this TO mode remains uncertain.

Previous experimental work by Neumayer and Cartier with IR absorption spectroscopy showed that amorphous HfO$_2$ exhibits a broad absorption band in the frequency range between ~200 cm$^{-1}$ and ~600 cm$^{-1}$, with its center at ~355 cm$^{-1}$. Upon annealing up to 1200$^\circ$C, the authors observed crystallization of the HfO$_2$ film into the monoclinic phase, which then exhibited up to ten distinct absorption bands in the frequency region ~183 cm$^{-1}$ and ~752 cm$^{-1}$. For the samples in Figure 4.9, the very broad peak seen in at frequencies below ~650 cm$^{-1}$ is therefore further confirmation of the amorphous nature of these samples.

From the first principles calculations of Reference [9], c-HfO$_2$ has a single phonon vibration mode at 286 cm$^{-1}$, while t-HfO$_2$ has three modes located at 117 cm$^{-1}$, 384 cm$^{-1}$ and 536 cm$^{-1}$ and m-HfO$_2$ has as many as 15 modes from 140 cm$^{-1}$ to 779 cm$^{-1}$. With the present experimental data available for analysis, it is difficult to accurately match the extracted LO and TO frequencies with any of these crystalline phonon vibration modes, though they are sufficient to estimate the static dielectric constants $\varepsilon(0)$ of the samples. Comparatively, The N-incorporated sample with $\Phi_{O_2} = 0.8$ sccm is observed to have the highest $\varepsilon(0)$, which is generally expected due to the formation of higher symmetry HfO$_2$ crystal structures in the film. As the O-content is increased and the crystal structure shifts to a mixture of monoclinic and cubic, $\varepsilon(0)$ is observed to decrease. Finally, it is found that the pure

<table>
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<th>$\varepsilon(\infty)$</th>
<th>3.54 (0.065)</th>
<th>3.11 (0.065)</th>
<th>2.71 (0.059)</th>
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<tr>
<td>$\omega_{\text{TO},1}$ (cm$^{-1}$)</td>
<td>355 (4.7)</td>
<td>347 (7.0)</td>
<td>365 (7.3)</td>
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<td>$\gamma_{\text{TO},1}$ (cm$^{-1}$)</td>
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<td>143 (16.1)</td>
<td>128 (16.7)</td>
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<td>$\omega_{\text{LO},1}$ (cm$^{-1}$)</td>
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<td>$\gamma_{\text{LO},1}$ (cm$^{-1}$)</td>
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<td>155 (12.4)</td>
<td>148 (13.8)</td>
</tr>
<tr>
<td>$\omega_{\text{TO},2}$ (cm$^{-1}$)</td>
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<td>590 (5.7)</td>
<td>589 (5.9)</td>
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<td>98 (8.4)</td>
</tr>
<tr>
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<td>691 (2.0)</td>
<td>690 (2.8)</td>
</tr>
<tr>
<td>$\gamma_{\text{LO},2}$ (cm$^{-1}$)</td>
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<td>123 (4.3)</td>
<td>131 (5.3)</td>
</tr>
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<td>$d$ (Å)</td>
<td>397 (2.1)</td>
<td>339 (2.1)</td>
<td>202 (5.0)</td>
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<td>$\varepsilon(0)^*$</td>
<td>12.32 ± 2.10</td>
<td>10.48 ± 1.33</td>
<td>7.99 ± 0.97</td>
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*Calculated from $\varepsilon(\infty)$, $\omega_{\text{TO}}$ and $\omega_{\text{LO}}$ by the LST-relation. Confidence intervals are calculated by summation of the relative errors of the constituent variables.
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HfO$_2$ sample has the lowest $\varepsilon(0)$ due to its microstructure being mainly amorphous with only weak signs of crystallization into m-HfO$_2$. While this trend of decreasing $\varepsilon(0)$ can be considered true in general, the values for these given in Table 4.1 are at the moment only a rough estimation, as the confidence intervals indicate. With the statistical distribution of $\varepsilon(0)$ taken as Gaussian functions, there is a nontrivial overlap in estimated $\varepsilon(0)$ between the two N incorporated samples, as depicted in Figure 4.10. Fortunately, the overlap between the pure HfO$_2$ sample and the former two is virtually nonexistent, but still, the presently estimated $\varepsilon(0)$ values are a great deal lower than previously reported figures. Recall from Chapter 2.2.1 that m-, c- and t-HfO$_2$, possess calculated $\varepsilon(0)$ of ~16 - 18, 29 and 70 respectively (in all cases assuming a high-frequency dielectric constant $\varepsilon(\infty)$ of ~5). Clearly, the present samples cannot achieve such high values of $\varepsilon(0)$, since they are not entirely crystalline. However, Ceresoli and Vanderbilt have performed first principles calculations on the structure and dielectric properties of amorphous HfO$_2$. Their results showed that, in terms of atom coordination numbers and local atomic arrangements, the amorphous phase is similar to the monoclinic phase, and both exhibit an average $\varepsilon(0)$ of ~21-22 (calculated with a $\varepsilon(\infty)$ of ~4.6 - 5). [64] From experimental work, Ino et al (Reference [38]), have calculated the dielectric constants for various HfON crystal structures, and found all of these to lay around 23. It may be argued that these high values of $\varepsilon(0)$ are due to the fact that calculations are performed for ideal materials, whereas real materials contain defects that may affect its dielectric properties. For example, the IRSE analysis from Reference [62] found pure amorphous HfO$_2$ to have an $\varepsilon(0) \approx 11.76$ (with $\varepsilon(\infty) \approx 3.5$). Also, one should keep in mind that if the lower frequency measurement data had been more accurate, or if the lower measurement frequency limit was pushed further into the far infrared, the lower frequency phonon vibration modes could be determined more accurately or even be found at lower frequencies. It is highly probable that this would increase the estimated value of $\varepsilon(0)$. Finally, it is also important to point out that the $\varepsilon(\infty)$ used in the calculations were higher than those determined by the present IRSE analysis. The authors of Reference [64] state that the value of these were estimated from experimentally determined refractive indices in the visible frequency range, according to the physical relation $n^2 = \varepsilon(\infty)$. In the present study, this relation may be used only if there are no additional features in the dielectric function from 2250 cm$^{-1}$ to visible frequencies. This range was not measured, but if it is assumed to be absent of any oscillations, the refractive index values from Figure 4.8 (n $\approx$ 2, which would give $\varepsilon(\infty) = 4$) used in the LST-relation with the phonon frequencies in Table 4.1 would result in slightly higher $\varepsilon(0)$ values for all three materials.

In conclusion, there is a general trend of increasing static dielectric constant with increasing N incorporation that can be correlated with the crystal structures present for a specific film composition.
5 SUMMARY

N-incorporated HfO$_2$ films with varying amounts of N incorporation have been synthesized by High Power Impulse Magnetron sputtering in an Ar–O$_2$–N$_2$ atmosphere, by varying the Ar/O$_2$ gas flow ratio during deposition while keeping the N$_2$ gas flow constant. Also, HfO$_2$ films were grown with the same deposition technique in an Ar–O$_2$ atmosphere. The structural, optical and dielectric properties of the films were characterized by X-ray diffractometry and Variable Angle Spectroscopic Ellipsometry, while their compositions were determined by Elastic Recoil Detection Analysis.

It was found that films grown at room temperature with low O$_2$ flow rates ($\Phi_{O2} = 0.4$ – 0.8 sccm) showed an amorphous structure with a certain degree of crystallization into a cubic-like HfO$_2$ crystal structure, most likely the tetragonal crystal structure. Their compositions were determined to Hf$_{37}$O$_{47}$N$_{16}$ and Hf$_{36.5}$O$_{59}$N$_{4.5}$ for $\Phi_{O2} = 0.4$ sccm and $\Phi_{O2} = 0.8$ sccm respectively, with at least an 8% O-vacancy content for both. For higher $\Phi_{O2}$ (> 1.2 sccm), the films also showed an amorphous structure, but with crystallization in the monoclinic HfO$_2$ crystal structure with the composition Hf$_{33.3}$O$_{66.5}$ with at least a 0.5% O-vacancy content, i.e. there was no longer any N incorporation. For HfO$_2$ films grown at room temperature, $\Phi_{O2} = 0.4$ sccm proved to be insufficient to synthesize pure HfO$_2$, and a phase separation into m-HfO$_2$ and Hf is observed for the composition Hf$_{51}$O$_{49}$. Already at $\Phi_{O2} = 0.8$ sccm, stoichiometric HfO$_2$ is formed with the composition Hf$_{33}$O$_{67}$ and an amorphous crystal structure, while for higher $\Phi_{O2}$, the composition is slightly shifted to higher Hf contents, reaching Hf$_{35}$O$_{65}$ for $\Phi_{O2} = 2.0$ sccm and showing indications of crystallization into m-HfO$_2$.

The crystalline quality of produced films was improved by applying an elevated substrate temperature of 400°C during the deposition process. With these samples, it was possible to make the definitive identification of the cubic HfO$_2$ phase in films with high N content (composition Hf$_{34.5}$O$_{59}$N$_{6.4}$, with at least a 3% O-vacancy content). For higher $\Phi_{O2}$, the films were again free of N incorporation, with a composition of Hf$_{34}$O$_{66}$ with at least a 2% O-vacancy content, and a crystal structure consisting of a mixture of the cubic and monoclinic structures, with a stronger crystallization into the latter. Films grown at 400°C in an Ar–O$_2$ atmosphere showed once again signs of phase separation for low $\Phi_{O2}$, with a composition of Hf$_{42}$O$_{58}$ at $\Phi_{O2} = 0.8$ sccm. For $\Phi_{O2} = 2.0$ sccm, the composition is also Hf$_{35}$O$_{65}$ with a strong m-HfO$_2$ crystal structure.

It is argued that the stabilization of high symmetry crystal structures for increasing N incorporation is due mainly to the effect of N on O-vacancies in the HfO$_2$ crystal lattice, but also to some extent due to the ability of N atoms to expand the average anion–cation bond length. N incorporation introduces an excess of charged O-vacancies, which have been shown to cause local lattice relaxations that have a strong effect on the stabilization of higher symmetry HfO$_2$ crystal structures. At increased deposition temperatures, c-HfO$_2$ is crystallized in favor of t-HfO$_2$ due to further ordering of atoms in the crystal lattice, according to the structural transformation order (with temperature) m–t–c. In relation to Reference [13], these results can confirm the DFT calculation predictions regarding the stabilization of high symmetry crystal structures in HfO$_2$ films with N incorporation and O-vacancy formation above a certain limit. However, c-HfO$_2$ is also observed for high temperature samples consisting predominantly of m-HfO$_2$. It is therefore suggested that this limit may be lowered by increasing the growth temperature.
Spectroscopic ellipsometry in the UV-IR range showed that the films possess refractive indices of ~2 - 2.14 in the visible frequency range of light (values taken at a wavelength of 550 nm), with increasing values for increasing N incorporations up to the composition Hf$_{36.5}$O$_{59}$N$_{4.5}$, while their absorption coefficients are approximately zero in the same frequency range. This implies that the films are transparent to visible light, and confirms that they are insulating. Films with higher N incorporations (composition Hf$_{37}$O$_{47}$N$_{16}$) were found to become conductive, possibly due to the formation of Hf or HfN at low reactive gas flows ($\Phi$$_{O_2}$ = 0.4 sccm, $\Phi$$_{N_2}$ = 1.5 sccm), or the effects of excessive O-vacancy/N incorporation on the electronic structure of the material.

Further ellipsometric studies in the mid-infrared frequency range revealed the films to possess transverse and longitudinal optical phonon resonance frequencies in the range of 347 cm$^{-1}$ to 701 cm$^{-1}$. By using these frequencies along with the high-frequency dielectric constant $\varepsilon(\infty)$ in the Lydanne-Sachs-Teller relation, a general trend of increasing static dielectric constant $\varepsilon(0)$ with increasing N-incorporation was observed. This is believed to be correlated with the structural properties of each film; films exhibiting high symmetry crystal structures possessed higher dielectric constants.
6 FUTURE POSSIBILITIES AND FURTHER INVESTIGATIONS

While the structural analysis of this work, backed by compositional analysis, contributes to the understanding of N incorporated HfO$_2$, additional measurements on the dielectric properties of this material are needed. If IRSE is to be employed once more, it will be necessary to synthesize thicker films with the same crystalline quality as those produced with 400º C substrate temperature. Especially in FIR wavelengths, the increased thickness will provide much better IRSE spectra by providing a larger beam interaction volume. The samples measured by IRSE in the present study were largely amorphous; thus, the experimentally determined static dielectric constants are strongly correlated to that of amorphous HfO$_2$. As one of the long term goals with this project is to achieve the previously reported high static dielectric constants of upwards ~30 (from experimental work on cation doped c/t-HfO$_2$), performing measurements on samples with good crystalline quality is of utmost importance.

It has been reported before that N incorporation reduces the band gap of HfO$_2$ by introducing additional energy states above the valence band. Therefore, spectroscopic ellipsometry with UV light or another suitable technique can be used to determine the band gap of films produced in this study, as this property is at least as important as the static dielectric constant for the material’s application as a gate dielectric.

In view of the findings of this study, through both experimental methods and theoretical background research, it would be interesting to perform extended DFT calculations to better understand the relationship between N incorporation, O-vacancy formation and crystal structure formation.

With this study, a rough roadmap of composition versus crystal structure has been found. For further studies, it would be interesting to produce samples with smaller steps in O$_2$ flow rate in the range 0 to 1 sccm for both N incorporated and pure HfO$_2$. In this way, a more detailed mapping of the transition of phase stability with O content can be created. This would necessitate precise control of the O$_2$ flow rate, which may entail the use of a feedback system based on monitoring O$_2$ partial pressure.

Finally, a further step in the research of Hf-based dielectrics would be to investigate the properties of HfO$_2$ films with both anion and cation doping, i.e. to synthesize Hf-M-O-N films. It has been reported before for N-stabilized ZrO$_2$, that the stabilizing effect of both types of doping do not conflict and are in fact additive. [65] Seeing as ZrO$_2$ and HfO$_2$ are isostructural, the same should apply for the latter material, and prime cation dopants are Si or P for stabilization of c-HfO$_2$ and Sc or Y for stabilization of t-HfO$_2$, for maximal effect according to past work. With the added benefits of N incorporation, such as suppression of O-ion diffusion, such a material could possibly provide a replacement for currently used Hf-based dielectrics.
7 REFERENCES


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