Fundamental Processes in Growth
of Reactive DC Magnetron Sputtered Thin Films

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James Mbiyu, NGARUIYA
B.Ed-Sc.(Hons), M.Sc.
aus Kiambu/Kenia

Berichter: Univeritätsprofessor Dr. Matthias Wuttig
Univeritätsprofessor Dr. Dieter Mergel

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Chapter 1

Introduction

The ever-increasing demand for thin film coatings stems from their ability to continue to offer high technological solutions to material limiting problems. The specific application depends on the film properties such as optical transmittance/reflectance, hardness, wear resistance, crystalline nature etc. The optical coating materials are chemical compounds such as metal oxides, metal fluorides, and certain sulfides that reflect on or transmit in selected portions of the spectrum. These materials show a behaviour that is illustrated by fig. 1.1, whereby the spectral width of the high transmittance region has great practical importance. Among the foresaid compounds, oxide films are of special interest because under proper deposition conditions they are not only fully transparent layers but also very hard and environmentally stable. In an increased number of applications these coatings not only modify the optical properties of a surface but also have to serve as protective coatings that can withstand adverse chemical and physical environments.

In particular, thin films of transition metal oxides are characterized by high refractive indices, large optical band gap, are wear resistant, have good adherence to glass etc., properties that endear them for use as optical coatings. Due to a combination of these properties they also find wide range of applications for example: tantalum pentoxide is practically the most promising capacitor material to be used in the near future in dynamic random access memories (DRAM) [1]. On the other hand successful preparation of the films for these applications at cost effective ways is still quite challenging. For example growth rates for sputtered transition metal oxide films are often low and frequently the film’s surface roughness is high. These properties result in high production costs and operational inefficiency due to high light scattering at the film surface. An innovative
Fig. 1.1 Schematic curve of transmission versus wavelength of an optical material. The spectral width of high transmittance region has great practical importance.

way to correct this is examining sputtering of transition metal nitrides. Transition metal nitrides have high growth rates and show metallic behaviour. They are used in areas where chemically inert and hard coatings are required. More recently [2], between these two extremes of thin film oxides and nitrides, transition metal oxynitride films have been synthesized and have attracted great attention. It has been shown that addition of nitrogen during the growth of the oxide film can result in improved film growth conditions and physical properties. The substitution of the anion in the lattice leads to an increased refractive index due to the higher polarizability of metal-nitrogen bonds [3] as compared to metal-oxygen bonds.

As partly inferred above, the method of choice in making these films has been direct current (DC) magnetron sputtering. Its currently the primary candidate for microelectronic device applications, due to its compatibility with conventional metallization schemes in integrated circuit processing, as well as hard coating applications. Other attractive features of this method include its wide area coating capabilities, automation, and deposition of adhesive and homogeneous films among others. Reactive sputtering provides an additional advantage in this context. It involves the direct current magnetron sputtering of a metallic target or alloyed ceramic target in a
reactive gas atmosphere. Films with controlled stoichiometry can therefore be produced with high accuracy. For example through this method, aluminium nitride films, which are some of the most promising piezoelectric materials for the fabrication of acoustic wave devices, have been produced. In particular films applicable where good surface morphology, preferred crystal orientations and low temperature deposition are required have been successfully produced [4].

Quite often, the production of films involves non-equilibrium methods of preparation for example in the direct current reactive magnetron sputtering of a metal target. Consequently the properties continue to be highly dependent on preparation parameters. To establish optimum parameters for any particular film application is not easy and it is even more challenging to understand the basic processes controlling film properties. The latter include for example type and energy of deposited species, film bombardment, substrate temperature etc. Yet it is this fundamental understanding of the deposition processes which is needed to maintain reproducibility and allow the transfer of a process from one system to the other. This is best underlined by a consideration of energetic particle bombardment on the surface of a growing film. The bombardment can result in a number of surface effects which include (i) displacement of lattice atoms, (ii) enhancement of atomic mobility, (iii) creation of lattice defects, (iv) recoil implantation of surface atoms into the substrate layer, (v) surface heating, and (vi) sputter de-sorption of contaminant species. These surface effects will in turn affect residual stress, microstrain, grain size, morphology, and texture of deposited films. Understanding the relationship between bombardment and film properties is therefore important to those processes associated with ion bombardment.

In a number of cases, it is the physical structure of the thin film, which is directly responsible for or related to the desired film property. For instance, in gasochromic films, which can be used in solar control glazings, nanoporous amorphous films are required for fast switching [5]. Deposition of anatase and rutile crystalline titanium oxide, on the other hand, is desirable for photocatalytic activity [6] and for high index of refraction, respectively. For ferroelectric films the crystalline orientation, i.e. the texture is of paramount importance [7]. Despite this importance of the physical structure of the thin film, there is presently only a qualitative understanding of the classification of the various
physical structures and, more importantly their origin. The understanding is still on a
more phenomenological level where film structures are strongly related to the deposition
apparatus parameters (e.g. discharge pressure or discharge power) rather than
fundamental physical parameters. Even the transfer of knowledge from one deposition
apparatus to another may create problems due to the complexity of the dependence of the
relevant atomic growth processes on deposition apparatus design and relevant system
parameters. Clearly, in this field there is a need for model experiments aimed to bring the
understanding of thin film growth to a more fundamental or atomistic level.

On the other hand acquisition of such knowledge can be quite challenging if such
knowledge is only based on one kind of measurement only. Hence there is a need for
combination of different characterization methods to gather as much information as
possible. This enables an understanding of the relationship between different film
properties and elucidates new and effective pathways to tailor the film properties. This
concept is best illustrated by Weis et al. [8] where optical spectroscopy (Infrared, Visible,
Ultraviolet), X-ray reflectometry (XRR), Atomic force microscopy (AFM), Rutherford
backscattering (RBS) and Auger electron spectroscopy have been used to characterize
optical properties, layer thickness, film surface roughness, density and quantitative
element distribution of an energy conserving low E-film deposited on glass. Such a
combination of analytical tools has allowed a complete description and understanding as
to why simulated spectra deviate from the measured ones.

The experiments and results presented in this thesis hope to contribute to an
understanding of some fundamental processes in the direct current magnetron reactive
sputtering of transition metal oxide and oxynitrides. Specifically the goal is to understand
film and structure formation for the reactively sputtered oxides and oxynitrides. To
achieve this, the correlation of film properties with the deposition conditions and material
properties is investigated. The films growth conditions considered are plasma properties,
reactive gas(es) partial pressure(s) and growth rates while film properties include
structure, thickness, density, surface roughness and morphology, composition,
backspattering and deposition stress.

Since we are interested in structure and film formation for the sputtered films, in
chapter 2 we provide an overview of sputtering as the method of film preparation. In the
same chapter we examine film growth morphologies and structures and models used to explain them. Film growth and structure formation require energy and for sputtered films an additional source of energy is the non-thermal means through particle bombardment. To understand better the effects of film bombardment we examine deposition stresses and the models used in literature to explain them. Closely associated with film bombardment is the backspattering phenomenon, which we shall also briefly examine. In chapter 3 we discuss the theoretical principles of characterization methods used. Through interaction of X-rays with matter, we discuss how the grown film crystallinity, density and roughness can be determined. The principles of backscattering, secondary neutral mass and forward recoil spectrometries for film composition determination are presented. A discussion on the deduction of deposition stress through use of substrate bending technique is provided. Lastly some basic principles of atomic microscopy, which was utilized to study the films morphology are reviewed. Chapter 4 details the procedures followed in film preparation and characterization with the aforementioned techniques. The result and discussions are presented in chapter 5 and 6. Specifically chapter five examines structure formation in sputtered transition metal oxides, while chapter 6 seeks to address film composition and formation mechanisms that improve on growth conditions and film properties of the sputtered transition metal oxides through addition of nitrogen during sputtering. Lastly in chapter 7 we give conclusions and outlook to this work.
Chapter 2

An overview on film preparation, growth and characterization

In the first chapter we have discussed about the need for a fundamental understanding of the observed film properties upon deposition. We have specifically seen that film formation and the resulting micro-structure would be very crucial for their functionality. In this chapter we examine the method of film preparation used in this work and review some of the film properties investigated. Initially we provide a summary on sputtering processes where invaluable definitions like the glow discharge and the hysteresis are made. We provide an atomistic approach to thin film growth and review some models advanced to explain the microstructure in sputtered films. To understand film structure would also entail defining the sources of energy to the growing film. For sputtered films one such source would be energetic particle bombardment. This non-thermal process of energy supply to the growing film may also cause stress. A significant attention to compressive stresses and models used is thus provided. Lastly a short review on backspattering/resputtering, also a consequence of sputtering, is presented.

2.1 Thin film production

2.1.1 Principle of sputter deposition

The ejection of atoms from the surface of material (the target) by bombardment with energetic particles is called ‘sputtering’. If the sputtering is due to positive–ion bombardment, it is referred to as cathodic sputtering. The ejected or sputtered atoms can be condensed on a substrate to form a thin film. Other processes associated with the bombardment of a target by highly energetic ions include: (i) secondary electrons, (ii) ion reflection at the target surface, (iii) ion implantation, with the ion permanently buried into the target, (iv) radiation damage in the structural rearrangement varying from simple vacancies and interstitial to more gross lattice defects and (v) emission of X-rays and photons. These processes can be summarized as illustrated in fig. 2.1.
Fig. 2.1 Processes generated by the impact of highly energetic particle on a target surface. The collision may terminate at the target or cause particle sputtering.

To obtain sputtering as a useful coating process some criteria have to be met. First, ions of sufficient energy must be created and directed towards the surface of a target to eject atoms of the surface of the material. To achieve this, a low pressure argon gas for example, can be present in a chamber and by application of a sufficiently large voltage between the target and the substrate, as discussed below, a glow discharge is set up in a way to accelerate the positive ions to the target to cause sputtering. The average ion energy is given by

\[ E = \frac{2\lambda_{fp}}{L} \cdot eV_c \]  

where \( L \) is the separation between the cathode and the anode, \( \lambda_{fp} \) is the mean free path of the sputtering ion, \( V_c \) is the cathode fall voltage and \( e \) electron charge. Secondly, the ejected materials must be able to get to the substrate with little impedance to their movement. The pressure \( p \) determines the mean free path, \( \lambda_{fp} \), of the sputtered particles, which according to the Paschen relation is proportional to \( 1/p \). In addition to pressure, the
target substrate distance determines the scattering of the sputtered particles on their way to the substrate and hence also the amount of energy that they deposit on the substrate.

Sputtering is characterized by the sputter yield $S$, which is the ratio of the number of ejected atoms to the number of incoming energetic particles, which are predominantly ions. For low bombardment energies, $E$, up to about 1 keV, equation 2.3 by Sigmund [9] is used to predict the sputter yield:

$$ S = \frac{3\alpha}{4\pi^2} \frac{m_i m_e}{(m_i + m_e)^2} \frac{E}{U_o} $$

where $U_o$ is the surface binding energy of the material being sputtered, and $\alpha$ is a monotonic increasing function of $m_i/m_e$ for $m_i$ and $m_e$ the ion and target atom masses respectively, with values in the interval of 0.17 and 1.4 for $m_i/m_e$ between 0.1 and 10. The sputtering rate from the target is given by $\Phi_t = S \cdot I_\|$ (where $I_\|$ is the ion current to the target).

Reactive sputtering, the method used in this work, involves addition of a reactive gas in the sputtering process thereby producing a material by reaction of the gas and the sputtered target material. The reaction may be controlled to just dope the film with the desired percentage of the gas or enough gas may be supplied to ensure complete reaction of the sputtered metal.

Disadvantages encountered in reactive sputtering include low film growth rates and arcing. The latter is caused by a breakdown due to high electric field strength in the thin insulating layer formed adjacent to the target erosion area during reactive sputtering. Low growth rates result from decreased sputter yield for the compounds due to higher binding energies as is apparent from equation 2.2. Arcing may be solved, for example by radio frequency (rf) sputtering, at the expense of deposition rate, which is much lower compared to the direct current mode sputtering. In rf sputtering the ions bombard the target surface during one cycle and in the next cycle the electrons neutralize the built up charge.
2.1.2 Glow discharge for sputtering

As mentioned above a glow discharge is formed by application of a potential between two electrodes (target and substrate). Depending on the pressure $p$ of the gas and the distance $d$ between the electrodes a breakdown voltage of

$$U_b = A \frac{pd}{\ln(pd) + B}$$  \hspace{1cm} 2.3

is required for a self-sustaining discharge. The constants $A$ and $B$ are material dependent. A typical direct current-voltage characteristic of such a diode structure and its visual appearance are shown in fig. 2.2. In particular fig 2.2 (a) shows that the normal discharge is only defined in a specific window of the voltage–current relation for a plasma discharge. Fig. 2.2(b) shows adjacent to the cathode, sheath formation at the front, which is referred to as the cathode dark space. If the electrodes are placed further apart as depicted one identifies the Faraday dark space and the positive column. These two are ‘consumed’ out upon the two electrodes being brought together in the realization of the usual glow discharge, leaving only the cathode dark space and the negative glow regions, which remain unchanged in lengths. The negative glow results from excitation and recombination processes taking place in this region. Here, energetic electrons repelled by the cathode potential can cause electronic excitations in atoms through collisions. Some of these electrons undergo relaxation thereby emitting photons. The minimum separation between the two electrodes is about twice the dark space thickness, less than which the dark space is distorted and the discharge is extinguished.

Between the two electrodes the cathode dark space is the most important region since all the applied voltage is dropped across it. This is illustrated in fig. 2.2 (b) plot for the voltage against cathode-anode distance. The ions and the electrons created at the breakdown upon voltage application produce more ions by collisions with the gas atoms in the negative glow. From this fall in the cathode voltage, the ions are energetic enough (equation 2.1) to strike the cathode and produce the sputtered species as well as emit secondary electrons, which are essential for sustaining the glow. To overcome the problem of low ionization at low pressures a magnetron source is used at the diode target. The electrons are trapped in its magnetic field and move in cycloidal curves immediately
Fig. 2.2 (a) Current voltage relationship for the various types of plasma discharges between two powered electrodes, (b) Glow region of a DC-glow discharge and the voltage variation with the cathode-anode spacing.
Figure 2.3 Basic principle of sputter deposition. Ions generated in plasma and accelerated towards a target sputter material, which condenses at the substrates.

above the target as shown in fig. 2.3. Through this increased path length ionization efficiency is vastly increased.

2.1.3 Hysteresis effect

In the simplest case of reactive sputtering, a mass flow of single reactive gas is supplied to the processing chamber. This is in addition to the inert gas ionized through voltage application thereby causing sputter erosion. The gas reacts with the sputtered target atoms to form the desired compound. However the sputter erosion rate from the target responds extremely non-linearly to the supply of the reactive gas. The process may even exhibit a hysteresis. Fig. 2.4 depicts such a process for a zirconium target [10]. The figure shows the variation of the mass deposition rate and oxygen partial pressure with increasing and decreasing oxygen flow. If the supply of the reactive gas is small (< $q_b$) almost elemental non-reacted target material is sputtered. Below $q_b$ no significant partial pressure of reactive gas is noted since all the reactive gas reacts with the sputtered metal atoms. Normally from calculations the reaction should follow the dashed line. However as the gas flow reaches the flow $q_b$ the process avalanches to sputtering the fully formed
Figure 2.4 Properties of the deposition of zirconium oxide as a function of the oxygen flow. The mass deposition rate and the oxygen partial pressure both show a pronounced hysteresis [10]. The dashed curve shows the path that would be followed for no avalanche.

compound at the target surface. Due to higher binding energy of the compound, the sputter yield decreases abruptly (equation 2.2). A similar situation appears when the supply of reactive gas is decreased from high to low flow rates. Instead, fully compound films will be deposited until the supply reaches the lower value $q_l$ when the flow is insufficient to maintain the compound target surface.

The physical reason for the appearance of the hysteresis is the strong pressure dependence of the compound formation on the substrate and chamber walls (receiving area), which in most cases are the potentially largest pumps for the reactive gas. This can be seen from equation 2.4 where the total pump system $S(F)$ for the reactive gas may be defined as

$$F \left[ t \alpha_i A_i + c \alpha_c A_c + S_d \right] = FS(F)$$

2.4
where $F$ is the flux of neutral gas reactive gas molecules, $t$ and $c$ are the metal fractions on the target and the receiving areas (includes substrate and walls) respectively, $\alpha_t$ and $\alpha_c$ are the sticking coefficients of nitrogen on the target and the receiving areas respectively while $S_d$ is the external pumping speed which is proportional to pressure. The terms in equation 2.4 describes the three different pumping processes, which together are in equilibrium with the mass flow of the reactive gas entering the chamber. The first term represents the getter pumping of the target surface $A_t$, the second represents the getter pump by the receiving areas $A_c$ while the third is simply the pumping of the vacuum pump. For constant pressure, it can be shown from equation 2.4 that it is the continuous compound formation on the receiving area that causes the hysteresis and not primarily the compound formation on the target.

We now turn to how sputtered particles condense on the substrate to form the thin film. We first examine what morphology is taken by the condensing atoms as limited by kinetics and thermodynamics and later focus on the macroscopic film structure development for films prepared by physical vapour deposition.

### 2.2 Thin film formation.

The realization of films proceeds through nucleation and growth stages, which are determined by both surface energetics and kinetics. While surface energetics predicts the thermodynamic equilibrium limit for the growth mode, the film growth is by definition a non-equilibrium kinetic process. The actual growth mode is determined by the growth condition, such as growth rate and temperature, and the material parameters of the film/substrate combination. In the following section various contributions, which influence or even control the growth morphologies are discussed.

#### 2.2.1 Thermodynamic criterion of growth modes

A thermodynamic criterion developed by Bauer [11] for the growth mode under equilibrium conditions is given by

$$\Delta \sigma = \sigma_f + \sigma_i - \sigma_s$$

2.5

where $\sigma_t$ is the surface free energy of the substrate, $\sigma_i$ is the free energy of the interface and $\sigma_f$ is the surface free energy of the film. If $\Delta \sigma \leq 0$, the adatoms are more strongly
bound to the substrate than to each other and the film tends to extend on (wet) the substrate to minimize the total energy. Under this condition, complete wetting of the substrate is favourable and the Frank-van der Merwe (layer-by-layer) growth should be observed. If the inequality has the opposite sign then the atoms are more strongly bound to each other than to the substrate. In this case the Volmer-Weber (island) growth is obtained, i.e. without wetting the substrate. Now, the film energy may get a contribution from, say strain energy (which is proportional to film thickness). Addition of this energy to $\Delta\sigma$ may result in a value smaller than zero until a certain thickness is reached beyond which the value is larger than zero. This way the Stranski-Krstanov (island plus layer) growth mode is obtained. The three growth modes are schematically shown in fig. 2.5.

![Fig. 2.5 Schematic growth modes of thin films: Morphology of a growing film for (a) Frank-van der Merwe (layer by layer), (b) Stranski-Krstanov (island plus layer) and (c) Volmer-Weber (island) growth upon increased coverage with monolayers (thickness).](image)

### 2.2.2 Kinetics aspects and microscopic models

In most practical cases, growth occurs far from equilibrium such that it is strongly influenced by kinetic processes. Therefore the final macroscopic state of the film is not necessarily the most stable but kinetically the most favourable and hence the need for understanding atomistic processes beside the thermodynamic principles. Growth of a film
starts with the arrival of atoms from the vapor. The atoms migrate on the surface until re-evaporation into vacuum, capturing by existing steps or clusters or nucleation into clusters occur as summarized in fig. 2.6. On a surface the potential for adatoms (binding energy) shows a modulation due to the atomic arrangement of the underlying substrate/atomic layers. Therefore to move from one adsorption site to a neighboring one, the adatom must overcome an energy barrier, $E_d$. According to the Gibb’s Boltzmann formula the probability of an adatom in equilibrium overcoming this energy barrier is proportional to $\exp(-E_d/k_BT)$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. Then the diffusion coefficient $D$ on a square lattice of lattice constant $a$ can be given by

$$D = \frac{a^2}{4} v_0 \exp\left(-\frac{E_d}{k_BT}\right)$$  \hspace{1cm} 2.6

where $v_0$ is assumed to be of the order of a typical vibrational frequency of the atom ($\sim 10^{13}$ s$^{-1}$) and depends weakly on temperature. An adatom migrating over a terrace

---

Fig. 2.6 A sketch of the elementary atomistic processes in nucleation and growth on a substrate.
as shown in fig. 2.7 site (a) would face a short-range attractive interaction when it approaches an ascending step. In contrast an adatom approaching a descending step fig. 
2.7 site (b), has to overcome an additional potential barrier to roll over the edge before it can attach itself to a step. This barrier is called the Ehrlich-Schwoebel barrier [12,13] and prevents adatoms diffusing to the lower terrace resulting in an island growth mode even though energetics favour layer by layer growth mode.

![Diagram of stepped fcc(100) surface and corresponding schematic potential](image)

Fig 2.7 Side view of a stepped fcc(100) surface and the corresponding schematic potential showing a decreased barrier near an ascending step due to the step-adatom attraction (a) and the Ehrlich-Schwoebel barrier $E_{ES}$ at the descending step (b).

Beside migration over a terrace and across a step edge, migrating atoms may meet and form a cluster, which may decay or develop into a stable nucleus. It is only above a critical cluster size that growth becomes much more important than decay. These stable clusters grow by further capture of adatoms. These atomistic processes can be summarized as in fig. 2.8. The process is analogous to homogeneous nucleation, where the total free energy change, $\Delta f$, accompanying the formation of a particle with radius $r$ is given by

$$\Delta f = 4\pi^2 \gamma + \frac{4}{3} \pi^3 \Delta F,$$  \hspace{1cm} 2.7
Fig. 2.8 A summary of the competition between nucleation and growth and the processes that govern them. The dashed lines denote rare processes. Nucleation is determined by arrival rate and capture of unstable nuclei. Capture of single adatoms by clusters lead to growth. A sub-critical nucleus may also decay.

where $\Delta F_v$ is the Gibb’s free energy change per unit volume and $\gamma$ is the surface energy per unit area of the interface separating the new and the parent phases. The two terms of equation 2.7 are plotted in fig. 2.9. If $\Delta F_v$ is negative, the free energy of the particle passes through a maximum. As the particle grows in size, its free energy also increases until a critical radius, $r^*$ is reached. Particles of radius less than $r^*$ will tend to dissolve, thus lowering the free energy while particles of radius larger than $r^*$ will lower their free energy by growing.
Growth requires thermal energy to overcome the potential barrier between the two phases, as graphically illustrated in fig. 2.10. It has been shown that the growth rate is given by [14],

\[ u = \xi n v p B V_{atom} e^{\frac{U_{g,12}}{k_b T}} (1 - e^{-\frac{N_{atom}}{k_b T}}) \]  

where \( n \) is the atom surface density, \( v \) is the frequency factor to change from one phase to the other, \( p \) is the probability of the successful change of an atom at the interface from one phase to the other, \( B \) is the probability that the changed atom stays in the second phase and \( V_{atom} \) is the volume of the atom. The factor \( \xi \) is less than one and accounts for the non-uniformity of atomic distribution at the interface of the two phases. The foregoing discussion has provided the atomistic picture of film formation. In the following section we show the effects of some of the control parameters on film structure during film preparation.
2.3 Thin film structure

Films prepared by physical vapour deposition show a wide range of microstructures and properties, both of which are highly dependent on the preparation conditions. In case of sputter deposition, which is the method of interest in this work, the transport of the atoms to the substrate is controlled by parameters such as the apparatus geometry and working gas pressure, while diffusion steps are controlled largely by the substrate temperature, but may be significantly influenced by energetic particle bombardment.

Various models describe the influence of the deposition parameters on the structure of the thin films. For example, for evaporated films a three zone structure model (SZM), which relates the microstructure of a thin film to the reduced temperature T/T_m, as a means of classifying the microstructures produced under different conditions is reported by Movchan & Demchishin [in 15]. According to this model microstructural development is controlled by shadowing effects (zone 1), surface diffusion (zone 2), and bulk diffusion (zone 3) as T/T_m increases. Though the SZM was developed primarily to explain the relation between microstructure and preparation conditions for the case of
crystalline metallic films, there have been recent reports to apply it to both amorphous and crystalline ceramic films and amorphous semiconductor films [16,17]. Although Movchan and Demchishin indicated only a single zone (zone 1) for \( T/T_m \) for evaporated films, Thornton [18] applied the same model to sputtered films and observed a second zone (zone T) that emerged as the pressure of the sputtering gas was decreased, fig 2.11. The generalized Thornton model for sputtered films has therefore in addition to the \( T/T_m \) ratio, the argon pressure, which determines the kinetic energy of the particles in the gas phase. The zone T structures are considered to be the internal structure of the zone 1 structures. Messier et al. [15] have revised the above models to encompass both the microstructure and nanostructure of the films (prepared at \( T/T_m \leq 0.5 \)), based on extensive preparation and characterization studies of both thin and thick films of tetrahedrally bonded amorphous semiconductors. In the model by Messier et al., three general structural units are recognized; nano-, micro- and macrocolumns and associated nano-, micro- and macrovoids. Fig. 2.12 shows schematic representation of these interrelated structural units along with representative micrographs for amorphous Ge (a-Ge) films prepared at \( T/T_m = 0.27 \).

![Microstructure zone diagram for metal films deposited by magnetron sputtering. T is the substrate temperature and T_m is the coating material melting point [18].](image)

20
Figure 2.12 Schematic representation of the general structure of a thin film prepared under low mobility conditions (T/Tm < 0.5). The scanning electron (SEM), transmission electron (TEM) and field ion micrographs (FIM) are for sputtered a-Ge films [15]. The FIM and defocused, phase contrast TEM show the small clusters within the nanocolumns, while larger scaled SEM and TEM show the micro- and macrocolumns.
The voids, i.e. the low density regions between the columns, are the primary controlling factors. The boundary of the zone 1 and T in the Thornton model is non-linear and Messier et al. [15] have shown that it varies in a fashion similar to the film bias potential as a function of gas pressure. Therefore under the influence of energetic particle bombardment as a result of substrate floating potential \( (V_s) \), Messier et al. have modified the Thornton model by replacing the gas pressure with \( V_s \) as illustrated in fig. 2.13. They therefore consider the \( V_s \) induced mobility to be a more fundamental process affecting the physical structure rather than pressure.

The parameters of temperature and pressure in the original structure zone models (SZM – MD and Thornton) were not unique but only represent empirical correlations made up to then. The basic processes of vapour to solid transformation will depend on the nature of the vapour species as they condense on the film surface and any energy input to the film surface such as substrate heating or ion and electron bombardment. An understanding of these primary parameters is therefore very important. For energetic particle bombardment, two cases come to the fore. The neutral gas species may be reflected from the target at energies up to the cathode potential. The probability and thus the flux of elastically backscattered neutral particles increases as \( M_i/M_T \), where \( M_i \) is the mass of the incident vapour species and \( M_T \) is the mass of the target. Negative secondary ions emitted at the target are a second source of substrate bombardment. They are repelled by the negative target potential, gain all or part of the cathode potential and arrive at the film surface primarily as neutrals.

We will return to the discussion of the species and effects of these particles on structure in chapter 5. Bombardment by such energetic particles during film growth can also lead to stress development. A study on stress development during thin film growth may thus provide evidence of presence, energy and nature of bombarding particles. In the following section we discuss residual film stresses in sputtered films and various models of explaining them.
Figure 2.13 SZM for thick films showing the effects of both bombardment due to the bias potential $V_b$, which is pressure dependent and thermal induced mobility represented by $T/T_m$ [15].

2.4 Stress in thin films

Residual stresses in functional coatings play an important role in the physical properties as well as the performance and lifetime of the coated component. Generally the resulting coating properties are strongly influenced by the deposition method and the selected deposition condition. The mechanical properties must therefore be adequate to guarantee mechanical stability and integrity for their period of use. The observed total mechanical stress can consist of three components as follows:

$$\sigma = \sigma_{ext.} + \sigma_{therm.} + \sigma_{intr.}$$

The external stresses ($\sigma_{ext.}$) arise from external forces, for example in case of poor assembly of a component supporting the film. Thermal stresses ($\sigma_{therm.}$) arise if large differences exist in the thermal expansion coefficients between the film and substrate material and is given by

$$\sigma_{therm.} = (\Delta\alpha)\Delta T E$$

where $\Delta\alpha$ is the difference in thermal coefficients, $\Delta T$ is the difference in deposition temperature and the surrounding temperature and $E$ is the Young’s modulus. The last and most important part is the intrinsic stress ($\sigma_{intr.}$) in the film itself. Intrinsic stress is a structure- and microstructure-sensitive property, which is caused by the mode of film growth and microstructural interactions influenced by some contamination. Usually the
intrinsic stresses are the dominant part of the total stress so that many investigations have specifically dealt with them, as is the case in this work.

The intrinsic stresses in sputtered films are related to structure zones discussed in section 2.3. A low-density zone I has voids in between columns leading generally to a coating under tensile stress. The tensile stresses are thought to arise from the interaction of the open columnar boundaries in coatings with the zone I structure. The higher density zones have fewer voids, but the extra bombardment also results in gas entrapment and ‘atomic peening’, giving compressive stresses.

Extensive studies of magnetron sputtering [19,20] have shown that energetic particles are the fundamental quantities that produce compressive stress. Therefore in order to understand the residual stress behaviour exhibited by the analyzed films, it is important to consider the broad models advanced to explain the various experimental studies showing compressive stresses.

2.4.1 Atomic peening model

In this model [21-23] stress in a sputtered film is dependent on the energy, flux and angle at which particles bombard the film. These parameters, in turn, depend on the total sputtering pressure. The energy of a sputtered atom as it passes through the sputtering atmosphere can be estimated from

\[ E_f = (E_O - k_B T_G) \exp\left[n \ln\left(\frac{E_f}{E_i}\right)\right] + k_B T_G \]  \hspace{1cm} 2.11

where \( E_O \) is the energy of the sputtered particle as it leaves the target, \( T_G \) is the sputtering gas temperature, \( E_f/E_i \) is the ratio of energies before and after a collision, and \( n \) is the number of collisions that take place in the gas and is given by

\[ n = \frac{d \rho \sigma}{k_B T_G} \]  \hspace{1cm} 2.12

where \( d \) is the distance traveled, \( \rho \) is the sputtering gas pressure and \( \sigma \) is the cross section assuming hard core interactions. At high pressure there is a loss in particle energy and an increase in oblique angle component of film bombardment due to scattering events in the plasma. Thus films deposited at high pressures are tensile due to an atomic shadowing effect of the growing film, which is a natural consequence of a random ballistic aggregation process as illustrated in fig. 2.14. At low pressure the relatively low particle scattering within the plasma allows high energy particles to strike the film at angles
approximately normal to its surface. This causes film densification by decreasing the voided regions in the microstructure through efficient atomic arrangement. A bombarding ion imparts energy to the atoms it collides with, creating a microscopically localized region of high atomic vibrational energy. This high-energy region, the thermal spike, radiates outward spherically as it dissipates energy. It is suggested that within the thermal spike region conditions are similar to the high pressure-high temperature conditions, which are used to form compounds like synthetic cubic boron nitride. It is also speculated that due to the high quenching rates associated with the dissipation of the spikes, $10^{14}$ K/s, any meta-stable structure created would be preserved.

![Diagram](image)

Fig. 2.14 A simulation of typical microstructures that evolve when monoenergetic atoms are introduced sequentially at random positions for incident kinetic energy $E$ of (a) 0.02 $\phi$, (b) 0.5$\phi$ and (c) 1.5$\phi$, where $\phi$ is the cohesive energy. In sputter deposition $E$ would be a function of total pressure [24]. (a) is characterized by overshadowing, (b) shows filling of voids (c) shows densified films.
2.4.2 Momentum transfer model

A bombarding ion can transfer its momentum to the atoms with which it collides, causing a series of atomic displacements, or collision cascades. The momentum transferred into the film by bombarding ions per depositing atom is given [19]

\[ P^* \propto J \sqrt{2m \eta E} \]  \hspace{1cm} 2.13

where \( J \) is the bombarding ion flux, \( m \) is ion mass and \( E \) is its energy. The maximum energy transfer from the ion to the film’s atom, \( \eta \), is given by

\[ \eta = \frac{4mM}{(m + M)^2} \]  \hspace{1cm} 2.14

with \( M \) being equal to the mass of the atoms being bombarded. This process has been modeled by a computer simulated two-dimensional molecular dynamics calculation. The model predicted a filling of the void structure and a densification of the film [24], as shown in fig. 2.14. This simulation points to a momentum model instead of a thermal spike model as a better description of the atomic processes involved in an ion assisted deposition. The momentum transfer model also describes better the resulting film density and related void network structures. Experiments have shown that a film property like refractive index, which is a measure of the packing density, varied linearly with the total momentum. Fig. 2.15 represents an idealized stress momentum curve, which depicts the variation of the intrinsic stress with momentum (\( P^* \)) [19]. The stress profile consists of three regimens. At low momentum (as might exist in high pressure sputtering, or sputtering from a light mass target with a heavy inert gas, or oblique deposition), films are characterized by a microstructure unable to support high stress. As momentum increases, densification occurs, accompanied by a conversion to zone T microstructure. In this zone voids collapse and the stress reaches a maximum. At moderately high momentum, the tensile stress decreases as compensating compressive stress caused by the atomic peening mechanism becomes operative. Conversion from tension to compression is observed as the microstructure densifies due to porosity annihilation by recoil implantation and knock-on processes.
2.4.3 A mathematical approach to compressive stress formation in thin films by ion bombardment

Davis [25] has developed a simple mathematical model to explain the formation of compressive stress in thin films deposited with simultaneous bombardment by energetic ions or atoms. The net stress is found to result from a competition between stress formation by knock on implantation of film atoms below the film surface and stress relaxation by thermal spike excited processes. An assumption of this steady state predicts that the magnitude of the compressive stress $\sigma$ is proportional to

$$\left[ Y/(1-\nu) \right] E^{1/3} / \left( R/f + kE^{2/3} \right)$$

where $E$ is the ion energy, $R$ the net depositing flux, $j$ the energetic bombarding flux, $k$ a material-dependent parameter, $Y$ the film material Young’s modulus and $\nu$ the Poisson ratio. Fig. 2.16 represents this prediction in compressive stress as a function of ion energy for different values of $R/f$. In general stress rises to a maximum with increasing ion energy and then decreases for all fluxes. Davis proposes two ways of stress reduction.
inherent from equation 2.15. When the energetic flux \( j \) is sufficiently low then \( R / j \) is large compared with \( k E^{5/3} \) and equation 2.15 can be approximated by

\[
\sigma(E) \propto \frac{Y}{1 - \nu} \frac{jE^{5/3}}{R}
\]

Equation 2.16 suggests that (i) the most obvious strategy to reduce stress is to reduce the energetic flux, as illustrated by varying \( R / j \) from 1 to 20. And (ii) for low energetic flux then stress varies as the square root of ion/atom energy, marked as region I in fig. 2.16. This stress variation with square root of ion energy is in agreement with the momentum transfer model discussed above. For a large energetic flux the term \( R / j \) will be negligible and the stress can be approximated by

\[
\sigma(E) \propto \frac{Y}{1 - \nu} \frac{1}{kE^{7/3}}
\]

implying that stress may be reduced by increasing the ion energy, which is depicted by region II in fig. 2.16. This stress reduction is due to more thermal spikes.

![Graph](attachment:image.png)

Fig. 2.16 Variation in compressive stress as a function of the kinetic energy of the impinging particles as predicted by the Davis Model. The three curves correspond to the different values of \( R/j \) as shown [25] and to case (i) in text. Region I corresponds to case (ii) in text while reduced stress at high energies for energetic flux is shown by the \( R/j=1 \) curve.
From the review of stress generation in sputtered thin films it can be concluded that energy and flux of sputtered particles are necessary to explain the deposition stress observed. Hence a study on the films stress may reveal effects of energetic particles on the microstructure as well. Further evidence of the presence of energetic particles can also be obtained from their effects on the film growth rate. This is now discussed next.

2.5 Resputtering in thin films

Under certain sputtering conditions negative ions will form near the target, and will be accelerated away by the negative bias of the target. Upon bombarding the growing film, these energetic ions may cause ejection of atoms from the surface, a phenomenon referred to as resputtering or backspattering. Resputtering effects can be classified into macroeffects or microeffects. Macroeffects are on the thickness of the film, which may range from a slight decrease in the film thickness to a total suppression of film growth and in some cases etching of the substrate. Microeffects are observed on the film surface morphology of the film and can include formation of etch pits, ripples, cones, and other surface morphological features on the growing film.

Jones et al. [26] have reported on the resputtering of SiO₂ and Si films by negative ions incident on a negatively charged film. Chapman et al. [27] have described the effects of accelerated and focused secondary electrons from a target bombarded by positive ions on a substrate. Hanak and Pellicane [28] have similarly reported on the effects of both the secondary electrons and the negative ions. They particularly found that in highly ionic materials such as TbF₃ and TbCl₃, negative ion resputtering would lead to substrate etching, which they attributed to F⁻ and Cl⁻ ions formed at the target. A more elaborate work on resputtering was carried out by Cuomo and co-workers [29] in the sputtering of rare-earth-gold alloys. They observed substrate etching in only certain of the alloys. They attributed these to negative ion resputtering and based on these data developed a model for predicting negative ion formation. They found substrate etching for compounds where electronegativity difference was higher than a certain value. Their model treats the compound as an ionic solid and hence calculate the energy required to transfer an electron from one element of the compound to the other. The ionization potential I of an
element A, would be the energy needed to remove an electron while formation of an ion B- would lead to energy gain equal to electron affinity of B, EA. The total energy required would thus be I-EA, and would be a measure of the difficulty to transfer an electron from A to B. They therefore found that for I-EA below a certain value there was negative ion formation. Later in their work Kester and Messier [30], from a range of materials examined the tenability of this model. They concluded that I-EA values are just but one of the many parameters that influence whether resputtering would occur, and to what degree. Nevertheless they found the model to be quite useful in comparing isostructural materials sputtered under identical conditions where one element in a compound is varied.

A simple way to test out resputtering phenomena showing macroeffects i.e. film thickness deviation would be to vary the total pressure. In such a case, the pressure dependent atomic deposition rate $r$ is well described by the Keller-Simmons formula [31]:

$$r = r_D + r_B = r_0 \frac{(pd)_0}{pd} \left\{ 1 - \exp \left( \frac{-pd}{(pd)_0} \right) \right\}, \quad r_B = r_0 \exp \frac{-pd}{(pd)_0}$$  

where $r_D$ and $r_B$ are the diffusive and the ballistic components of the rate. $r_0$ the deposition rate without scattering losses, $p$ is the total pressure, $d$ the distance between target and substrate, and $(pd)_0$ the characteristic pressure-distance product. This product is (a) element-specific determined by microscopic parameters of the deposition process (namely masses and diameters of the atoms involved in the collisions of the sputtered atoms between the target and substrate. There is (b) an effect of the power of the discharge, which affects (i) the gas density and the temperature of the argon atmosphere and (ii) the energy of the sputtered atoms on the other. Both microscopic and process parameters determine the free path and the scattering angle of the sputtered atoms. According to the Keller-Simmons model, the energetic ballistic component of growth decreases exponentially with pressure. It can therefore be concluded that the energy flow carried by particles causing significant impulse transfer to the atoms of the growing film show similar exponential dependence.


Chapter 3

Theoretical background

We aim at obtaining an atomistic understanding of the film and structure formation for reactively sputtered transition metal oxides and oxynitrides. The novelty for a combination of techniques is already highlighted in chapter 1. In this chapter we discuss the theoretical principles of the methods used in analyzing the films. To determine the film crystallinity, density, thickness and roughness, we extensively used the interaction of X-rays with matter and for which we provide the relevant theory and how these film properties are discerned. To determine the films composition three techniques were used and whose principles are discussed. These are the Rutherford backscattering, the secondary neutral mass and the forward recoil spectrometries. We have in chapter two discussed extensively compressive stress in sputtered thin films whereby the reviewed models attribute the stress generation to energetic particle bombardment. This points to an additional means of imparting energy to growing films, which may have consequential effects on other film properties. We therefore examine how the deposition stress is determined through stress-induced substrate bending approach. Lastly, we present the principles of atomic force microscopy in analyzing the films surface morphology.

3.1 Interaction of X-rays with matter

The energy of an X-ray photon, $\varepsilon$, is related to its wavelength $\lambda$ by

$$\lambda = \frac{12.4}{\varepsilon}$$

where $\varepsilon$ is in keV and therefore $\lambda$ in angstroms, which is comparable to material lattice constants. Consequently X-rays can undergo diffraction thereby revealing the structure of the probe. X-rays are generated both by the deceleration of electrons in metal targets and by the excitation of the core electrons in the atoms of the target. A copper target has a
strong line at 1.5418 Å (CuKα). In addition its high melting point and good heat conduction makes it a good target. Another important source of coherent and highly intense source of X-rays is the synchrotron radiation. Diffraction of X-rays falls into two basic processes namely (i) diffraction at interfaces or X-ray reflection and (ii) diffraction from crystal lattices for the transmitted X-rays. In the following sections, the theories of the methods are considered in detail.

3.1.1 X-ray diffraction

This method reveals a sample’s crystallinity through characteristic interference patterns obtained due to the phase difference between the X-ray photons scattered at each individual lattice plane. The position, shape and intensity of these reflection peaks provide detailed information about the structural properties of the sample on an atomic scale. Fig. 3.1 (a) shows the condition for constructive interference from two parallel beams diffracted elastically by parallel crystal planes with distance \(d_{hkl}\) apart and is given by

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

where \(\theta\) is the angle of the lattice planes with respect to the incident X-ray beam of wavelength \(\lambda\). Equation 3.2 is referred as Bragg’s equation after W.L Bragg (1913). A crystal is made of repeated identical units. We therefore need only consider diffraction from a single unit cell to see the effect. A unit cell is formed by three lattice vectors \(\vec{a}, \vec{b}\) and, \(\vec{c}\), which can describe the periodicity within the crystal structure. The corresponding three dimensional periodic structure created by this unit cell is referred to as a Bravais lattice [32], which consist of all points with position vectors \(R\) of the form

\[
R = u\vec{a} + v\vec{b} + w\vec{c}.
\]

Where \(u, v\) and \(w\) are integer values which lead from one unit cell to a corresponding point in another unit cell of the lattice.

From X-ray diffraction experiments, it is possible to extract direct information about the sample structure in reciprocal space. Hence the need to connect real and reciprocal space:
Fig. 3.1 (a) A schematic representation of Bragg diffraction at crystal planes with inner planar spacing \( d_{hkl} \), and (b) the Ewald construction of the Bragg condition in reciprocal space.

\[
\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}, \quad \vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})}, \quad \vec{a}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}
\]

The reciprocal lattice consists of all points with position vectors \( G \) of the form \( G_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \) where \( h, k \) and \( l \) are the Miller indices. The reciprocal lattice has all the properties of a real lattice. Every reciprocal space vector corresponds to an infinite number of parallel, equally spaced lattice planes in real space. The normal vector of these lattice planes has the same direction as the corresponding reciprocal space vector \( G \) and the spacing of the lattice planes is given by \( d_{hkl} = \frac{2\pi}{|G|} \). If the scattering vector \( \vec{K} \) is equal to a reciprocal lattice vector \( G \), the Bragg condition for constructive interference is satisfied. The reciprocal lattice concept was introduced by Ewald and it makes it possible
to visualize the Bragg’s condition. Figure 3.1(b) shows the Ewald construction illustrating Bragg’s condition.

It is clear from Figure 3.1 that if $2\theta$ is the angle separating the incident and diffracted beams,

$$2|k_0|\sin\theta = |G_{hkl}| = \frac{2\pi}{d_{hkl}}$$  \hfill 3.4

which leads to $2d_{hkl} \sin\theta = \lambda$, the Bragg’s law. Hence, a point in the reciprocal space is equivalent to an infinite number of equally spaced parallel lattice planes in a real space.

To establish now the atom positions and the intensity of the Bragg peaks, X-ray scattering by single electron and finally all the atoms within the unit cell need to be considered. According to J. J Thompson the intensity of coherent radiation scattered from an electron is given by

$$I = \frac{I_0 e^4}{m_e^2 r^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{2}$$  \hfill 3.5

where $I_0$ is the intensity of the incident beam, $e$ is the electron charge, $m_e$ is electron mass, $c$ is the speed of light and $r$ is the distance from the scattering electron. A phase difference in the scattered waves would be expected as a result of the different electron positions. Therefore to determine X-ray scattering by the atom, we introduce the atomic wave factor $f_o$. The factor is a Fourier transform of the electron density distribution $\rho_e$ within the atom and normalized in units of the amount scattered from a single electron and given as

$$f_o = \int_{\text{atom}} \rho_e e^{i\vec{k} \cdot \vec{r}} d^3 r$$  \hfill 3.6

For a radial symmetric distribution, $f_o$ can be calculated by angular integration to yield

$$f_o = \int_0^{r_{\text{max}}} \rho_e(r)r^2 \frac{\sin(Kr)}{Kr} dr$$  \hfill 3.7

where $K = 4\pi(sina)/\lambda$. Now for $r \to 0$, $\sin(Kr)/Kr = 1$ and $f_o$ is equal to number of electrons in the atom and corresponds to scattering without phase difference. This also holds true for $K \to 0$, i.e. scattering in the forward direction. An increase in the scattering vector $K$ results in lower values of $f_o$. Hence the intensity of the scattered radiation
decreases with increasing incident angle. The atomic form factor has now to be corrected for anomalous scattering with real \((\Delta f')\) and imaginary \((\Delta f^\ast)\) terms. The effective atomic scattering factor becomes

\[
|f| = (f_o + \Delta f')^2 + (\Delta f^\ast)^2
\]

From the atom the next larger scattering unit is the unit cell, which scatters intensity from each of the constituent atoms depending on the atomic form factor \(f\) and phase due to position. An addition of the scattered waves with respect to their phase difference results in the scattering from the unit cell and referred to as structure factor \(F\).

\[
F(K) = \sum_j f_j e^{i\vec{k}\cdot\vec{r}_j}
\]

for \(f_j\) the atomic form factor of the atom at position \(\vec{r}_j\). The resulting diffraction from a set of planes can now be written as

\[
F_{hkl} = \sum_j^n f_j \cdot \exp[2\pi i(hx_j + ky_j + lz_j)]
\]

where \(n\) is the number of atoms in the unit cell. \(F_{hkl}\) is complex and expresses both the amplitude and the phase of the resultant wave. Its square is proportional to the intensity of the beam diffracted by all the atoms of the unit cell in a direction predicted by the Braggs law. From equation 3.10 it is easy to show expected and forbidden peaks when coordinates of the atoms are substituted. Another important deduction is that the positions of the atoms only affect the intensities and not the directions of the diffracted beams. Other factors that may affect intensity include the thermal vibrations, polarization, multiplicity, Lorentz and absorption [33-36]. For example Debye and Waller introduced a parameter \(B\) in the atomic scattering factor due to temperature in the form

\[
f = f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right)
\]

where

\[
B = 8\pi^2 u^2
\]

for \(u\) the vibrational amplitude. Now taking into account all these factors, the total or integrated intensity \((I_{tot})\) diffracted by a polycrystalline sample for a specific reflection is given by
\[ I_{\text{tot}} = \int [I(\theta) - I_B] d\theta = I_o \cdot C \cdot LP \cdot B \cdot A \cdot A_a \cdot F_{hkl}^2 n_{hkl} p_{hkl} \]  

where \( I_o \) is the intensity of the incident x-rays, \( C \) is a constant determined mainly by the scattering power of one electron, \( LP \) is the Lorentz-polarization factor, \( B \) is the temperature factor, \( A \) is the factor determined by size of the scattering volume and absorption, \( A_a \) is the absorption between source and detector outside sample, \( F_{hkl} \) is the structure factor, \( n_{hkl} \) is the number of equivalent planes \((hkl)\) in the crystal lattice and \( p_{hkl} \) is the fraction of crystals with their reciprocal lattice vector parallel to the scattering vector in comparison with a random sample for which \( p = 1 \).

Quantities that can be extracted from the X-ray diffraction spectrum include; angular peak position, peak width at half maxima (FWHM), line profile of the Bragg reflections and total intensity, among others. From these quantities micro-structural information on the sample can be obtained. These include for example, interatomic distances, grain size and orientation, strain and stress, some of which are briefly discussed below.

Lattice constants or d-spacing, characteristics of the symmetry and the dimensions of the unit cell are determined by inserting the measured angular position \( \theta \) in Bragg’s equation. From the d-spacings, phases are identified by using JCPDS (Joint Committee for Powder Data Standards) Powder Diffraction File. The reflections can then be indexed by Miller indices. With the help of computer programs the best fitting lattice parameters can be simulated by applying least square methods.

The deviation of the measured d-spacing from the strain free bulk material is an indication of the presence of macrostrain. Such strains and stresses may result from film deposition, heat treatment, chemical treatment or phase transformation. The component of strain tensor in the direction of diffraction vector \((hkl)\) is given by

\[ \varepsilon_{hkl} = (d_{hkl} - d_{o,hkl}) / d_{o,hkl} \]  

where \( d_o \) is the interplanar spacing of the unstrained lattice. A change in the inter-planar spacing leads to a change in the Bragg angle according to Bragg equation. Equation 3.14 can thus be written as

\[ \varepsilon_{hkl} = (\Delta d_{hkl}) / d_{o,hkl} = -\cot \theta \Delta \theta \]
which implies a global shift of peaks. The corresponding in plane stress component $\sigma_{11}$ is given by

$$\sigma_{11} = \frac{E_{hkl} \varepsilon_{11}}{(1-\nu_{hkl})} \quad \text{or} \quad \sigma_{11} = \frac{E_{hkl} \varepsilon_{33}}{2\nu_{hkl}} \quad 3.16$$

where $\varepsilon_{11}$, $\varepsilon_{33}$, $\nu_{hkl}$, $E_{hkl}$ are the in-plane, out of plane strain, Poisson’s ratio and elastic modulus, respectively.

If the grain size is small, the X-rays interfere only partially leading to peak broadening. The full width at half maximum ($FWHM$) for a peak at angle $\theta$ is given using the Scherrer equation:

$$FWHM = \frac{0.89 \lambda}{L_{hkl} \cos \theta} \quad 3.17$$

where $L_{hkl}$ is the grain size. In case of single crystal thin films $L_{hkl}$ is the film thickness while for textured films it is equal or less than the film thickness.

The preference of a film to grow in certain directions (texture), is obtained from an ordinary XRD scan by comparing the observed peak intensities with powder samples. However for a complete description of the preferred orientation pole figure measurements are necessary. A pole figure shows the grain orientation distribution for a selected Bragg reflex and is measured by tilting and rotating the sample while monitoring the diffracted intensity for the selected Bragg reflection. For example fig. 3.2 shows a) a polycrystalline film, which shows all expected peaks as for a powder sample and the pole figure shows a broad peak due to the random orientation, (b) a fiber texture, where all crystallites have a specific set of $hkl$ planes roughly parallel to the film surface but different orientations. The pole figure shows a strong peak at the centre and a continuous ring at specific angle of $\psi$ due to random orientation of the crystallites. Fig. 3.2 shows (c) a sheet texture, where all crystallites have specific set of $hkl$ planes parallel to the surface but with different orientations on the film surface. XRD shows peaks from different orders of $hkl$ planes. The corresponding pole figure shows a strong peak at the center and distinct peaks depending on the symmetry of the unit cell, and lastly (d) shows single crystal, where XRD shows same pattern like fiber texture but no ring in pole figure. The sharp peaks show the symmetry of the unit cell.
Fig. 3.2 Schematic representation of the real space and the reciprocal space of (a) a polycrystalline film, which shows all expected peaks as for a powder sample and the pole figure shows a broad peak due to the random orientation, (b) a fiber texture, where all crystallites have a specific set of hkl planes roughly parallel to the film surface but different orientations. The pole figure shows a strong peak at the centre and a continuous ring at specific angle of ψ due to random orientation of the crystallites, (c) sheet texture, where all crystallites have specific set of hkl planes parallel to the surface but with different orientations on the film surface. XRD shows peaks from different orders of hkl planes. Pole figure shows a strong peak at the center and distinct peaks depending on the symmetry of the unit cell, (d) single crystal, where XRD shows same pattern like fiber texture but no ring in pole figure. The sharp peaks show the symmetry of the unit cell.
3.1.2 X-ray reflectivity (XRR)

3.1.2.1 Density by XRR

At an interface between two different media, part of the incident electromagnetic radiation is reflected and another part is transmitted through the interface. The most important quantity describing the propagation from one layer to the other is the scattering vector, which may be written as

$$K = \frac{\omega}{c_0} \sqrt{\varepsilon_2(\omega) - \varepsilon_1(\omega) \sin^2 \alpha}$$  \hspace{1cm} 3.18

where $\alpha$ is the angle of incidence measured from the surface normal, $c_0$ is the phase velocity, $\omega$ the radiation frequency while $\varepsilon_1$ and $\varepsilon_2$ denote the dielectric function of the two media respectively. In the visible range $\omega$ is usually varied to obtain those values of $K$ that will give rise to constructive interference. In X-ray characterization due to the monochromatic radiation it is customary to vary the glancing angle $\theta$ between the surface and the incident beam instead of $\alpha$. Now for measurements in air $\varepsilon_2 = 1$ equation 3.18 therefore becomes

$$K = \frac{\omega}{c_0} \sqrt{\varepsilon - \cos^2 \theta}$$  \hspace{1cm} 3.19

where $\varepsilon_1 = \varepsilon$, the dielectric function of the film. Since X-ray frequencies are much higher than in the dielectric function, we consider high frequency limit where the dielectric function shows a Drude like behaviour and the harmonic oscillator susceptibility is given by

$$\chi_{\text{ho}}(\omega) = -\frac{\omega_p^2}{\omega^2 + i\omega\omega_r}$$  \hspace{1cm} 3.20

where $\omega_p$ is denotes the plasma frequency and $\omega_r$ the damping. For low damping equation 3.20 reduces to

$$\chi_{\text{ho}}(\omega) = -\frac{\omega_p^2}{\omega^2}$$  \hspace{1cm} 3.21

The real part of the dielectric function in the X-ray regime is of the order of $10^{-5}$ for solids [37], while the density of air is lower by three orders of magnitude. Thus the dielectric function is of the order of $10^{-8}$, and the assumption that dielectric function of air
is equal to 1 is still valid. As a consequence, for glancing angles smaller than a critical angle $\theta_c$ the scattering vector becomes imaginary, and the total reflection occurs. The value of $\theta_c$ then depends on $\omega_p$ by

$$\cos^2 \theta_c = 1 - \frac{\omega_p^2}{\omega^2}$$

3.22

For low angles equation 3.22 can be approximated to

$$\theta_c = \frac{\omega_p}{\omega}$$

3.23

Now the plasma frequency depends on the electron density $n$ through the equation

$$\omega_p^2 = \frac{e^2 n}{\varepsilon_o m}$$

3.24

where $e$ is the electronic charge and $m$ is the effective mass of the electrons. If the composition of the material is known, it is possible to correlate electron density and mechanical density $\rho$

$$n \propto \rho$$

3.25

and therefore with $\theta_c$, which is easily determined as shown in the typical X-ray reflectivity pattern of a thin film on a substrate, fig. 3.3.

3.1.2.2 Film Roughness by XRR

The reflectivity of X-rays from a flat smooth surface is given by the Fresnel reflectivity [38]

$$R_f = |r|^2 = \frac{|\theta_i - \theta_r|^2}{|\theta_i + \theta_r|^2}$$

3.26

for $s$ and $p$ polarized X-rays and for $\theta \approx \theta_c$, so that $\sin(\theta) \approx \tan(\theta) \approx \theta$. For $\theta > \theta_c$, the reflectivity reduces to simple asymptotic form

$$R_f \approx r^2 \approx \left(\frac{2\theta}{\theta_c}\right)^{-4} = \left(\frac{2K}{K_c}\right)^{-4}$$

3.27

such that the reflectivity for an ideal surface is a function of the scattering vector \(K^{-4}\) above the critical scattering vector, $K_c$ determined by the critical angle $\theta_c$.
Fig. 3.3 Typical XRR pattern of a thin film on a substrate. The density, thickness and surface roughness of the films calculated from the critical angle, period of oscillations and intensity decay respectively.

The above model for reflectivity only describes flat, homogeneous and isotropic surfaces. In real measurements, such conditions are not met: in general, the real surfaces are rough, inhomogeneous and anisotropic, while the most significant role is played by interface roughness. Surface roughness causes a deviation from the ideal surface leading to reduced reflectivity and diffuse scattering. Névot [in 39] has advanced a model to account for the roughness. They describe the vertical roughness by assuming that the height profile of the film varies around the mean thickness according to a Gaussian height distribution with a half width of $\sigma$, as shown in fig. 3.5. This roughness reduces the reflection at the interface to $R_f \exp(-4K\theta_{rp}\sigma)$ compared to the Fresnel reflection, $R_f$. $\theta_{rp}$ is the real part of $\theta_r$ and $K$ wave number in the air/vacuum side.
Fig. 3.4 Interface roughness according to Névol. The distribution of peaks and valleys on a mean interface level is described using the gaussian function and its parameter $\sigma_n$.

### 3.1.2.3 Thickness by XRR

Above the critical angle the X-rays can penetrate into the film and reflections from the second interface are considered as shown in fig. 3.5. Fringes are observed as consequence of interference from rays reflected from the two interfaces. As mentioned earlier (equation 3.18) the scattering vector is varied by changing the angle of incidence instead of frequency as in optics. A major advantage of XRR is the small deviation of the refractive index from unity, which means that the spacing of the interference fringes is determined by the film thickness only unlike in optics where films have to be appreciably thick so as to decouple thickness and refractive index. The position of the extrema (fig. 3.3) are given by

$$\theta_m^2 = 2\delta + (m + k)^2 \frac{\lambda^2}{4t^2}$$  \hspace{1cm} 3.28

where $m$ is an integer and represents the order of the extremum, $k$ takes the values 0 or 1/2 for minima or maxima respectively for density of substrate less than that of film, while $t$ is the film thickness. Thus thickness of the film can be deduced from the period of oscillations $\Delta \theta = 2\pi n / t$ (where $n$ is the refractive index of the film).
3.2 Composition analysis

3.2.1 Rutherford backscattering (RBS)

RBS is based on classical scattering in a central force field. Aside from the accelerator providing a collimated beam of MeV particles, whose corresponding wavelength is orders of magnitude lower than solid interatomic distances, the instrumentation is easy. Semiconductor nuclear particle detectors are used which have an output voltage pulse proportional to the energy of the particles scattered from the sample into the detector. The scattering is governed by Coulomb repulsion between the positively charged nuclei of the projectile and target atom. The kinematics of the collision and the scattering cross section, necessary parameters for backscattering, are independent of chemical bonding. Therefore measurements are insensitive to electronic configuration or chemical bonding between atoms within the target. In the following sections we first consider energy transfers during collisions as they provide the identity of the target atom. Scattering cross section is then considered, which is the basis of the quantitative aspect of Rutherford backscattering. A short discussion on depth profiling follows.
3.2.1.1 Kinematics of Elastic Collisions

With reference to fig. 3.6, the conservation of energy and momentum parallel and perpendicular to the direction of incidence are expressed by the equations

\[
\frac{1}{2} M_1 v^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2 \quad 3.29
\]
\[
M_1 v = M_1 v_1 \cos \theta - M_2 v_2 \cos \phi \quad 3.30
\]
\[
0 = M_1 v_1 \sin \theta - M_2 v_2 \sin \phi \quad 3.31
\]

Eliminating \( \phi \) first and then \( v_2 \), the particles velocity ratio becomes:

\[
\frac{v_1}{v} = \left( \pm \left( M_2^2 - M_1^2 \sin^2 \theta \right)^{1/2} + M_1 \cos \theta \right) / (M_2 + M_1) \quad 3.32
\]

The ratio of the projectile energies for \( M_1 < M_2 \), where the plus sign holds, is:

\[
\frac{E_1}{E_0} = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right]^2 \quad 3.33
\]

The energy ratio, called the kinematic factor \( K=E_1/E_2 \), shows that the energy after scattering is determined only by the masses of the particle and target atom and the scattering angle.

Fig. 3.6 schematic representation of an elastic collision between a projectile of mass \( M_1 \), velocity \( v \), and energy \( E_0 \) and a target mass \( M_2 \), which is initially at rest. After the collision, the projectile and the target mass have velocities and energies \( v_1, E_1 \) and \( v_2, E_2 \), respectively. The angles \( \theta \) and \( \phi \) are positive as shown.
3.2.1.2 Scattering cross section

This gives the connection between the number of target atoms and detected particles. The differential cross section, $d\sigma/d\Omega$, of a target atom scattering an incident particle through an angle $\theta$ into a differential solid angle $d\Omega$ centered about $\theta$ is given by

$$\frac{d\sigma(\theta)}{d\Omega} \cdot d\Omega \cdot N_s = \frac{\text{number of particles scattered into } d\Omega}{\text{total number of incident particles}}$$

Where $N_s$ is the number of target atoms per unit area. For a small detector solid angle, an average differential scattering cross section can be defined as

$$\sigma(\theta) = \frac{1}{\Omega} \int_\Omega \frac{d\sigma}{d\Omega} \cdot d\Omega$$

The number $N_s$ is related to the yield, $Y$ i.e. the number of detected particles by

$$Y = \sigma(\theta) \cdot \Omega \cdot Q \cdot N_s$$

Where $Q$ is the total number of incident particles in the beam determined by a time integration of the current of charged particles incident on the target.

The scattering cross section can be calculated from the force that acts during that collision between the projectile and target atom. In most cases for backscattering spectroscopy, the distance of closest approach during the collision is well within the electron orbit so that the force can be described as unscreened Coulomb repulsion of two positively charged nuclei with charge given by the atomic numbers $Z_1$ and $Z_2$ of the projectile and target atoms. Derivation details can be found in literature [38], where it is shown that the unscreened scattering cross section is given by

$$\sigma(\theta) = \left(\frac{Z_1 Z_2 e^2}{4E}\right)^2 \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$

and when corrected for electron screening is given by $\sigma_{sc}$ where

$$\sigma_{sc} = \sigma(\theta) F$$

where $F$ is a correction factor and tabulated for various energies for the different targets.

$E$ is the elastic scattering energy, which remains the same before and after collision.
3.2.1.3 Backscattering depth profiles

The depth scale is established by the energy loss \( \frac{dE}{dx} \) of incident ions at high energies (0.5-5 MeV) during the passage through the solid. The energy lost in the penetration is directly proportional to the thickness of material traversed so that a depth scale can be assigned directly and quantitatively to the energy spectra of detected particles. For light ions penetrating a solid, such as He\(^+\) used in this work, the energetic particles lose energy primarily through excitation and ionization in inelastic collisions with atomic electrons referred to as ‘electronic energy loss’. The radii of atomic nuclei are so small compared with atomic dimensions that nuclear scattering is rare compared to interactions with electrons, such that in a first approximation, nuclear interactions may be neglected in the slowing down process. Treatments of inelastic collisions and target atoms are separated into fast and slow collisions, the criterion being the projectile velocity in relation to electron orbital velocity in the target atom. For high energy particles, the stopping cross section decreases with increasing velocity since the particle spends little time in the vicinity of the target atom. For low energy particles stopping power is proportional to velocity. It can be shown that the energy loss per unit path length, \( \frac{dE}{dx} \) is [40]

\[
- \frac{dE}{dx} = \frac{4\pi Z_1^2 e^4 n}{mv^2} \ln \left( \frac{2mV^2}{I} \right)
\]

where \( n \) is the number of electrons per unit volume, \( V \) is velocity of projectile, \( m \) is mass of electron, \( I \) average excitation energy of the electron, \( e \) electronic charge and \( Z_1 \) atomic number of the projectile particles. In thin film analysis, to a good approximation, the total energy loss \( \Delta E \) into a depth \( \Delta x \) is proportional to \( \Delta x \) and the total thickness of the film can therefore be obtained if \( \Delta E \) the corresponding energy difference is known.

3.2.2 Forward Recoil spectrometry – hydrogen and deuterium depth profiles:

In elastic collisions particles are not scattered in a backward direction when the mass of the incident particle is equal or greater than that of the target particle atom. The incident energy is primarily transferred to the lighter target atom in a recoil collision resulting in its forward emission direction. In such a case, forward recoil spectrometry method is used as a nondestructive method of obtaining depth profiles of light elements.
(hydrogen and deuterium) in solids using the geometry shown in fig. 3.7. A mylar foil (≈ 10 μm) is placed in front of the detector to block the penetration of the abundantly scattered helium ions while permitting the passage of the hydrogen ions. Depth profiles are determined by the energy loss of the incident He ion along the inward path and the energy loss of the recoil hydrogen or deuterium ion along the outward path.

![Diagram of experimental setup](image)

Fig. 3.7 Experimental geometry for forward recoil spectrometry experiments to determine the depth profiles of hydrogen (¹H) and deuterium (²H) in solids.

### 3.2.3 Secondary Neutral Mass Spectrometry (SNMS)

Whereas high energy (~MeV) ions penetrate the order of microns into a solid as is the case of RBS discussed above, low energy ions (~ KeV) scatter almost from the surface layer. The species eroded from surface layers provide a direct measure of the components that have been removed. Sputtered species are emitted as neutrals in various excited states, as ions (negative or positive, singly or multiply charged) and as clusters. The energy distribution of the sputtered particles is given by

$$
\frac{dN}{dE} = \frac{E}{(E + U)^{3-2\alpha}}
$$

3.40
where $U$ is the bond strength of the atom, $E$ is the corresponding kinetic energy and $a$ an element correction factor between 0 and 1.

Collection and analysis of the ionized sputtered species or the neutrals gives rise to the acronyms SIMS for secondary ion mass spectrometry and SNMS for secondary neutral mass spectrometry. SNMS was preferred because, when analyzing oxides, the secondary ion yield may vary by several orders of magnitude depending on the oxygen concentration. SNMS avoids these matrix effects by deducing composition from the sputtered neutral particles. However, the mass analysis system still requires ions for detection. Therefore the emission (sputtering) and ionization (charge transfer) processes are decoupled by ionizing the sputtered neutral atoms after emission from the sample surface. The post-ionization factor $\alpha_A^0$ for the sputtered species $A$ depends on the plasma parameters, electron ionization and the travel time of species $A$ through the ionizer. Values of $\alpha_A^0$ close to $10^{-1}$ are achieved for near noble ions and $10^{-2}$ for transition metal ions like tantalum. The measured signal $I_A^0$ of the neutral species $A$ can be written as:

$$I_A^0 = i_p Y_A \frac{\alpha_A}{\alpha_A^+} (1 - \alpha_A^+ - \alpha_A^-) \eta_A^0$$

3.41

where $i_p$ is the primary beam current, $Y_A$ is the sputter yield of $A$, $\alpha_A^+$ and $\alpha_A^-$ are ionization yields for the formation of secondary ions and $\eta_A^0$ is the instrumental factor. Since $\alpha_A^+ \ll 1$ and $\alpha_A^- \ll 1$ then $(1 - \alpha_A^+ - \alpha_A^-)$ can be treated as unity.

3.3 Mechanical stress induced substrate bending

This section describes how the intrinsic stress in the grown thin film causes substrate bending and how the same is used to determine the magnitude of the stress involved. The derivation is based on the work of Timoschenko and Woinowsky-Krieger [41]. A force $\vec{F}$ causing stress in the film will induce bending moments $M_x$ and $M_y$ in the plane along the x- and y-axes of the system given by:

$$M_x = M_y = \vec{F} \cdot \vec{r}$$

3.42

Due to these bending moments, the substrate will bend and attain a given curvature along its x- and y-axes. Since the stress in the film gives rise to a force acting on the substrate,
it therefore acts as a shear stress \( \tau \) on the substrate. The bending moments can therefore be calculated as:

\[
M_x = \frac{1}{2} \tau_x w d_f d_s
\]

(3.43)

\[
M_y = \frac{1}{2} \tau_y l d_f d_s
\]

(3.44)

where \( l \) is sample length, \( w \) is width, while substrate and film thicknesses are denoted \( d_s \) and \( d_f \), respectively. The relation between the bending moments and the radii of curvature of the substrate depends on the nature of the substrate. If, for example anisotropic substrates are used, anisotropy and the resulting directional dependence of the Young’s modulus and the Poisson’s ratio must be considered. For in plane isotropic substrates, for example such orientations such as hexagonal (0001), cubic (100), and (111), the following expressions are valid for the bending moments when radii of curvature are considered:

\[
M_x = \frac{E_s d_s^3 w}{12(1-v_s^2)} \left( \frac{1}{R_x} - \frac{1}{R_y} \right)
\]

(3.45)

and

\[
M_y = \frac{E_s d_s^3 w}{12(1-v_s^2)} \left( \frac{1}{R_y} + \frac{1}{R_x} \right)
\]

(3.46)

combining the last four equations yields:

\[
\sigma_x = \frac{E_s d_s^2}{6(1-v_s^2)d_f} \left( \frac{1}{R_x} + \frac{1}{R_y} \right)
\]

(3.47)

and

\[
\sigma_y = \frac{E_s d_s^2}{6(1-v_s^2)d_f} \left( \frac{1}{R_y} + \frac{1}{R_x} \right)
\]

(3.48)

The last two equations link the stress components \( \sigma_x \) and \( \sigma_y \), i.e. the in plane stresses, which work as shear stresses \( \tau_x \) and \( \tau_y \) on the substrate, to the radii of curvature along the \( x \)- and \( y \)- axes. For isotropic stress, for example in amorphous or polycrystalline films, \( \sigma_x = \sigma_y \). The foregoing equations reduce to

\[
\sigma = \sigma_x = \sigma_y = \frac{E_s d_s^2}{6(1-v_s)d_f} \frac{1}{R}
\]

(3.49)
This equation is known as the Stoney equation [42]. Due to the non-availability of perfectly flat substrates, an initial radius of curvature $R_0$ has to be considered and Stoney equation becomes:

$$\sigma = \frac{E_s d_f^2}{6(1-v_s)d_f} \left( \frac{1}{R} - \frac{1}{R_0} \right)$$  \hspace{1cm} 3.50

Equation 3.50 is used in this work to compute the deposition stress for our films.

### 3.4 Atomic Force Microscopy (AFM)

In contrast to scanning electron microscopy, AFM can image electrical insulators without problem. It uses two modes of operation namely contact and tapping modes. In contact mode, a sharp tip of radius less than 10 nm at the end of a cantilever scans the surface of a sample as illustrated in fig. 3.8(a). The sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information). The force between the tip and the sample is less than $10^{-9}$ N. An optical detection system is employed to map out the surface morphology. The reflection of a laser beam at the back side of the cantilever is detected by a quadrant photodetector. This signal is used as an input for a feedback loop, which keeps the deflection of the laser beam from the center of the detector constant by moving the cantilever up and down with help of a piezo transducer. The voltage applied to the piezo is proportional to the height. In tapping mode, illustrated in fig. 3.8(b), the cantilever oscillates driven by a piezo crystal. The drive frequency is close to the resonance frequency of the cantilever leading to amplification of small amplitudes. When the tip approaches the surface, damping is increased and the amplitude of the oscillation decreases. This reduction in oscillation amplitude is used to identify and measure surface topologies. A feedback loop adjusts the tip-sample separation to maintain a constant amplitude and force on the sample.

The force between the sample and the tip is due to several interactions and depends on the distance apart. For distances larger than approximately 10 μm, fluid film damping occurs due to the ambient air between the cantilever and sample. Between 100 nm and 1 μm, electrostatic forces may appear if sample and tip are charged. This effect may be exploited to image ferroelectrics. Attractive capillary forces are experienced at 10
to 100 nm distances due to water vapour film that covers a sample upon exposure. At a
distance of 1 nm, van der Waals forces become predominant and the subsequent damping
are exploited in the tapping mode imaging. Lastly, at even lower distances repulsive
Coulomb forces can be observed.

(a) Contact mode                   (b) Tapping mode

Fig. 3.8 Principle of the two fundamental modes of AFM operation.
Chapter 4

Experimental procedures

In this chapter the experimental methods used in film preparation and characterization are discussed. Films were produced by reactive direct current magnetron sputtering of metal targets. Characterization methods included X-ray diffraction and reflection, Rutherford backscattering spectroscopy, wafer curvature method for deposition stress and the atomic force microscopy (AFM).

4.1 Reactive magnetron sputtering

4.1.1 The sputter system

The sputter system used in this work is illustrated by the schematic drawing of fig. 4.1. It is a self constructed system [43] and can be mounted with up to six cathodes. A rotatory feedthrough platform installed in the chamber allows for sputtering on 24 substrates. A protection bottom plate with only one aperture, positioned directly below the substrates shields them from the plasma. Typical sizes of the targets are 75 mm diameter and 6 mm thickness. The magnetrons are water cooled. The system is pumped down by 360 l/s turbo molecular pump (Leybold Turbovac 360) connected to a rotary pump for pre-pumping. The chamber has a base pressure of $10^{-4}$ Pa as measured by a cold cathode/Pirani pressure gauge system. A plasma power supply with arc suppression produced by ELAN is used to apply high voltages (600V/1.2 A) to the target. It can operate in both constant power and current modes.
4.1.2 Other accessories

As supplements to pressure monitoring gauges the chamber is also mounted with Ionivac and Pfeiffer pressure gauges. Gas flows into the chamber are regulated via the four mass flow controllers (MFCs), while the gas composition is determined by the quadrupole mass analyzer (QMS) connected to the chamber via a differential pressure valve. A microbalance oscillator (XTC) by Leybold, which uses 6 MHz plano quartz crystal is used to determine the mass deposition rate.

Fig. 4.1 A schematic drawing of the deposition chamber used: Top (left) and side (right) views. The mass spectrometer (QMS) can be connected to the chamber via a gate valve for residual gas analysis and via the Angle bypass for process monitoring. The numbers mark position within the chamber.

4.2 Films preparation

After loading the system with clean substrates, which differed in type as per analytical method, the system was pumped down to the base pressure. Argon was used as the sputter gas. The targets were pre-sputtered in Ar for a minimum of 15 minutes to remove any surface oxide, which may have formed during system venting. Target characterization was a prerequisite in sample preparations so as to determine the appropriate oxygen flow rate, stoichiometry and thickness. The characterization entailed examining the target behaviour upon increasing and decreasing oxygen flow. Sputtering
was done at constant current mode. Prior to exposing a substrate the target is conditioned with the reactive gases at the chosen deposition conditions. The mass deposition rate from the quartz crystal balance, the cathode voltage as reflected by the power supply and the oxygen partial pressure as determined from the quadrupole mass analyzer were determined as functions of oxygen flow. As already pointed out in chapter 2, these parameters identify various sputtering regimes. The appropriate oxygen flow, giving the right stoichiometry, and sputter times, for particular thickness, can thus be achieved and monitored. The substrates used included ordinary microscope glass slides, quartz glass, 150 µm thick glass, silicon wafers (100), graphite sheet and thin steel sheets. Ordinary microscope and quartz glass slides were used for optical and X-ray analysis depending on the optical band gap of the coating being analyzed. In order to achieve better theoretical simulations to X-ray reflection patterns, Si (100) wafers were preferred to glass because of their surface uniformity. The 150 µm thick glass substrates could freely and continuously deform depending on stress and were thus used to quantify the deposition stress. The low background signal from graphite made the substrates appropriate for analyzing oxygen and nitrogen contents in the films through RBS measurements. From the steel sheets, the coating could be peeled with ease for further analysis like for powder diffraction.

4.3 X-ray measurements

A Philips X’pert MRD system was used. The system is fully computer controlled and can be used in different configurations depending on the measurement required. It employs the CuKα radiation and has two channels for the conventional Bragg-Bretano and grazing angle geometry. The X-ray beam can be incident on the sample on line or point focus. This work utilized the line focus, which is used for phase analysis and reflectometry measurements. The point focus is used for texture and stress determination. Fig. 4.2 shows a photograph of the system. All slits are programmable except the manual slit. The secondary beam can pass through optics 1 or 2 depending on the measuring geometry. An important feature is also that the sample can be translated in any of the three directions. Grazing angle geometry was utilized to determine the phase and
structure of the films, while X-ray reflectivity was used to determine density, thickness and film roughness. In the following sections, the procedures used are discussed.

4.3.1 X-ray reflectometry
To determine the quantities already mentioned using this procedure, namely density, thickness and roughness, the most challenging aspect is the sample alignment. Details are as already published [44]. In brief: The sample is mounted on a vertical sample stage (see fig. 4.2) and aligned for the direct beam by performing a 2-Theta scan which means setting angle 2θ to zero. This means maximum intensity (I₀) gets to the detector. An
Omega scan requires translation of the sample to the beam path and obtaining half the intensity \((0.5 I_0)\) when the sample is parallel to the beam. A further scan referred to as a Psi scan, provides a further parallel alignment. It involves the sample being moved further into the beam path and upon performing the scan, the detector should collect minimum intensity since the sample blocks much of the intensity. A test for successful alignment is a scan near the critical angle. The test is executed by locking the detector at an angle of \(2\theta = 0.4^\circ\) and performing an omega scan. The emerging curve is referred to as rocking curve and is expected to be peaked at \(\omega = 0.2^\circ\). A deviation from this value shows misalignment of the sample and the alignment procedure should be redone. The rocking curve also gives information about the curvature of the sample’s surface. First, from the full width half maximum (FWHM) intensity values, a flat, concave or convex surface can be distinguished. Secondly, a non-uniform surface, as shown in fig. 4.3 with open circles, has more than one peak. This can be collected by use of a knife-edge near the sample surface by reducing the area illuminated by the beam. The result is illustrated in figure 4.3 by the curve with filled circles.

![Graph](image)

**Fig. 4.3** a) Typical rocking curve of a sample with non-uniform curvature while (open circles) and with knife edge (closed circles).
A reflectivity scan collected with a knife-edge becomes easy to fit and hence to extract the necessary parameters. Figure 4.4 depicts such a measurement and fitting using Wingixa program. The density and thickness determined with this precise procedure yield precision better than 0.05 g cm$^{-3}$ and 1 Å, respectively.

![Figure 4.4 Typical X-ray reflectivity data and simulation for a zirconium oxynitride sample.](image)

The film density, thickness and roughness can be obtained with very high precision.

4.3.2 X-ray diffraction

The grazing angle diffraction geometry was used to measure the intensity of the diffracted beam. The beam path was as depicted in fig. 4.5. The sample was fixed at a grazing incidence angle, $\theta$, of less than 1$^\circ$ and the detector scan performed. With this geometry the Bragg reflections occur in all other planes apart from the planes parallel to the surface. In addition at grazing angle for the incident beam, there is less effective penetration of the X-rays and the diffraction pattern is from the near surface rather than the interior. Due to this, there is less attenuation of the incident intensity and the signal to
noise ratio is therefore considerably improved. On the other hand by varying the incident angle, the penetration depth could be changed making it possible to probe different depths. The technique can therefore be exploited to investigate multi-layers. Grazing incidence leads to irradiation of a large volume, which implies higher intensity reaching the detector. All expected peaks could therefore be easily observed. The foregoing advantages made this geometry to be preferred to the conventional Bragg-Bretano. The sample was aligned as already discussed for XRR. Depending on samples thickness the incident angle, $\omega$, was varied between 0.4 and $0.75^{\circ}$, which was adequate to reveal film structure.

Fig. 4.5 Geometry of the grazing incidence diffraction method. The incident angle $\omega$ is small and is kept constant while the detector collects the intensities at all the angle within $2\theta$. There is large area illumination of the sample surface.
4.4 Stoichiometry determination

4.4.1 Rutherford backscattering spectroscopy

To ascertain film stoichiometry upon variation of the reactive gas partial pressure, we utilized Rutherford back scattering (RBS). Its theoretical aspects are as already described in section 3.2.1. The RBS system used consists of three main components namely: a source of helium ions, an accelerator to convert the ions to high energy particles and a detector to measure the energy of the backscattered ions. A tandemron accelerator was used with 1.4 MeV \(^4\)He\(^+\) particles and a current of 14 mA. The backscattered particles were detected at an angle of 170\(^\circ\) with respect to the incident beam. The detector was a semiconductor device with an energy resolution of 10 keV.

Fig. 4.6 shows a block diagram of the typical measuring setup used. There are two ion lens optical components placed between the accelerator and sample chamber. A magnetic field separates the He\(^-\), He and He\(^+\) beams, while a quadrupole lens shapes the incident beam and focuses it into the sample chamber. In the inset, the particles that are backscattered from the sample surface are detected.

To illustrate typical RBS measurements and the importance of choice of substrates, fig. 4.7 shows two spectra of (a) tantalum oxide on Si (100) substrate and (b) zirconium oxide on graphite. In the figures the normalized yield is plotted versus the energy of the backscattered particles. The stoichiometry of the films is determined by measuring the heights of the metal elements and substrates and normalization of the scattering cross section for the respective elements. To increase the sensitivity of oxygen, use of graphite is evident as compared to the silicon substrate, which interferes with the oxygen signal. The use of graphite was particularly important in the composition analysis of transition metal oxynitrides, due to the closeness of nitrogen and oxygen peaks in the spectra.
Fig. 4.6 Block diagram of RBS instrument. There are two ion lens optical components placed between the accelerator and sample chamber. A magnetic field separates the He', He and He' beams, while a quadrupole lens shapes the incident beam and focuses it into the sample chamber. In the inset, the particles that are backscattered from the sample surface are detected.

4.4.2 Secondary neutral mass spectroscopy:

Some of the samples prepared were analyzed for composition through secondary neutral mass spectrometer VG Microtech SIMSLAB300 from Vacuum Generators. Fig. 4.8 shows a schematic drawing of the system used. During depth profiling, sputter erosion was carried out using a scanned Ar+ ion beam (VG EX05 ion gun) of 3.5 keV primary energy with a current of 700 nA at an angle of 60°. By biasing the nose cone positive, the secondary ions can be removed from the trajectory to the post-ionization chamber and hence only neutrals enter the SIMS 300 Transfer Optics Mass Analyzer. The quantification is characterized by a linear correlation between the number of post ionized neutrals and the atomic distribution on the surface of the sample. To render the neutral accessible for mass analysis, the neutrals are post ionized by electron collision. In this SNMS system an electron energy of 40 eV was used to post-ionize the neutrals.
Fig. 4.7 Typical RBS measurements showing a) tantalum oxide on Si(100) and b) zirconium oxide on graphite. Use of graphite increases sensitivity due to non-overlap of signals as observed for Si substrates.
Fig. 4.8 Schematic diagram of the secondary neutral mass spectrometer. For detection purpose the neutrals ejected from the sample are post ionized with electrons as shown in the enlarged ionization unit.

4.5 Stress measurements by wafer curvature method

From Stoney’s equation (3.50) it is easily seen that a method based on measuring the curvature of the sample would yield a direct way to determine the biaxial stress in the sample. Methods to determine wafer curvature include capacitive deflection method, the scanning laser beam and others based on profilometry. The scanning laser beam method was used in this work. Its applicability for a variety of setups without complications was among other advantages leading to its local assembly as reported and tested out by T. P. L. Pedersen in his Ph. D. Thesis [45]. In the following section, details of the set up and measurements are discussed.

As the name suggests, the system is based on scanning a laser beam across the surface of a sample. Fig. 4.9 shows a photograph of the setup with the main components numbered. A 5 mW HeNe laser (1), emits a monochromatic beam with a wavelength of 633 nm and a beam radius of 0.81 mm and a divergence of 1.0 mrad. The rotating polarizer (2), in front of the laser, adjusts the intensity of the polarized laser light. A mirror (3) reflects the beam onto the galvanometer (4), which controls tilting of a mirror by application of current. From the galvanometer the beam is reflected through 90° by a beam splitter (5), passes through a plano convex lens (6) before additional mirrors (8)
Fig. 4.9 A photograph of the stress measuring unit displaying all the optical components as numbered (1) laser, (2) polarizer, (3) mirror, (4) galvanometer, (5) beam splitter, (6) plano convex lens, (7) sample, (8) additional mirrors and (9) detector unit.
direct it to the sample (7). Upon reflection by the sample, the beam passes through the plano convex lens and the beam splitter and finally falls on the detector unit (9). The detector unit consists of a one dimensional position sensitive detector (PSD) in front of which a cylindrical lens and a 633 nm band pass filter are placed.

The design allows a perfect alignment of all the components with respect to the optical axis. This way the relative position of the beam can be determined. The design ensures also an increased signal to noise ratio. For example, just scanning a centimeter the system can measure accurately curvatures of $10^{-3}$ m$^{-1}$. The minimum detectable changes in stress are of the order of 2 MPa for films of 100-200 nm thickness on a substrate of 150-200 μm. The beam splitter allows both the galvanometer and the PSD to be positioned at the focal distance of the plano convex lens, but at different locations. This means that despite the laser beam being moved by an angle $\alpha$ by the galvanoscanner, each angle results in a beam parallel to the optical axis, once the beam passes the lens.

The movement of the beam on the PSD is linked to the radius of curvature $R$ of the sample by geometry of the system through the equation:

$$\frac{x}{s} = \frac{2f}{R}$$

where $x$ is the distance the beam moves on the PSD, $s$ is the length of the scan, while $f = 1.0165$ m is the focal length of the plano convex lens at the laser wavelength and is determined by calibration of the system. The system is damped for vibrations through use of a heavy table and sand cushions. A box covering the system ensures constant background signal in the intensity measurements beside reducing air motion effects. When making deposition stress measurements, which were made for this work, a few precautions were taken. As expressed in equation 3.50 for determination of stress, samples selection was necessary to give as low bare substrate curvature as possible. Secondly this intrinsic stress of the substrate is inhomogeneous across the substrate. By a proper sample holder, same position on substrate could be scanned before and after deposition. No other measurements were carried in between substrate and coated substrate scanning, in order to preserve the setup.
4.6 Instrumentation of atomic force microscope

To examine the topology of the surfaces in this work the Digital Instruments Dimensions 3100 atomic force microscope was used in tapping mode operation. In this mode, as already mentioned in section 3.4, the damping of an oscillation is measured. Consequently to intensify the interaction of tip and sample, either the drive amplitude can be increased or the set point amplitude can be decreased. The modification of the former gives better results for the valleys while the latter influences the peaks. The change in voltage needed to control the piezo crystal is then proportional to the sample topology. This way a topological image of the surface is obtained.
Chapter 5

Structure formation for DC magnetron sputtered transition metal oxide films

As already mentioned in chapter 1 some applications crucially depend on the physical structure of the film. For example we noted that tungsten oxide films would have to be nanoporous and amorphous for successful use as gasochromic coatings in solar control glazings. Titanium oxide films specifically in the polycrystalline anatase structure are the best suited for photocatalytic applications. It is thus imperative to understand under what conditions such films can be grown. Desired materials should have wide applications as known for transition metal oxides. The method of film preparation would also have to be cost effective. In this chapter we therefore examine structure formation for the transition metal oxide films grown at room temperature by direct current reactive magnetron sputtering. To achieve this we first provide preparation and characterization reports of oxide films for two neighbouring elements – hafnium and tantalum. We follow this with a comparative analysis to the deposition conditions and film properties, which we also extend to reports of other group IV to VI elements, as carried out in the research group. From these findings we propose a model for structure formation in these films.
5.1 Deposition and Characterization of Tantalum Oxide Films

5.1.1 Introduction

The preparation and characterization of tantalum oxide (TaO$_x$) films continues to receive considerable attention due to their high refractive index and large dielectric constant. Tantalum pentoxide (Ta$_2$O$_5$) has been practically the most promising capacitor material to be used in the near future in dynamic random access memories (DRAM) [1]. Ta$_2$O$_5$ finds other important applications as a high temperature resistance material, as an antireflecting coating for solar cells, in optical wave-guides and as an oxygen sensor, among others [46]. For successful integration of this material in microelectronic devices and in other areas, extremely reliable thin films are desired.

A lot of the available literature on Ta$_2$O$_5$ has focused on its improvement for technological applications [1,46-49]. The literature shows a wide variation in the reported structural, dielectric and insulating properties of both amorphous and crystalline states of Ta$_2$O$_5$ [47]. An understanding of process–structure-property correlations is hence important in order to understand and compare various thin film properties reported in the literature and exploit Ta$_2$O$_5$ thin films for device applications.

In this work, tantalum oxide films were prepared by reactive DC magnetron sputtering. Pignolet et al. [50] have reported on rapid thermally processed thin films of reactively sputtered Ta$_2$O$_5$, while Chang and Liu [46] have reported on structures of Ta$_2$O$_5$ thin films formed by reactive sputtering of tantalum (Ta) metal. Deposition parameters such as the cathode potential, oxygen partial pressure, target-substrate distance, etc. have a major influence on the microstructure and properties of the films. In this report the oxygen content in the Ar/O$_2$ mixture used to sputter a metallic tantalum target was varied during deposition. The structural, compositional, and deposition stress properties of the as-deposited films were studied by a number of techniques. The target behaviour upon varying the oxygen flow was in addition examined.

Tantalum oxide films were prepared by reactive DC magnetron sputtering from a metallic tantalum target (76 mm diameter). The Ta target was sputtered at constant total pressure and constant cathode current of 0.8 Pa and 300 mA, respectively. The sputtering atmosphere consisted of argon (Ar) and oxygen (O$_2$). The substrates, one side polished Si (100) wafers, and 150 μm thick glass were held 78 mm above the target. The silicon
wafer samples were used for Rutherford back scattering and X-ray measurements due to high temperature post deposition annealing studies that followed. The change in curvature of the 150 μm thick glass substrates upon film deposition made them suitable for the determination of film stress. The deposition was carried out at room temperature.

Thickness, density and surface roughness of the films were determined by use of X-ray reflectivity method. Typical film thicknesses for good X-ray reflectometry (XRR) spectra were less than 100 nm. The deposition rate was simply obtained by dividing the XRR thickness by deposition time. The stoichiometry of the films was determined from the heights of the tantalum and oxygen peaks from data obtained by RBS method. The grazing angle geometry was utilized to obtain the XRD patterns for the as-deposited and annealed tantalum oxide films. Measurements were performed at an incidence angle of 0.75° and typical XRD patterns were recorded from 2θ = 20° to 80°. A typical film thickness to obtain XRD spectra with good signal to noise ratio was about 500 nm. The deposition stress was determined by the wafer curvature method.

5.1.2 Target characterisation and deposition characteristics:

Fig. 5.1(a) shows the mass deposited per second on a quartz crystal microbalance as a function of increasing and decreasing oxygen flow. The total sputtering pressure as measured by an Ionivac pressure gauge was kept constant at 0.8 Pa for all oxygen flows. Data were recorded for both increasing and decreasing oxygen flow. The mass deposition rate was found to first increase up to 2 sccm oxygen flow and then a significant drop up to around 6 sccm O₂ flow was observed. Initially up to 2 sccm oxygen flow there was an increased reaction at the substrate between the oxygen and the metal ions sputtered from the target. This would explain the initial increase in mass recorded. In this region the target surface and the tantalum metal sputtering are not significantly affected by the oxygen flow. Above 2 sccm oxygen flow the target starts to oxidise. Since the binding energy of the oxide is higher than that of the metal, the sputtering yield decreases (equation 2.3) and the deposited mass starts to drop as observed. The rate gradually drops further and is almost a constant above 20 sccm. Additional target behaviour is obtained from fig. 5.1(b). The figure shows the variation of potential of the DC electrode (target)
Fig. 5.1 a) Deposited mass of tantalum oxide films per second per cm² as a function of oxygen flow, b) Variation of the cathode voltage of the tantalum target as a function of oxygen flow for a constant cathode current of 300 mA, c) Oxygen partial pressure as a function of oxygen flow during reactive sputter of tantalum.

required to achieve the sputter current of 300 mA at different oxygen flow rates. The cathode potential initially increases rapidly up to 2 sccm oxygen flow. It further increases gradually until a certain critical oxygen flow (6 sccm), which corresponds to a fully oxidized target, is reached and beyond which it remains almost constant. This cathode potential behaviour is in contrast with many other reactively sputtered elements. When the system changes from elemental sputtering to compound sputtering the voltage drops
for many reactively sputtered metals and subsequently stays at an almost constant value. Similar results to our observations have been reported by Venkataraj et al. [51] in reactively DC sputtered niobium (which has similar chemical properties as tantalum) oxide films.

Oxidation of the Ta target surface results from small additions of O\textsubscript{2} to the Ar sputtering discharge and gives rise to dramatic changes in both plasma and film growth conditions. In order to maintain a constant current, the cathode potential increases rapidly. Since the voltage is proportional to the inverse of the secondary electron coefficient, $\gamma$, in cold cathode discharges, the observed increase in voltage may indicate that $\gamma$ for tantalum oxide is less than $\gamma$ for metallic tantalum. Fig. 5.1(c) displays the oxygen partial pressure measured by a mass spectrometer as a function of oxygen flow. A general increase of the partial pressure with oxygen flow, which is not linear, is observed. The partial pressure increases with increasing oxygen flow. Moreover the data for increasing and decreasing oxygen flow coincide fairly well implying stable sputtering conditions with the absence of hysteresis.

Though fig. 5.1a contains valuable information on the deposition rate, it is not enough to determine the quantitative sputter rate. Results from quartz crystal microbalance measurements could not reveal the film composition and density variation with different oxygen flows. We therefore determined the actual sputter rate by dividing the thickness obtained by X-ray reflectometry by the sputter time. In fig. 5.2 we depict the results of the sputter rate variation with oxygen flow. Initially the rate increases rapidly from 0.29 nm/s when the metal was sputtered in pure argon (0 sccm O\textsubscript{2}) to 0.74 nm/s at 2 sccm (metallic mode). This is followed by a steep drop between 2 and 6 sccm and a gradual one for higher oxygen flows. The rate levels out and is slightly below 0.1 nm/s at 20 sccm. It is worth to note that the trends depicted for fig. 5.1(a) and fig. 5.2 are qualitatively quite similar. As earlier mentioned X-ray reflectometry measurements were also used to examine density variations for the films at various oxygen flows and is discussed in the following section.
5.1.3 X-ray reflectivity:

Fig. 5.3 shows the X-ray reflectivity spectra for tantalum oxide films deposited on silicon at 6 and 20 sccm oxygen flow rates. The figure also shows the corresponding simulations done by a three layers model, which includes a roughness layer, a homogeneous TaO$_x$ layer and the substrate. There is a good agreement between the theory and experiment, which demonstrates adequate description of the relevant properties of the tantalum oxide films. From the position of the total reflection edge we can determine the film density with high accuracy. Fig. 5.4 depicts the variation of the film density with increasing oxygen flow rate. At 0 sccm the density was 15.1 g/cm$^3$, which corresponds to 91% of the bulk density of pure tantalum (16.6 g/cm$^3$). Between 0 and 2 sccm oxygen flow the film density decreases rapidly from 15.1 to 8.1 g/cm$^3$. Above 2 sccm oxygen flow the density has a very slow decrease with increasing O$_2$ flow. In this range a composition close to Ta$_2$O$_5$ was found as shown below by the RBS results. The bulk density of this phase is 8.2 g/cm$^3$, as compared to the average density of 7.1 g/cm$^3$ (~87 %) beyond 6 sccm oxygen flow. At low oxygen flow rates, 0 - 2 sccm, the relatively
higher density of the films could be explained by the substoichiometric films obtained within this range as revealed by RBS measurements. These results indicate that the density change was caused by the changing film stoichiometry rather than by different void fractions. The almost constant density above 2 sccm may imply the presence of the same crystalline or amorphous structure. In the next section we hence examine the structure evolution with the oxygen flow.
Fig. 5. Variation of tantalum oxide film density upon increasing oxygen flow. The dashed line denotes the bulk density of tantalum pentoxide while the black curve is a guide to the eye.

5.1.4 Structural properties:

We employed XRD to map the phase composition and structure of TaO_x layers grown on Si(100). Grazing angle X-ray diffraction (GA-XRD) is sensitive to the presence of small volume fractions of randomly oriented polycrystalline grains since it avoids strong reflections emanating from the substrate. An incident angle of 0.75° was chosen for this analysis. The effective penetration depth of X-rays at this angle is 410 nm, which was less than the thickness of the films (500 nm). Typical XRD patterns recorded for samples at 6, 10, 20 and 30 sccm oxygen flow are displayed in fig. 5.5. The figures show two broad peaks for the four oxygen flows. This is indicative of an amorphous structure of the as-deposited films at all oxygen flows. Pignolet et al. [50] have also reported amorphous films for Ta_2O_5 films deposited on unheated substrates. Upon annealing the films in steps of 100 °C under flowing argon, the films were found to crystallize at around 700 °C as shown in fig. 5.6. The peaks are identified as the orthorhombic phase of tantalum pentoxide [52]. In the next section, the films composition is examined.
Fig. 5.5 Grazing angle X-ray diffraction pattern of tantalum oxide films prepared at 6, 10, 20 and 30 sccm oxygen flow rates. The broad peaks indicate amorphous structure for all the flows.

Fig. 5.6 Grazing angle X-ray diffraction pattern for a tantalum oxide film prepared in the oxidic mode and annealed for one hour at 700 °C in argon.
5.1.5 Film composition:

Rutherford backscattering spectroscopy (RBS) can provide information about the composition and contamination profile of the film. From RBS measurements the relative composition of tantalum and oxygen was obtained. In fig. 5.7(a) and (b) typical RBS spectra of tantalum oxide films on a Si substrate at 6 and 30 sccm oxygen flow are presented. The normalized yield is plotted versus the energy of the backsputtered particles. The stoichiometry and the concentration across the films have been obtained by simulation. A strong signal near 1.30 MeV shows the position of tantalum. The spectra show a clear signal for energies below 0.7 MeV. This is characteristic of the silicon substrate. The oxygen signal is detected near 0.50 MeV, overlapping with the silicon one. The faint signal at 0.95 MeV corresponds to argon. Table 5.1 summarizes the ratio of oxygen to tantalum (O/Ta) at various oxygen flow rates and the amount of Ar incorporation. From the figures and the table it is clear that the O/Ta atomic ratio increases very rapidly upon increasing oxygen flow rate. Within error bars, tantalum pentoxide is realized above 2 sccm oxygen flow, which is in close agreement with the density, which decreases very slightly above 2 sccm oxygen flow, as shown in fig. 5.4.

We also note argon incorporation in the films from 2 sccm oxygen flow and above. Trapping of the sputtering gases in growing films is a well known phenomenon [53]. Argon can be expected to be trapped in the film during the sputtering deposition process. This occurs because a fraction of the Ar ions, which strike the target surface are neutralized and reflected from it. These energetic Ar neutrals arrive at the substrate and are trapped by the incoming sputtered particles. The mass of Ta atoms (180.9) is high compared to argon (40), so during the collision process, i.e. when Ar ions hit the Ta target surface, energy transfer is only partial and some of the Ar neutrals are reflected. If the masses of the ions and target are similar, as in the case of a silicon target a smaller fraction of the sputtering gas ions will be reflected from the target and consequently less gas will be incorporated in the film.

The absence of Ar gas at 0 sccm can possibly be accounted for by the reflected ions’ accelerating voltage (≡ cathode potential) and hence the depth into which an argon atom is implanted in the growing film. We propose that at the high cathode potential observed from 2 sccm and above (fig. 5.1b), deep implantation of argon atoms takes
Fig. 5.7 Typical RBS spectra of tantalum oxide films sputtered at a) 6 and b) 30 sccm oxygen flow rates, and the development of the film stoichiometry with oxygen flow. The red curve is the simulation. The films showed argon contamination as shown by the faint peak around 0.95.
<table>
<thead>
<tr>
<th>Oxygen flow (sccm)</th>
<th>Stoichiometry (O/Ta ratio) [± 0.2]</th>
<th>Argon content [±0.04]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>0.08</td>
</tr>
<tr>
<td>6</td>
<td>2.3</td>
<td>0.08</td>
</tr>
<tr>
<td>10</td>
<td>2.65</td>
<td>0.08</td>
</tr>
<tr>
<td>20</td>
<td>2.65</td>
<td>0.08</td>
</tr>
<tr>
<td>30</td>
<td>2.55</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 5.1. O-Ta ratio and Ar incorporation in the tantalum oxide films prepared under different oxygen flow rates.

place and hence the detected quantities of Ar. Gas incorporation and the bombardment of the growing film by the fast particles should have a profound effect on the deposition stress in the growing film. Therefore in the next section we discuss the deposition stress variation with oxygen flow.

5.1.6 Stress measurements:

Stress in the films was measured by a wafer-curvature set up. Films were 100 nm thick and deposited at different oxygen flows on 150 μm thick glass substrate. All stress values displayed in fig. 5.8 were negative which is evidence that the films possess compressive stress. The stress decreases with increasing oxygen flow rate changing by one order of magnitude by 6 sccm oxygen flow. Beyond this flow the stress was found to be independent of the oxygen flow and remained almost constant at −250 MPa. According to d’Heurle [in 54], compressive stress can be caused by knock-on processes by impinging ions and atoms. Sigmund [in 21] observes that atom implantation below the film surface is related to the ion flux and energy (see equation 2.15). The compressive stress caused by the implanted atoms is associated with an increase in the strain energy of the film. Therefore a reduction in the stress by movement of the implanted atoms to the surface is energetically favoured. Such atoms are thought to be in metastable states and upon receiving excitation energy can escape to the film surface. The intense local heating
Fig. 5.8 Variation of deposition stress for tantalum oxide films prepared at different oxygen flow rates. The stress shows a rapid decrease and then stabilizes at ~ -250 MPa. This is attributed to stress relaxation due to impinging energetic ions during film growth.

or thermal spike accompanying a bombarding ion can provide the energy required to release implanted atoms from their metastable positions.

An increase in stress relaxation with increasing ion energy is therefore expected as modeled by Davis, fig. 2.16. We have observed an increased cathode voltage and a simultaneous decrease in film stress with increase in oxygen flow. We therefore propose that, energetic oxygen ions (see section 5.4), accelerated by the observed cathode voltage, account for stress relaxation as discussed above. Furthermore, our XRD results show the films to be amorphous which could imply that the decrease in stress in the films could also partly be due to viscous flow in the amorphous phase.

5.1.7 Conclusion:

Through a number of analytical techniques the effects of varying the oxygen flow in the preparation of tantalum oxide films have been studied. Samples were prepared on glass and silicon substrates at different oxygen flow rates for constant total pressure and sputter current.
The target showed increased voltage, which was attributed to decreased secondary electron emission coefficient. There was no significant hysteresis for the tantalum target, which may be explained by the metal’s reactivity. The getter reactions explained the initial increase in the film deposition rate followed by a decreased rate, characteristic of oxidized surfaces due to decreased sputter yield with increased binding energy. Fully oxidized films were obtained above 2 sccm oxygen flow and were characterized by argon contamination and low stress. The films were also smooth, amorphous and with approximately 87% of the bulk tantalum pentoxide. The increased cathode voltage was thought to account for the necessary energy to cause the argon implantation and also stress relaxation through atomic peening mechanisms. This latter argument will be revisited later in section 5.4. The films were found to crystallize at around 700 °C.

5.2 Preparation and Characterization of Hafnium Oxide films

5.2.1 Introduction

Hafnium is a neighbouring element to tantalum in the periodic table and its oxide is a promising material in optical, electrical and photocatalytic applications. It belongs to oxides from group IV elements together with TiO₂ and ZrO₂, which are widely applied for such usages. Hafnium oxide has such interesting properties as high refractive index, thermodynamic stability, high dielectric constant, high heat of formation (1133.9 kJ/mol) and a relatively large band gap (5.68 eV) suitable for optical coatings [55]. In this section the deposition of hafnium oxide (HfOₓ) films upon varying the oxygen flow is presented. Films were prepared at a constant total pressure of 0.8 Pa and a sputter current of 500 mA at a substrate target distance of 70 mm.

5.2.2 Target characterization and deposition characteristics

Target characterization and deposition characteristics involve monitoring the target voltage for a constant current, mass deposition rate, the oxygen partial pressure as well as the quantitative film deposition rate with the oxygen flow. In this work oxygen flow was used as the variable parameter and its mixture with argon as the sputter gas. Fig. 5.9(a) shows the mass of hafnium oxide (HfOₓ) deposited per second on a quartz crystal
microbalance. The data was recorded for increasing and decreasing oxygen flow. The total pressure was kept constant by systematic variation of the sputter gas flow. The figure shows no significant change in mass deposition rate up to 1.7 sccm oxygen flow, where a sudden drop is observed. Thereafter the rate remains constant. This steep reduction characterizes transition from metallic to oxidic mode sputtering as already discussed in chapter 2 for reactive sputtering of metal targets. Upon decreasing the oxygen flow, a reverse behaviour is observed, though the sudden jump now occurs at a lower oxygen flow. This occurrence of the transition from metallic to oxidic and vice versa at different oxygen flows gives rise to the hysteresis effect. The oxidized target provides a source for oxygen and coupled with the low sputter rate of the oxide makes the transition to metallic to occur at a lower flow. Fig. 5.9(b) depicts the variation of the cathode voltage necessary to maintain the current constant at 500 mA with varying oxygen flow. The initial slight decrease is followed by a 30 V jump in voltage at 1.7 sccm flow when the mass deposition rate falls. The rise in cathode voltage implies an increased sputtering power, which should be reflected as a slight increase in the deposition rate. However as a result of the oxide formation, this anticipated change in deposition rate is overshadowed by the lower sputter yield characteristic of oxides in comparison to metals. The lower sputter yield is because of the oxide’s higher binding energy. The observation in voltage increase is also in contrast to the commonly observed behaviour where voltage is observed to fall upon target oxidation [ZnO [56], Al₂O₃ [57], MgO [58] etc]. The latter has been attributed to increased secondary electron emission for the oxide as compared to the metal. For increased voltage some researchers observe that it could be as a result of a thicker resistive oxide layer formation, which would require more power to be removed. On the other hand, in glow discharges, secondary electrons maintain the discharge. Therefore an increase in cathode voltage could also be as result of a depletion of these electrons in order to sustain the constant current. It is proposed in this work that the observed increase in the cathode voltage is due to reduced secondary electron emission coefficient to the oxides that show this behaviour. This will be discussed in detail in section 5.3, where voltage changes for reactively sputtered transition metals from groups IV to VI are considered.
Fig. 5.9 The variation of (a) deposited mass of hafnium oxide films per second per cm², (b) the cathode voltage, and (c) the oxygen partial pressure as functions of the oxygen flow. Hafnium target shows a pronounced hysteresis.

Finally, fig. 5.9(c) displays the changes observed in the oxygen partial pressure as revealed by a quadrupole mass spectral-analyzer. In the metallic mode (0 – 1.7 sccm oxygen flows), the partial pressure increases dismally with the flow due to getter reactions within the metallic mode. Upon target oxidation, there is a jump in the partial
pressure, which increases linearly with the flow thereafter. The hysteresis effect observed in fig. 5.9(a) is also evident in both figures 5.9(b) and (c).

The results of the mass deposition rate are quite qualitative and do not therefore translate into actual film deposition rate at various oxygen flows. This is because the quartz crystal microbalance uses only one density value as an input. However the film density varies with the oxygen flow rate and the accompanying film stoichiometry. This means that the elastic constants of the deposits vary and hence the oscillation frequency of the quartz. Therefore to quantitatively determine the film deposition rate, film thickness at various oxygen flows was obtained by X-ray reflectivity in conjunction with theoretical simulations. Figure 5.10 depicts the deposition rate of HfO_x films as a function of increasing oxygen flow. Films prepared in the metallic mode show a slight increase in the deposition rate with increasing oxygen flow. This is as a result of oxygen incorporation upon its reaction with the sputtered metal atoms. The sudden drop is observed at the same flow, as noted earlier with the mass deposition rate, while the oxidic mode sputtering is characterized by a low deposition rate of about 0.1 nm/s.

Fig. 5.10 Deposition rate of hafnium oxide films as a function of increasing oxygen flow. The rate increases due to getter reactions followed by an abrupt decrease upon target oxidation.
5.2.3 Film density and surface roughness

The films density and surface roughness were obtained, as already discussed, from theoretically simulated X-ray reflectivity measurements from samples prepared at various oxygen flows. Fig. 5.11 shows X-ray reflectivity measurements for samples prepared at 1 and 1.8 sccm oxygen flow together with the theoretical simulations. There is very good agreement between theory and measurement, which indicates adequate and precise description of the film properties. The sample prepared at 1 sccm, fig. 5.11(a), is in the metallic mode of sputtering. The spectrum shows a slow decay with increasing X-ray incidence angle (inset figure), which is an indication of low roughness. For the sample prepared, fig. 5.11(b), in the oxidic mode the oscillations decrease rapidly which is due to increased film surface roughness.

The variation of the films roughness with oxygen flow is summarized in fig. 5.12(a). After the low roughness associated with films prepared in the metallic mode, a steep increase is observed around 1.7 sccm oxygen flow, when oxidic regime sputtering begins. Further confirmation of this observation is obtained from atomic force microscopy pictures shown in fig. 5.13. The three images show film surface prepared at (a) 0 sccm oxygen flow, (b) 1.5 sccm oxygen flow and (c) 3.0 sccm oxygen flow. The differences in roughness are clearly discernible and follow the trend observed in fig. 5.12(a). This can further be linked to the observed different crystalline structures as discussed in section 5.2.3. From the critical angle of X-ray reflectivity spectra, the films density could be obtained with great accuracy and the result are as shown in fig. 5.12(b). The density is observed to rapidly decrease from 13.5 gcm\(^{-3}\) at 0 sccm, corresponding to hafnium metal films, up to 10 gcm\(^{-3}\) at 1.7 sccm oxygen flow. Between 0 and 1.7 sccm oxygen flows, the films understoichiometric as revealed by composition measurements in section 5.2.4. For the flows thereafter, the film density hardly changes and is approximately 10 gcm\(^{-3}\) on average, which within errors is comparable to the bulk value of 9.68 gcm\(^{-3}\) for hafnium oxide (HfO\(_2\)). This result departs from other reports like in tantalum oxide where densities of sputtered films possess an average of 80-90 % of the bulk density. The densification may be attributed to a high flux of energetic particles sputtered from the oxidized target as discussed later in structure formation for sputtered transition metal oxides in section 5.4.
Fig. 5.11 X-ray reflectivity measurements from samples prepared (a) 1.0 sccm and (b) 1.8 sccm oxygen flow. The inset in figure 1(a) shows appreciable interference patterns even for higher angles of incidence for x-rays, which means the films at this flow were smooth.
Fig 5.12 Variation of films (a) roughness and (b) density as determined by X-ray reflectivity measurements. The density decreases upon oxygen incorporation and is comparable to bulk value of hafnium oxide above 1.60 sccm oxygen flow. The roughness increases abruptly after 1.6 sccm oxygen flow.

5.2.4 Structural properties

By use of grazing incidence angle geometry for X-rays, the crystal structure evolution with the oxygen flow was determined. Fig. 5.14 summarizes these observations for measurements made at 0.4° angle of incidence. At the least oxygen partial pressure (0 sccm oxygen flow), the peaks observed correspond to metallic hafnium. For 1.0 and 1.5 sccm oxygen flows, the patterns are characterized by a single broad peak, which indicates that the films were amorphous. For films prepared in the oxidic mode (1.8, 2.5 and 4 sccm oxygen flows), peaks corresponding to monoclinic hafnium oxide are observed. The formation of crystalline films at room temperature is a surprising observation for hafnium oxide films. This is because hafnium oxide has a high heat of formation, which is evidence for very strong oxygen metal bonds and the rearrangement of such bonds at room temperature, a prerequisite for formation of crystalline phase, appears rather unlikely and an amorphous structure would thus be expected. Nevertheless a monoclinic crystalline phase is observed for the hafnium oxide.
Fig. 5.13 AFM pictures for hafnium oxide film prepared at various oxygen flows. At 0 scem oxygen flow films show small grains, which give rise to small roughness. The films are completely smooth at 1.5 scem flow while large grains and pit like holes are observed at 3.0 scem flow. This leads to significantly higher roughness.
Fig. 5.14 Grazing angle X-ray diffraction pattern for HfO$_x$ films prepared at 0, 1.0, 1.5, 1.8, 2.5 and 4 sccm oxygen flows. The peaks for the film prepared at 0 sccm oxygen flow are for hafnium metal. Within metallic mode sputtering films were amorphous. Crystalline monoclinic hafnium oxide films are observed in the oxidic mode.
The main peak detected corresponds to the plane $(\overline{1} 1 1)$ at $28^\circ$ while weak peaks of (002) and (200) planes are detected at $34^\circ$ and $35.5^\circ$, respectively. To account for the observed crystallization occurring at room temperature upon reactive sputter of the metal, an atomistic approach is provided in section 5.4. In this model, based on a broad data from transition metal oxides, oxygen ions sputtered from the oxidized target, are accelerated by the cathode potential and their bombardment on the growing film is proposed to result in the crystalline structures.

5.2.5 Film stoichiometry

Two methods were used to analyze the relative composition of hafnium and oxygen in the films. These were the Rutherford backscattering and the secondary neutral mass spectroscopy. Typical RBS spectra measured for 2.2 and 4 sccm oxygen are shown in fig. 5.15. The normalized yield is plotted versus the energy of the backsputtered particles. Simulation was used to obtain the stoichiometry. The strong signal, whose leading energy edge lies near 1.30 MeV, corresponds to hafnium. The oxygen signal is detected at 0.5 MeV overlapping the one of silicon, which has a leading energy edge at 0.7 MeV. A notable observation is the reduced yield for the hafnium at the interface, shown by the receding energy edge in the spectra. This could be thought as interface mixing, though not confirmed by the silicon energy leading edge, which would have shown a distorted yield as characteristic proof for such a phenomenon. A summary of the ratio of oxygen to hafnium from both the RBS and SNMS measurements is depicted in fig. 5.16. Within errors, there is a close agreement between the two measurements. Specifically in the metallic mode there is very good agreement and slightly more oxygen detected by RBS than SNMS in the oxidic mode. There is increasing oxygen incorporation in the films with increasing oxygen flow within the metallic mode. From 1.7 sccm oxygen flow, films were fully stoichiometric within measurement errors. These results in stoichiometry collaborate the trend observed with the film density. There are large error bars for the oxygen concentration as a consequence of the weak Rutherford cross section for oxygen and the difficulty to precisely subtract this peak from the background caused by the underlying Si substrate. Similarly appreciable error bars are to be observed for SNMS.
Fig. 5.15 Typical RBS spectra measured and simulated for samples prepared at (a) 2.2 and (b) 4sccm oxygen flow. The black curve shows the measurement while the red shows the simulation. Hafnium peak is observed near 1.3 MeV while oxygen at 0.5 MeV overlapping that of Silicon substrate.
Fig. 5.16 Summary of oxygen to metal ratio with the oxygen flow as revealed by Rutherford backscattering (RBS) and secondary neutral mass spectroscopy (SNMS). Films are understoichiometric below 1.7 sccm oxygen flow.

5.2.6 Deposition stress

The stress in the films was determined by the wafer curvature method. Films were approximately 100 nm thick and deposited on 150 µm thick glass and in general showed compressive stress as indicated by the negative values as shown in fig. 5.17. Pure metal films were characterized by high compressive stress of approximately \(-1300\) MPa while films made just before the transition from metallic to oxidic mode sputtering show a decreasing stress with increasing oxygen flow. From 1.7 sccm oxygen flow the films showed an abrupt increase in stress with all the films in the oxidic mode characterized by high stresses. This behaviour in stress is only comparable to that of zirconium oxide [59]. To try and understand this, we recall that, within the metallic mode, the films were amorphous as shown by X-ray diffraction and understoichiometric as revealed by both RBS and SNMS measurements. Consequently structure and stoichiometry may account for the reduced stress in terms of viscous flow and the unsaturated bonds, which may be easier to deform. The abrupt increase in stress occurs at the transition point from metallic
Fig. 5.17 Variation of deposition stress with increasing oxygen flow for hafnium oxide films. Stress decreases with increasing oxygen flow followed by an abrupt increase above 1.7 sccm oxygen flow. The stress build up in the oxidic mode is attributed to a large flux of ions at moderate energies.

to oxidic mode of sputtering. Films within this region are also fully stoichiometric and crystalline. As further discussed in section 5.4, oxygen ions sputtered from the oxidized target and accelerated by the moderate cathode voltage are proposed to lead to stress build up in the films through the process of ‘atomic peening’ as reviewed in chapter 2.

5.2.7 Conclusion

A number of techniques are employed in characterizing reactively dc magnetron sputtered hafnium oxide films. In target characterization, a significant hysteresis, whose width is only comparable to that of zirconium target [10] among reactively sputtered transition metals, was observed. The hysteresis behaviour could be associated with the high reactivity of the metals and the oxides high heat of formation known for zirconium and hafnium in comparison to the other transition metals. Moderate target voltage change
was measured, which showed an increase upon target oxidation. This is attributed to depletion in secondary electron as a result of reduced secondary electron emission coefficient of the oxide layer, which covers the target. Film deposition rate showed a typical behaviour: high in the metallic mode and showing a sudden drop upon target oxidation. This is well accounted for by the getter reactions in the metallic mode as a result of oxygen incorporation, while the increased binding energy of the oxide formed on the target leads to decreased deposition rate. Films obtained in the metallic mode were amorphous, understoichiometric and smooth. Their density was also shown to decrease with increasing oxygen flow. In the oxidic mode the films had almost bulk density, had monoclinic crystalline structure, were rough and stoichiometric HfO₂ within measurement errors. The bulk-like density contrasted with the 70-90 % reported for other reactive direct current magnetron sputtered transition metal oxide films [51, 60, 61].

5.2.8 Comparison between tantalum and hafnium oxides deposition

The two targets showed similar general sputter behaviour upon variation of oxygen flow. The significant regions characterizing reactive sputtering namely metallic, transition upon target oxidation and the oxidic mode were all evident. From the mass deposition rate, hafnium oxide showed abrupt change into the oxidic mode while tantalum oxide proceeded more progressively. Hafnium showed a marked hysteresis, which was absent for tantalum. This may possibly be correlated with the respective metal’s reactivity. The target voltage increased in both cases albeit much higher for tantalum despite the lower sputter current. This will be discussed in detail in section 5.3, where the change in cathode voltage is accounted for in terms of change in secondary electron emission coefficient. The deposition rate was higher for tantalum at the start of the oxidic mode as compared to hafnium, which means that its possible to deposit transparent tantalum oxide films at quite a high rate of about 0.3 nm/s compared to 0.1 nm/s for hafnium oxide in the oxidic mode. The trend observed in mass deposition rate is replicated in the actual film deposition rate for both oxides.

For the film properties, on one hand hafnium oxide films were quite dense (~bulk density), crystalline in the oxidic mode, rough and they showed high compressive stresses. On the other hand tantalum oxide had a density lower than the bulk (~87 %),
were amorphous, smooth, and showed low compressive stresses. In the metallic mode both were characterized by understoichiometric amorphous films while stoichiometric films were found within measurement errors for films prepared in the oxidic regime.

The target voltage is one of the fundamental parameters during sputtering that has a direct influence on the film properties. As seen in equation 2.3, the sputter yield and thence the sputter rate, directly depend on it. A fundamental parameter that controls target voltage is the emission of the secondary electrons from the sputtered target. The knowledge of secondary electron emission yield is therefore paramount in understanding the fundamental processes during film preparation. Section 5.3 provides an analysis on the variations in target voltage for the different transition metal oxides examined in the research group and provides an empirical computing procedure for the coefficient.

5.3 Secondary electron emission yields in reactive sputtering of transition metal oxides:

In the reactive sputtering of metal targets, the reactive gases flow rate influences the discharge voltage, deposition rate and film composition and a hysteretic mode transition between the metallic and oxide modes may even occur. These observations are best illustrated by the results of tantalum and hafnium oxides depositions as presented in sections 5.1 and 5.2. These discharge characteristics provide useful information on target condition upon varying the reactive gas partial pressure. Theoretical descriptions exist which attempt to explain these processes. Berg et al. [62] originated with a simple qualitative model, which considers the balance of reactive gas from adsorption and desorption reactions at the target and the substrate electrodes. From their model, deposition rate and the film composition are calculated as functions of the reactive gas flow rates. The Berg’s model has since been further developed by them [63,64] and other researchers [65-67]. However the models neglect changes in plasma properties against the reactive gas flow and therefore fail to sufficiently describe the experimental results quantitatively. To correct these shortcomings, Ershov and Pekker [68] modified the Berg’s model by including the plasma chemistry. But according to Matsuda et al. [58] the modification seems to have overstated the plasma chemistry thereby complicating the
analysis. Matsuda et al. have corrected this by including in the reactive sputtering model changes in secondary electron emission for a magnesium target.

Of importance to note also is the explanation by Rao and Mohan [69] for reactive sputtering and which is also widely quoted. They correlated film properties and the glow discharge characteristics for reactively sputtered cermet films of Cu-Cu$_2$O at different oxygen partial pressures. In their explanation, they represent the cathode potential variation with the oxygen partial pressure, in three phases as shown in fig.5.18.

Fig. 5.18 Proposed model of reactive sputtering process in terms of cathode potential and oxygen partial pressure by Rao and Mohan [69]. Region I is characterized by increased cathode voltage due to secondary electron depletion by oxygen atoms. Target oxidation leads to emission of more secondary electrons and hence the decrease in voltage. Region III has increased voltage due to resistance of the formed oxide layer.

They identify the first phase as the region where cathode voltage initially increases before it starts to decrease at a certain oxygen partial pressure. They attribute this voltage increase to negative ion formation, during which some of the secondary electrons emitted by the cathode get attached to the oxygen atoms with consequent depletion in the number of electrons. This results in the higher cathode potential to achieve the required cathode current, which is essentially positive argon current. In the second phase, the target
poisoning starts and hence an oxide layer starts building up on the target surface. They point out that, since oxides have a higher electron emission yield than the corresponding metal, both the total number of electrons as well as the ionization increases, resulting in the drop in the cathode potential. They also observe a corresponding drop in the deposition rate because of the lower sputtering yield of the oxide. A third phase is identified by an increase in the cathode potential as oxygen partial pressure is further increased. They attribute this to need to break the growing insulating oxide layer.

From our series of studies involving eight transition elements of groups IV-VI, these models do not seem to explain our results. Upon target oxidation, which is the point at which deposition rate is observed to drop, we do not observe a decrease in the cathode potential, as already illustrated for tantalum and hafnium in figures 5.1(b) and 5.9(b). The cathode potential is observed to stay at the same high value upon transition with little or no decrease as the oxygen flow is increased. The magnitude of target voltage change also differs for different transition metal targets. We propose that the deviation of our results from the proposed models is a result of these models not including the effects of the differences in secondary electron emission coefficients. This section seeks to account for the differences observed in target voltage behaviour by providing a computing procedure for the oxides secondary electron emission coefficients. The availability of the coefficients for the oxides should contribute to better modeling of reactive sputtering processes as illustrated by Matsuda et. al [58].

The mechanisms of secondary electron emission have been understood quite well for metal targets in the past two to three decades. This is owing to development of various techniques for particle bombardment and analysis at low and at medium-to-high energies on metal surfaces [70]. On the other hand very few investigations for metal oxide targets have been carried out [71,72]. Ellmer and Mientus [57] have established discharge characteristics for Al, Au, Cr, Cu, Fe, Mo, Pt, Ti, and Zn. In this section an analysis of discharge characteristics from a systematic study of a series of elemental transition metal targets in groups IV-VI during reactive magnetron sputtering in Ar/O₂ mixtures is performed.

Columns II and III in table 5.2 show the magnitudes of the target potential in the metallic and oxidic modes for constant sputter current. A common feature for all of them
is the increase in the target voltage upon target oxidation. This observation is in contrast to what has been reported for other elements like Zn [56] and Al [57]. The latter show decreased discharge voltage, which is associated with an increased electron yield for the oxidized surface. Such increase in electron yield is found for dynodes for secondary electron multipliers, only that, in dynodes, electrons are the incident particles and not ions.

For ions of higher energies it is generally stated that an oxidized surface has a higher electron yield due to increased mean free path for electrons and a smaller work function of insulators compared to metals. This statement does not seem applicable in the ion-energy range below 1 keV which characterizes dc magnetron discharges. This is because the electron emission is due to potential emission (caused by Auger neutralization, as for example depicted in fig. 5.19). Such emission occurs if the potential (ionization) energy $E_i$ of the impinging ion is higher than the twofold workfunction $\phi$ of the target material [57]. The electron yield in the energy range 100-1000 eV is essentially independent on the ion energy. Hagstrum [73] and Baragiola et al. [74] have independently developed empirical relations for secondary electron emission coefficient, $\gamma_{pot}$, for potential electron emission in metals presented as follows:

$$\gamma_{pot}=0.016(E_i-2\phi) \quad 5.1(a)$$

$$\gamma_{pot}=0.032(0.78E_i-2\phi) \quad 5.1(b)$$

which yields similar results (see the $\gamma_m$ values in table 5.2) except for the metals with $\phi \geq 5$eV. Typical values of $\phi$ are shown in table 5.2 for the various transition metals used in this work. According to these relations and under the assumption that, the discharge voltage is determined by the electron yield, if all the other parameters (magnetic field, geometry, power, pressure) are fixed there should exist a correlation between the discharge voltage and the electron work function of the metals. This relation is now derived below.

The ignition of the glow discharge relies on ionization caused by secondary electrons from the target as they are accelerated across the dark space. This can be modeled by considering the amount of ionization caused by a flux $N_e(x)$ electrons passing through a thin slab of thickness $\Delta x$ located from the cathode. If the density of neutrals is
Fig. 5.19. Schematic illustration of an Auger process. A hole is created in the L level when the atom is excited by some incident energy $E$ and is filled by an electron from the valence band. The energy released ejects another electron in the valence band out of the atom. The process is denoted as LVV. The letters on the right hand side denote the electronic levels and $\phi$ the work function. The fermi level and conduction band are labeled as $E_F$ and $E_C$ respectively on the left hand side.

If $n$ and the ionization cross-section (assumed energy independent for simplicity) is $q$, then the number of ionizing collisions is equal to $N_e(x) n q \Delta x$, which means that

\[
\frac{dN_e(x)}{dx} \Delta x = N_e(x) n q \Delta x
\]

\[
\int \frac{dN_e}{N_e} = \int nq dx
\]

\[
N_e(x) = N_e(0) \exp (nq x)
\]  

5.2
So each electron that leaves the target is multiplied by \( \exp(nqL) \), where \( x = L \) is the electron’s effective ionization path length. For each ionization, a new ion is formed as well as a new electron. For each electron that leaves the target, \( \exp (nqL) - 1 \) ions will be formed. For each ion that strikes the target, \( \gamma \) secondary electrons will be emitted. These events are schematically shown in fig. 5.20. Hence each ion that strikes the target will lead to the generation of \( \gamma (\exp nqL - 1) \) ions. For the ignition of the discharge it is necessary that electron multiplication factor \( \gamma (\exp nqL - 1) \) is greater than one. From this condition one obtains:

\[
\gamma = \left[ \exp(nqL) - 1 \right]^{\frac{1}{\gamma}}
\]  \hspace{1cm} 5.3

For magnetron discharge, \( L \) is much longer than the dark space length, \( l_{ds} \), because of the cycloidal electron path form in the crossed electric and magnetic fields. Hence

\[
L >> l_{ds} \Leftrightarrow L = kl_{ds}
\]  \hspace{1cm} 5.4

where \( k \) is a constant of proportionality.

For the calculation of the length of dark space, \( l_{ds} \), Child-Lagmuir equation [75] can be used to give:

\[
l_{ds} = \sqrt{\frac{8.6 \times 10^{-9} AV^{\frac{3}{2}}}{I}}
\]  \hspace{1cm} 5.5

where \( A \) is the effective target area, \( V \) is approximately the applied voltage and \( I \) is the current. Since we sputter in the constant current mode and \( A \) can be considered constant for a given target, from equations 5.3 to 5.5 it can be shown that the secondary electron emission coefficient for the metal oxide \( \gamma_{mo} \) is

\[
\gamma_{mo} = \left[ \left( \gamma_m^{-1} + 1 \right) \left( \frac{V_m}{V_o} \right)^{\frac{1}{2}} \right]^{-1}
\]  \hspace{1cm} 5.6

where \( V_m \) and \( V_o \) are the target voltages in the oxidic and metallic modes respectively, and \( \gamma_m \) is the metal’s secondary electron emission coefficient, which is directly calculated from the metal’s work function and the ionization potential of the sputter gas argon as shown by Hagstrum and Baragliola.

In table 5.2, values computed with this procedure are depicted. In general for the considered transition metal oxide covered targets, the coefficients, \( \gamma_{mo} \), for the oxides are lower as compared to those of the metal, \( \gamma_m \), sputtering. They are also relatively higher in
Fig. 5.20 schematic representation of the ion pair production in the dark space of length, L. For each ion that strikes the target γ electrons are emitted. For each ionization, a new electron as well as a new ion is formed.

those oxides where change in voltage is not large i.e. group IV elements. These values are empirical and form the first attempts, outside the work of Ellmer and Mientus [57] on Ti and Mo oxides, in computing the coefficient for a large number of transition metal oxides. In comparison, Ellmer et al. values of titanium and molybdenum oxides are slightly higher at 0.06 and 0.01 than results obtained by this work (0.043 and 0.006) despite a similar computing procedure. The differences may be attributed to exact electrical discharges encountered since they depend on a number of factors e.g. target history etc. The influence of the ions sputtered from the target on the plasma impedance and therefore on the target potential has also been neglected.
<table>
<thead>
<tr>
<th>Element</th>
<th>Target Voltage [V]</th>
<th>φ [eV]</th>
<th>$\gamma_m$ = (0.016*(E$_{Ar}$ -2φ) [eV]</th>
<th>V$<em>{MO}$/V$</em>{M}$</th>
<th>$\gamma_{mo}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metallic V$_M$</td>
<td>Oxidic V$_{MO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>301</td>
<td>393</td>
<td>4.33</td>
<td>0.114 (0.116)</td>
<td>1.306</td>
</tr>
<tr>
<td>V</td>
<td>290</td>
<td>473</td>
<td>4.3</td>
<td>0.115 (0.118)</td>
<td>1.631</td>
</tr>
<tr>
<td>Zr</td>
<td>264</td>
<td>294</td>
<td>4.05</td>
<td>0.123 (0.134)</td>
<td>1.114</td>
</tr>
<tr>
<td>Nb</td>
<td>314</td>
<td>555</td>
<td>4.3</td>
<td>0.115 (0.118)</td>
<td>1.767</td>
</tr>
<tr>
<td>Mo</td>
<td>281</td>
<td>521</td>
<td>4.6</td>
<td>0.105 (0.099)</td>
<td>1.854</td>
</tr>
<tr>
<td>Hf</td>
<td>270</td>
<td>281</td>
<td>3.9</td>
<td>0.127 (0.144)</td>
<td>1.041</td>
</tr>
<tr>
<td>Ta</td>
<td>220</td>
<td>409</td>
<td>4.25</td>
<td>0.116 (0.121)</td>
<td>1.859</td>
</tr>
<tr>
<td>W</td>
<td>345</td>
<td>613</td>
<td>4.55</td>
<td>0.1078 (0.102)</td>
<td>1.777</td>
</tr>
</tbody>
</table>

Table 5.2 Summary of target voltages in metallic, V$_M$ and oxidic modes, V$_{MO}$, metal work function, φ and the electron emission coefficients in metal, $\gamma_m$ and metal oxide, $\gamma_{mo}$. In brackets are the $\gamma_m$ the values computed with equation 5.1(b).
5.4 Summary and Analysis on Structure Formation in Transition Metal Oxide Films

5.4.1 Introduction

In section 5.1 and 5.2, we have discussed the deposition of tantalum and hafnium oxide films, respectively. Despite these elements being neighbours in the periodic table, they have exhibited some fundamental differences in their deposition conditions and film properties as summarized in section 5.2.8. We therefore for example in section 5.3 sought to understand the origin of the differences in the cathode voltages. We have attributed this to the differences in secondary electron emission coefficient, which we have now quantified. In this section we address the differences in film structures. We have seen that tantalum oxide deposition leads to amorphous films while hafnium oxide films were found crystalline. We now want to address the question of when are films deposited crystalline or amorphous by use of the direct current reactive magnetron sputtering. The discussion here will be broad and including all other reported structures of transition metal oxides within the research group as illustrated by the table below.

<table>
<thead>
<tr>
<th>TiO₂</th>
<th>V₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>Nb₂O₅</td>
</tr>
<tr>
<td>MoO₃</td>
<td></td>
</tr>
<tr>
<td>HfO₂</td>
<td>Ta₂O₅</td>
</tr>
<tr>
<td>WO₃</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3 Summary of oxides investigated for their growth in thin film structure upon reactive direct current magnetron sputtering of their metal targets in an argon oxygen atmosphere at room temperature.

The analyzed oxide films were prepared by reactive DC magnetron sputtering from the corresponding elemental targets in the oxidic mode regime. Details of the
experimental set-up have already been described in chapter 4. The sputtering atmosphere was a mixture of argon and oxygen. The films for structure and deposition stress analysis were prepared at pressure (p) and substrate-target distance (d) product, (pd), in the range of 52 to 78 mmPa and at constant current sputter mode. To obtain sufficient signal for an unequivocal structure identification film thicknesses of approximately 500 nm were employed. Furthermore the X-ray diffraction patterns were recorded in grazing angle geometry to increase the signal-to-noise ratio. The wafer curvature method was employed to determine the deposition stress. Finally, deposition rates were obtained at different total pressures from thicknesses determined using X-ray reflectometry.

5.4.2 Results and discussion

Figure 5.21 shows a summary of grazing angle X-ray diffraction (XRD) spectra for some of the transition metal oxide films prepared in the oxidic mode. Both zirconium [10] and hafnium [this work] are observed to form monoclinic crystalline oxide films, while niobium [51] and tantalum [this work] form amorphous oxides as revealed by the two broad humps observed in the spectra. In addition, we have found tungsten, vanadium and molybdenum [61] to form amorphous oxide films (see table 5.4). Titanium oxide was found to be a borderline case, which can crystallize to mixed phases of anatase and rutile at low total but high partial oxygen pressure, whereas it is amorphous [77] at other sputtering conditions. These results show a systematic trend where oxides of group IV can be deposited with crystalline structure at room temperature while those oxides of groups V and VI are amorphous. This trend is surprising because none of the models for structure formation reviewed in chapter 2 seems to explain this trend. To begin with, the sputter pressures for our oxides do not vary significantly. They only range between 0.8 and 1 Pa. Furthermore there is also no trend to explain the results when one examines the product of pressure and target-substrate distance as shown in table 5.4. This shows the first incompatibility with Thornton’s model for our films.
Fig. 5.21. Grazing angle X-ray diffraction pattern for a) zirconium [10], b) niobium [49], c) hafnium, and d) tantalum oxide films prepared in the fully oxidic mode. The spectra reveal a monoclinic structure for both zirconia and hafnia. The two broad peaks observed for niobia and tantalum are characteristic of amorphous films.

Secondly, we consider the homologous temperature, the other parameter in the Thornton model. The importance of homologous temperature is for example also evident in molecular beam epitaxy (MBE) studies for the growth of metal films. The studies reveal a sequence of atomic barriers that govern the film morphology. This is illustrated in fig. 5.22 for homoepitaxial growth of platinum on platinum (111) and aluminium on aluminium (111) at different deposition temperatures [78,79]. The figure shows increased island size with temperature due to increased diffusion. The relevance of the homologous temperature in metals is not surprising since notably in metals the melting temperature scales linearly with the cohesive energy as depicted in fig. 5.23 [80]. However when we consider the homologous temperature for oxides, it is lowest for HfO$_2$, as revealed in table 5.4. Hence one would expect this oxide to be the best candidate for the formation of an amorphous film if the Thornton model is applicable. Experimentally, however, HfO$_2$ is one of the two oxides growing with a monoclinic crystalline structure (fig. 5.21), while most other oxides have an amorphous structure as depicted in table 5.4. These results can also not be reproduced by comparing the heats of formation as would be the case for
<table>
<thead>
<tr>
<th>Oxide</th>
<th>Crystal structure</th>
<th>pd [mmPa]</th>
<th>$T_h$</th>
<th>$\Delta H_f$ [eV]</th>
<th>IP$_M$–EA$_O$</th>
<th>$V_{\text{oxidic}}$</th>
<th>$\Delta V/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Amorp./cryst (anatas&amp;rut)</td>
<td>78/58</td>
<td>0.14</td>
<td>9.9</td>
<td>41.79</td>
<td>400/383</td>
<td>0.33/0.27</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Crystalline (monoclinic)</td>
<td>52</td>
<td>0.10</td>
<td>11.4</td>
<td>32.86</td>
<td>294</td>
<td>0.12</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>Crystalline (monoclinic)</td>
<td>52</td>
<td>0.10</td>
<td>11.63</td>
<td>31.83</td>
<td>276</td>
<td>0.02</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>amorphous</td>
<td>62</td>
<td>0.31</td>
<td>8.28</td>
<td>63.75</td>
<td>430</td>
<td>0.65</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>amorphous</td>
<td>52</td>
<td>0.17</td>
<td>9.94</td>
<td>49.06</td>
<td>550</td>
<td>0.77</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>amorphous</td>
<td>62</td>
<td>0.14</td>
<td>10.68</td>
<td>-----</td>
<td>370</td>
<td>0.76</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>amorphous</td>
<td>78</td>
<td>0.28</td>
<td>7.79</td>
<td>66.52</td>
<td>570</td>
<td>0.90</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>amorphous</td>
<td>78</td>
<td>0.17</td>
<td>8.7</td>
<td>-----</td>
<td>630</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Table 5.4. A summary of the observed structure of different transition metal oxides; the product, pd [mmPa] of pressure, p, and substrate-target distance, d; the homologous temperature, $T_h = T_{\text{growth}} / T_{\text{melt}}$, where $T_{\text{growth}}$ and $T_{\text{melt}}$ are film growth and target melting temperatures respectively; the heat of oxide formation per metal atom, $\Delta H_f$ in eV; the value (IP$_M$ – EA$_O$) in eV, where IP$_M$ denotes the metal’s ionization potential and EA$_O$ denotes the oxygen’s electron affinity [80], $V_{\text{oxidic}}$ is the cathode voltage in oxidic mode and the ratio $\Delta V/V$ describing the change in voltage divided by initial voltage at 0 sccm oxygen flow. The dashed line (---) indicates that data are not available from our references.

Fig 5.22 Temperature dependence of island densities [78,79]. The islands increase in size with increasing temperature due to increased diffusion.
deposition through chemical vapour deposition. As shown in table 5.4, ZrO₂ and HfO₂ are characterized by the highest heats of formation of all oxides considered. A low standard free energy of formation, |ΔG|, which is related to the heat of formation, fosters a low nucleation rate of larger critical sized nuclei whereas a high rate of heterogeneous nucleation results in polycrystalline or amorphous films [81]. In addition such strong bonds formed by compounds characterized by high heat of formation would not be easy to rearrange. This implies a need to examine the additional features in the growth process of sputtered films, which are not inherent in Thornton model and not found in the CVD processes. The characteristic feature that distinguishes sputtering from for example a CVD process is the impact of energetic particles formed in the sputtering process. We hence propose that it is the energy deposited at the growing film by these particles that governs the structure of the transition metal oxides produced by DC reactive sputtering at room temperature. A basic observation pointing towards the role of energetic particles is the nano-crystalline nature of the zirconia and hafnia as revealed by fig. 5.21. Below we provide further experimental findings and theoretical arguments in support of the foregoing statements.
The first and foremost question is; which energetic particles bombard the growing film and influence the film structure? Possible candidates are positive or negative ions and electrons as well as neutrals. Most of the positive ions are accelerated towards the target and can hence be directly excluded. Others are accelerated towards the growing film by the small positive potential of the plasma. Their energy is typically ~ 20 eV [82, 83] and a significant thermal effect on the growing film seems unlikely. Some of the positively charged Ar ions that bombard the target can be neutralized and reflected at the target surface and hence could impinge on the growing film with sufficient energy as fast neutrals. The formation of such energetic neutrals should however mainly depend upon the target mass as is known for the atomic peening mechanism, that causes compressive stresses in sputtered metal films [54]. Hence neighboring oxides such as zirconia and niobia should be exposed to a similar amount of Ar neutrals with comparable energies and consequently exhibit similar structure, which is in contrast to our finding. Therefore only negative ions or electrons can be responsible for the structure formation of the growing film. Secondary electrons formed [27, 84] are trapped by the magnetic field and those that escape could cause substrate heating. However, previous studies have shown that the temperature rises to only 70 °C for zirconium oxide [10] and 100 °C for tungsten oxide [5] sputtering. Hence only negative ions have to be considered and the only reasonable candidate is oxygen. Such oxygen ions will only have sufficient energy for a structural modification if they are formed at or very near the target surface.

The situation can then be hypothesized as follows:

i) That during the reactive sputtering, sputtering is from an ionic compound, which is the oxidized target.

ii) That the Ar⁺ ions eject from the oxide a significant number of negative oxygen ions whose flux depends on the particular oxide being sputtered.

iii) That these oxygen ions experience an accelerating voltage equivalent to the applied target potential

iv) That the ions bombard the growing film thereby depositing energy, which depends on ion flux and energy resulting in the different structures.
Fig. 5.24. Variation of the target voltage of a) zirconium [10] and b) niobium [51] targets as a function of increasing (↑) and decreasing (↓) oxygen flow for constant cathode currents. ∆V is the change in voltage. Modest changes in voltage, as observed for the zirconium target, imply modest energy imparted to the oxygen ions. On the other hand large cathode voltages as observed for niobium lead to very energetic ions. Curves (c) and (d) illustrate the evolution of deposition stress for zirconium and niobium oxide with the oxygen flow rates respectively. Stress builds up for zirconium oxide films but stress relaxation is observed for niobium upon target oxidation.

An immediate proof that ions formed at the target are crucial for film formation and related properties can be demonstrated by the evolution of the deposition stress. This is shown in figure 5.24(c) & (d) for zirconium and niobium respectively, where deposition stress is shown as a function of the oxygen flow.

For the zirconium target, the films show a decreasing stress with increasing oxygen flow up to a critical flow at which the stress increases abruptly. This flow marks the onset of complete target oxidation. The fully oxidized films are characterized by high deposition stresses of the order of −1500 MPa. There is clearly a dependence of stress on
the target condition as revealed by the corresponding target voltage for increasing oxygen flow in figure 5.24(a). The compressive nature of the stress is as shown by the negative values. We hence propose that an increased flux of oxygen ions from the oxidized target accounts for the stress build-up and crystallization in zirconium oxide films. Indeed Tominaga and Kikuo have demonstrated a steep increase in oxygen ions at a flow correspond to target oxidation for zirconium as shown in fig. 5.25 [85]. Niobium films, on the other hand, show decreasing stress with increasing oxygen flow up to the flow corresponding to complete target oxidation, beyond which the stress remains constant. As in structure formation a systematic trend also emerges for the deposition stress as shown in table 5.5, where crystalline films have high deposition stresses whereas amorphous oxide films have comparatively low stresses.

To interpret the deposition stress and the emerging trend, we have to consider both the source and magnitude of the energy of the sputtered oxygen ions as well as their flux. First we discuss their energy.

![Graph showing the variation of ion current, Io, due to energetic oxygen as a function of oxygen partial pressure ratio for Zr target. There is a steep increase in the oxygen ion flux upon target oxidation at R_{th} % oxygen partial pressure ratio [85].]

Fig. 5.25 Ion current, Io, due to energetic oxygen as a function of oxygen partial pressure ratio for Zr target. There is a steep increase in the oxygen ion flux upon target oxidation at R_{th} % oxygen partial pressure ratio [85].
<table>
<thead>
<tr>
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<td></td>
<td></td>
<td>-300 MPa</td>
<td>-100 MPa</td>
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</table>

Table 5.5 Summary of deposition stress in transition metal oxides. Stress is generally compressive (negative values) and specifically high for crystalline films (ZrO₂ & HfO₂).

Tominaga et al. [86] have already demonstrated through time of flight measurements that oxygen ions sputtered from an oxidized zinc target obtain their energy from the repulsion by the cathode potential. Similarly here, the ion energy of the sputtered oxygen ions can be correlated with the target voltage, which on the other hand could be directly correlated with the secondary electron emission coefficient as discussed in section 5.3. The amorphous oxides have relatively high cathode voltages while only moderate voltages are observed for crystalline oxides. This trend is evident for all the elements as can be seen from table 5.4 where we list both the absolute values of the cathode voltage in the oxodic mode, $V_{\text{oxidic}}$ and $\Delta V/V$. The ratio $\Delta V/V$ takes care of the sputter currents used and is obtained by normalizing the change in cathode voltage, between the metallic and oxidic modes, with the voltage in the oxidic mode. Oxygen ions are therefore accelerated by high cathode potentials for the case of group V and VI, bombard the growing film and result in stress relaxation via thermal spikes as well as the amorphous structure due to damage caused by this bombardment. For group IV oxides, the moderate voltages provide moderate energy for film crystallization and atomic rearrangement that causes stress build up. The stress results may be summarized by fig. 5.26, where stress is plotted against ion energy assuming that the ions bombard the growing film at energies equivalent to the target potential. This observed stress-energy relation is in qualitative agreement with the proposed model by Davis [25] as discussed in section 2.4.3. Zirconium and hafnium oxides stresses fall in region I (for high flux - as
Fig. 5.26. Compressive stress from the different transition metal oxides as a function of energy. The energy is obtained from the cathode voltage, which accelerates the oxygen ions sputtered from the oxidized target. No scattering from the sputter gas is considered.

will be shown below) while the other oxides fall in region II (where low stress are due to stress relief via thermal spikes due to high ion energies).

The subsequent question is if an independent experiment can provide further evidence for such ion energies and their influence on the oxide films. To address this, we have examined the films growth rates by monitoring the variation of the deposition rates with total pressure as shown in fig. 5.27. The data points illustrate the deposition rate measurements performed for (a) titanium, (b) hafnium, (c) niobium and (d) molybdenum oxide films while the dashed curves are the fittings obtained through Keller Simons relation [31]. The relation, as already discussed in section 2.5, predicts a decreasing deposition rate with increasing pressure due to increased particle scattering. Titanium and hafnium oxide deposition rates show a progressive decrease in agreement with the theoretical relation. However, the deposition rates for niobium and molybdenum oxides first show an increase at low pressures followed by a decrease at higher pressures. The deviation at low pressures illustrates backspattering, which is deposit removal or erosion due to high kinetic energy of incident particles. This implies that some oxide films encounter higher energetic particles, that cause backspattering, which provides us with an
Fig. 5.27 Variation of the deposition rates (data points) with total pressure for (a) titanium oxide, (b) hafnium oxide (c) niobium oxide and (d) molybdenum oxide sputtered at 55 mm substrate-target distance and 800 mA sputter current in the oxidic mode. The dashed curves are simulations of the measured data by use of the Keller-Simons relation.

unequivocal proof of the differences in oxygen ion energies. In the foregoing discussions we correlate the ion energies which lead to stress generation, relaxation and resputtering with the cathode voltage. However before these events happen at the growing film, it should be noted that the sputtered and the cathode potential accelerated oxygen ions would first undergo thermalization along their path to the growing film as revealed in equation 2.11 This is principally dependent on pressure and any shift on energy due to this would be proportionately the same for all oxides since the pressure \( (p) \) and target-substrate \( (d) \) products is not significantly different. For incident ion of energy \( E \), the Davis model predicts that the exact stress generated in the growing film would also depend on the nature of the material. Beside the Young’s modulus there is also a characteristic excitation energy \( E_o \), which is contained in \( k \) of equation 2.11 and is the energy for the movement of an atom resulting from events in the collision cascade of an impinging ion. Such energy \( E_o \) would be different for the different oxides depending on the bond strengths, which we consider highest for group IV oxides. For the resputtering
phenomena, the sputter rate depends on the surface binding energy, which should show a similar dependence as the bond strength. In light of these considerations therefore, we can only make qualitative statements and conclusions as we have done. However, to completely account for the differences in structure and stress values, it is important to address the oxygen ion formation and the relative flux from the different targets.

The probability to form such ions will depend upon an activation barrier. With respect to the oxide layer formed at the target, this barrier is difficult to calculate due to coulombic attraction and band formation. However it can be reasonably correlated with the barrier depicted schematically in fig. 5.28 where the metal and the oxygen atom have to be ionized to form an ionic compound.

![Energy diagram](image)

Fig. 5.28. Energy levels involved in the electron transfer from metal, M, to oxygen, O, in the formation of the target oxide $M^+O^-$. $IP_M$ is the metal’s ionization potential and $EA_O$ is the oxygen’s electron affinity. The energy barrier [$IP_M - EA_O$] can be correlated with the ease or difficulty of oxygen ion formation upon sputtering of the oxidized solid target. Hence [$IP_M - EA_O$] is correlated with flux of oxygen ions incident on the growing film.
The activation barrier for this charge transfer is the ionization potential for the metal atom in the relevant oxidation state IPₑ, minus EA₀, the electron affinity of the oxygen atom. Therefore (IPₑ – EA₀) would be a measure of the difficulty or the ease of transferring an electron from the metal to the oxygen and hence for oxygen ion formation. Here we make the reasonable assumption that the differences between energy levels in the oxides stable structural phases are relatively low in comparison to the activation barrier for oxygen ion formation. A very similar diagram has been suggested by Cuomo et al. [29] to describe negative ion formation and backspattering in different metallic alloys while Kester and Messiah [30] have also shown the model to be accurate in compounds where only one element is changed, as is the case in the oxides considered here. In table 5.4 we correlate the activation energy (IPₑ – EA₀) for oxygen ion formation with the observed structure of the different sputtered oxides. We observe crystalline films where the activation barrier is low and amorphous films where the barrier is relatively high.

We have so far used the secondary electron emission yield to account for the target voltage, which we see as the energy source for sputtered ions in the foregoing model. However it may be argued that, the secondary electrons can get attached to the oxygen ions and hence lead to the increased ions. The flux of these ions would thus scale with the yield and hence highest for group IV oxides. However such ions would be formed in a region where the electron density is highest. For the DC discharge this would be in plasma. Such ions would therefore not have enough energy to lead to the different properties observed for the oxide films. Therefore, once again, only those ions formed at the target would have necessary energy leading to observed structures.

5.4.3 Role of other factors

Although the energetic ion bombardment of the growing film is advanced as the reason for the observed differences between the studied oxide structures, other factors may likely be involved and may as well dominate the film structure formation processes. Such an effect may be hydroxide formation, especially for films grown at low temperature and vacuum conditions as in this work. The crucial role of hydrogen in structure formation has been demonstrated through deposition of aluminium oxide [87].
In the report, Schneider et al. have demonstrated that the content of hydrogen increased with oxygen partial pressure in both the film and plasma stream. The hydrogen content was analyzed by nuclear resonance reaction in the films and time of flight mass spectroscopy in plasma. On the basis of their measurements and thermodynamics they suggested formation of aluminium oxide-hydroxide compound film, which they proposed to account for the large scatter in data reported in literature for refractive index and chemical stability of alumina films.

To try and separate these possible effects, hydrogen content in films of crystalline zirconia and amorphous niobia was determined. The method used was elastic recoil detection analysis (ERDA), which is a forward-scattering analysis and therefore capable of detecting the light hydrogen atoms. The results are as shown in fig. 5.29, where the atomic density is plotted against depth. In the spectra, the low atomic density shows the hydrogen content, followed by oxygen and the highest density is that of the metal. The amorphous niobium oxide films reveal an atomic density of 1.8 % hydrogen while the

![Graph showing atomic density vs depth](image)

**Fig. 5.29.** ERDA spectra on niobium and zirconium oxide films on Si (100). No significant difference in hydrogen content was observed between the amorphous niobium oxide film and crystalline zirconium oxide film. Observed film structures cannot therefore be attributed to effects of hydroxide formation.
crystalline zirconium oxide reveals 2.0 % hydrogen. Hence no significant difference in hydrogen content was found, which rules out hydroxide formation as a possible cause of the differences observed in structure.

5.4.4 Comparison with other findings

Finally these findings are compared with previously published data. Cuomo et al. [29] have already explained systematic trends in the backspattering rate of different metallic alloys by the ease of negative metal ion formation. Kester and Messiah [30] have validated the use of Cuomo model in titanate perovskites. They found the model to be most appropriate in compounds where only one element is changed at a time, which is similar to change of metallic element in the oxides analyzed in this case. As already mentioned elsewhere, Tominaga et al. [86] have demonstrated that when sputtering from an oxidized target that oxygen ions are sputtered and bombard the growing film at energies equivalent to the target potential. In another report, Tominaga and Kikuo [85] have also shown that the flux of these oxygen ions increases steeply at a flow corresponding to target oxidation, as earlier mentioned, for a zirconium target. Furthermore, the effect of energetic ions bombarding a growing film have been aptly demonstrated by Hultman et. al. [88]. They reported the change of film texture of a sputtered TiN film upon increasing the ion flux at low energies. They realized the (200) plane of sodium chloride structure of TiN, which is expected at high temperatures where adatom mobility is sufficient to form crystallites bounded by low-energy planes during nucleation and or liquid-like coalescence. At high energies for the ions, they showed the development of (111) surfaces, which have higher surface energy attributed to kinetic limitations. Alvisi et al. [89] have shown that the presence of impinging ions substantially modifies the thermodynamic condition for ion (Xe+) assisted hafnium oxide films deposition. Raising the transferred momentum caused the original crystalline structure to collapse into an amorphous state, which is probably due to damage induced by the ion bombardment.
5.4.5 Conclusion

The new finding of our study is that in reactive DC magnetron sputtering at room temperature the flux and energy of oxygen ions bombarding the growing film determine the film structure. Energy is provided by cathode voltage, which in turn is determined by the secondary electron emission yield. The oxygen ion flux is determined by the ease or difficulty of their being sputtered ionized from the oxidized target. This in turn depends on the metal’s ionization potential at the relevant oxidation state and oxygen electron affinity. A low flux of high energy ions for groups V and VI leads to amorphous films. The ion energies in this case are sufficient to produce thermal spikes to release stress and cause backspattering at low total pressure. The high flux at moderate energies leads to increased diffusion of depositing atoms and hence film crystallization and compressive stress build-up as observed for group IV. We observed no apparent backspattering for these films. This finding enables the development and improvement of routes towards optical coatings with tailored film structure also in cases where high substrate temperatures have to be avoided.
Chapter 6

Composition and formation mechanism of zirconium oxynitride films

6.1 Introduction

In previous chapter we sought a systematic understanding of the film structure formation for the DC reactively sputtered transition metal oxide films. In this chapter we now address their low growth rates and high surface roughness, which constitute their drawbacks for successful exploitation. To solve the problem of low growth rates, a common approach is to exploit sputtering within the transition from metallic to oxidic modes regime. This method requires investment in equipment for control and feedback so as to access this regime. An additional problem in DC reactive sputtering is arc formation, which may terminate the discharge. To overcome the arcing problem, expensive methods like pulsed sputtering have been explored. However, a simple and inexpensive solution to these problems can be obtained through addition of nitrogen to the argon –oxygen atmosphere during sputtering. This results in high growth rates and remarkable improvement in films properties.

For example in fig. 6.1 [2], the effects of substituting oxygen with nitrogen during sputtering of a zirconium target are illustrated. The deposition rate is observed to increase by a factor of three. The film density and refractive index also found to increase while film roughness remarkably comes down. In addition, glancing angle X-ray diffraction measurements on these films revealed retention of the same monoclinic ZrO$_2$ structure, fig. 6.2, despite a reasonably high percentage of nitrogen flow (50% of the reactive gases) into the chamber. There was also increased grain growth as shown by the XRD spectra peak intensities as summarized in fig. 6.3 for increasing nitrogen flow.
Fig. 6.1. The variation of the deposition rate, the film density, the refractive index and the film surface roughness with decreasing oxygen (lower x-axis) flow and increasing nitrogen flow (top x-axis) in the reactive dc magnetron sputtering of a zirconium target [2].

The aim in this chapter is to seek a plausible explanation to account for the remarkable differences in reported growth conditions and film properties. To achieve this goal the films composition and structure (from film powder) were therefore further examined so as to reveal nitrogen’s role, amount and lattice position. The amount of nitrogen incorporated is compared to thermochemical predictions and process simulations. While the thermochemical approach is best suited to describe equilibrium thermodynamics, the process simulations involve an expanded Berg-Larsson model for reactive sputtering, which addresses kinetics. The possible nitrogen lattice position was
Fig. 6.2 Grazing angle x-ray diffraction pattern for an incidence angle of 0.75 for (a) 3.5 scem oxygen flow, (b) zirconium oxynitride (O$_2$:N$_2$ = 50:50) and (c) 3.5 scem nitrogen flow [2]. There is retention of ZrO$_2$ structure at high nitrogen flows.
Fig. 6.3 Intensity of the (011) diffraction peak as a function of increasing nitrogen flow and decreasing oxygen flow [2]. The peak intensity increases with increasing nitrogen flow, an indication of improved film crystallinity.

analyzed by simulating the XRD spectra from film powder. Such XRD measurements and analyses would reveal any disturbance of the lattice as a result of nitrogen inclusion. The zirconium oxynitride films were prepared by reactive direct current magnetron sputtering of a zirconium target in an argon-oxygen-nitrogen atmosphere. Sputtering was performed at room temperature with a constant current of 900 mA and a total pressure of 0.8 Pa as determined by an ion gauge. The latter was achieved by regulating the Ar flow rate into the chamber while systematically changing the oxygen and the nitrogen flows. Initially 3.5 sccm oxygen flow only was let in, which resulted in fully oxidized films and then prepared the oxynitrides by replacing oxygen partially with nitrogen, but keeping the total flow of oxygen and nitrogen constant at 3.5 sccm. The nitrogen flow was thus increased from 0 to 3.5 sccm while oxygen was decreased from 3.5 to 0 sccm. The distance between the target and the substrate was kept at 70 mm.
6.2 Results and discussion

6.2.1 Composition

From Rutherford backscattering spectroscopy (RBS), the stoichiometry of the films has been obtained by reproducing the measured data with a simulation. Fig. 6.4 shows three such spectra where the films were produced at (a) 3.5 sccm oxygen, (b) 0.5 sccm oxygen and 3.0 sccm nitrogen and (c) 3.5 sccm nitrogen flows. The normalized yield is plotted against energy (upper axis) and the channel (lower axis).

The strong signal near 1.2 MeV in all the figures shows the presence of zirconium, while in figures 6.4(a) and (b) the oxygen signal is observed near 0.5 MeV. From figure 6.4(c) the nitrogen signal is detected at 0.45 MeV. The small atomic mass difference between nitrogen and oxygen makes a simultaneous quantitative analysis particularly difficult. Nevertheless, the nitrogen signal is seen to the left of that of oxygen, albeit with lower yield in the oxynitride film, fig. 6.4(b). In fig. 6.5 the data points summarize the results from all spectra analyzed.
Fig. 6.4 Typical RBS spectra of films produced at (a) 3.5 sccm oxygen flow (b) 0.5 sccm oxygen and 3.0 sccm nitrogen flows and (c) 3.5 sccm nitrogen flow. Notice in (b) the low nitrogen peak in despite the high nitrogen content in the sputter atmosphere.
Fig. 6.5. The variation of the oxygen (left y-axis) and the nitrogen (right y-axis) to metal ratio as function of increasing oxygen and decreasing nitrogen flow. The continuous curves have been produced by simulation with an extended Berg-Larsson model (see text for further details) and the dashed line represents predictions of thermochemistry as computed from the metal’s sputter rate and the partial pressures of the reactive gases. The inset shows the effect of temperature on predicted stoichiometries of the film.

Here the nitrogen (right y-axis) and the oxygen (left y-axis) to metal ratios are plotted against the corresponding oxygen (top x-axis) and nitrogen (bottom x-axis) flow. From the figure it is clear that there is very little nitrogen incorporation in the growing films below 2.25 sccm nitrogen flow (1.25 sccm oxygen flow). Below this nitrogen flow, the films grown are mainly oxidic. Above 2.25 sccm nitrogen flow, nitrogen incorporation increases rapidly. The films consist of stoichiometric zirconium nitride at 3.5 sccm nitrogen, when no oxygen was introduced in the chamber.

The results provide interesting observations because, at 1.75 sccm flow for both oxygen and nitrogen and as illustrated by figs. 6.1 - 6.3, the films are characterized by very remarkable properties. The density is almost equal to that of bulk zirconium oxide,
the roughness has decreased, the sputter rate has more than doubled and the crystal grains have increased in size. There was also an increase in refractive index and decrease in band gap [2], yet very little or no nitrogen is incorporated within the films up to 2.25 sccm N₂ flow, according to the RBS results. It is therefore imperative to understand the mechanism of film formation giving rise to these observations. We do this by first examining the predictions of equilibrium thermochemistry. Though reactive sputtering is a non-equilibrium reaction, thermodynamics provides a ‘vector’ along which the system tends to and therefore an important starting point in analysis.

6.2.2 Thermodynamic consideration

Tabulated thermochemistry data provide information about two zirconium oxides: ZrO and ZrO₂ and one zirconium nitride: ZrN. Due to lack of data on zirconium oxynitrides, we will assume that when sputtering metallic zirconium in a reactive process in an argon atmosphere containing oxygen and nitrogen, in principle any of those but no other compounds are produced, and we can think of the resulting film as a mixture of those compounds. What can thermodynamics tell us about the ratio of those constituents? At constant temperature and pressure the chemical reactions will proceed in such a way that the change in Gibbs free energy (ΔG) takes on its minimum value.

It is therefore instructive to examine the ΔG values of some basic reactions that might take place in the sputtering chamber. The high energetic argon-ions may dissociate some of the oxygen and nitrogen molecules such that although we offer molecular gases, reactions between zirconium atoms and atomic gas species are also possible. In table 6.1 we show possible reactions and the change in ΔG values for reactions taking place at a temperature of 300 K and 1 Pa pressure. The temperature dependencies of these values are also plotted in fig. 6.6. From these dependencies it can be deduced that, in the whole temperature range the formation of ZrO₂ reduces the Gibbs free energy the most, whereas the change in Gibbs energy for the formation of ZrO is relatively small.
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</table>

Table 6.1. Possible reactions and the change in Gibb’s free energy, $\Delta G$, for reactions taking place at a temperature of 300 K and 1 Pa pressure in KJ/mol and eV/mol [90].

Combining all the basic reactions given above leads to the following description of the reacting system:

$$a_1Zr + a_2O_2 + a_3O + a_4N_2 + a_5N \rightarrow b_1Zr + b_2ZrO_2 + b_3ZrO + b_4ZrN + b_5O_2$$
$$+ b_6O + b_7N_2 + b_8N$$

6.1
Fig. 6.6. The dependence of the change in Gibb’s free energy, $\Delta G$, on temperature for various possible reactions between zirconium sputtered in oxygen and nitrogen atmosphere [91]. In the whole temperature range the formation of ZrO$_2$ reduces the Gibbs free energy the most and hence the most favourable to be formed.

The coefficients $a_i$ are given by the process parameters. For example $a_1$ depends on the sputtering rate of Zr-atoms from the target while $a_2$, $a_3$, $a_4$, $a_5$ depend on the respective partial pressures of oxygen and nitrogen in the chamber. The coefficients $b_i$ on the right hand side of the reaction equation (2) are determined in a way to minimize $\Delta G$ in addition to being dependent on the choice of the coefficients $a_i$.

The foregoing implies that, if the number of oxygen atoms (either in the form of molecules or atoms) is double or more than that of Zr-atoms in the chamber, it is energetically most favorable to form only ZrO$_2$. If the number of O-atoms is not sufficiently high, the entire oxygen is consumed to form as much ZrO$_2$ as possible, while the remaining Zr-atoms form ZrN, provided that there is enough nitrogen in the chamber.

We conclude therefore that it is the flow (partial pressures) of oxygen and that of nitrogen during the sputtering process that will determine the stoichiometry of the generated films. The stoichiometry can be computed [92, 93] through polynomial fittings of stoichiometry, density and sputter rate as a function of flow rates to obtain the average
number of zirconium atoms arriving on the growing film. A value of 1 was assumed for the sticking coefficient of zirconium atoms. A further fitting of oxygen and nitrogen partial pressures as a function of the flow rates helps in estimating the average arrival rate of oxygen or nitrogen atoms per cm$^2$/s impinging on the film. In fig. 6.5, the dashed curves illustrate the results obtained by use of these inputs in a simple computer program. When this prediction and the RBS analyses (data points) are compared, we clearly observe nitrogen incorporation in the films earlier than energetically expected. This observation can be interpreted that, in the time scale of the reactions i.e. in the mean duration of time between arriving atoms, zirconium has no time to choose the perfect bonding partner, which would be oxygen in this case. The subsequent bonding of zirconium and nitrogen and eventual burial in the matrix before replacement leads to nitrogen incorporation. This would imply that beside energetics, reaction kinetics also play a significant role in film formation during the reactive sputtering of the oxynitrides. These processes may be schematically presented as shown in figure 6.7. The sample temperature does not have a very significant influence as illustrated by the inset of fig. 6.5 for reactions at 350 and 750 K. The figure reveals that, the flows at which nitrogen incorporation start, change by marginal values despite a 400 K temperature difference. The important role of kinetics in these reactions is addressed in more details in the next section.

6.2.3 Process Simulations

Most approaches to model reactive sputter deposition processes [58, 94-96] are based upon the principles introduced by Berg and Larsson [97, 98]. In this model the material fluxes of the metal and a reactive gas are analyzed. From the resulting rate equations the variation of partial pressure, deposition rate and stoichiometry with reactive gas flow rate can be calculated for a given ion current. This model has been successfully applied to various experiments [43, 99], adapted to new problems like deposition from alloy targets [94] and refined by including plasma chemistry [98], the behaviour of the cathode potential [58] and realistic pressure distributions [96]. In the present work, the influence of a second reactive gas has been considered to describe the stoichiometry of the deposited oxynitride films upon variation of oxygen and nitrogen flow rates.
Fig. 6.7 Schematic diagram showing the processes during zirconium oxynitride deposition. Due to the higher reactivity of oxygen it is mainly zirconium-oxygen bonds that are formed. For a formed zirconium-nitrogen bond it may be substituted with oxygen or get buried in the matrix leading to nitrogen incorporation than would be thermodynamically expected.

The first step is to determine the target coverage with oxide, \( \theta_i^O \) and nitride, \( \theta_i^N \). It is also necessary to introduce sticking coefficients \( \alpha_{Me}^O \) and \( \alpha_{Me}^N \) at metallic surfaces for oxygen and nitrogen, respectively. In addition, replacement coefficients \( \alpha_{MeN}^O \) and \( \alpha_{MeO}^N \) have to be considered, which describe the reaction of the metal nitride with oxygen and of the oxide with nitrogen, respectively. The surface concentration of metal oxide, \( MeO_{D^o} \) and nitride, \( MeO_{D^n} \) molecules with stoichiometry \( D^{O} \) and \( D^{N} \) per unit time can be written as:
\[
\frac{\partial (nD^O \theta^O)}{\partial t} = 2\alpha_{Me}^O F_{O_2} (1 - \theta^O - \theta^N) + 2\alpha_{MeN}^O \theta^N F_{O_2} - F_{MeO} \tag{6.2}
\]

\[
\frac{\partial (nD^N \theta^N)}{\partial t} = 2\alpha_{Me}^N F_{N_2} (1 - \theta^O - \theta^N) + 2\alpha_{MeN}^N \theta^O F_{N_2} - F_{MeN} \tag{6.3}
\]

where \(F_i\) represents the flux of species \(i\) and \(n\) the surface concentration of metal atoms. Since the formation of oxides is generally much more favorable than that of nitrides, \(\alpha_{MeO}^N = 0\) will be assumed, i.e. nitrogen cannot replace oxygen once the oxide has been formed. Solving of the equations (6.2, 6.3) for the steady state yields

\[
\tilde{\theta}_i^N = \frac{2\alpha_{Me}^N F_{N_2}}{2\alpha_{Me}^N F_{N_2} + jY_{MeN}} \tag{6.4}
\]

\[
\theta_i^N = \tilde{\theta}_i^N (1 - \theta_i^O) \tag{6.5}
\]

\[
\theta_i^O = \frac{2\alpha_{Me}^O F_{O_2} + 2(\alpha_{MeN}^O - \alpha_{Me}^O) F_{O_2} \tilde{\theta}_i^N}{2\alpha_{Me}^O F_{O_2} + 2(\alpha_{MeN}^O - \alpha_{Me}^O) F_{O_2} \tilde{\theta}_i^N + F_{MeO}} \tag{6.6}
\]

where \(\tilde{\theta}_i^N\) abbreviates the target nitride coverage acquired in the oxygen free atmosphere, \(j\) is the sputter current density and \(Y_{MeN}\) is the sputter yield for the nitride. In analogy to the target coverage (6.2, 6.3), the wall coverage \(\theta_i^O\) and \(\theta_i^N\) can be written as

\[
\frac{\partial (nD^O \theta^O_c)}{\partial t} = 2\alpha_{Me}^O F_{O_2} (1 - \theta^O_c - \theta^N_c) + 2\alpha_{MeN}^O F_{O_2} \theta^N_c \tag{6.7}
\]

\[+ F_{MeO} D^O \frac{A_i}{A_C} (1 - \theta^O_c) - (F_{Me} + F_{MeN}) D^O \frac{A_i}{A_C} \theta^O_c \]

\[
\frac{\partial (nD^N \theta^N_c)}{\partial t} = 2\alpha_{Me}^N F_{N_2} (1 - \theta^O_c - \theta^N_c) + F_{MeN} D^N \frac{A_i}{A_C} (1 - \theta^N_c) \tag{6.8}
\]

\[- (F_{Me} + F_{MeO}) D^N \frac{A_i}{A_C} \theta^N_c \]

where \(A_i\) and \(A_C\) are the active area of target and walls, respectively. The mass deposition rate \(r_m\) and the stoichiometries \(x_O\) and \(x_N\), for the deposited film, for oxygen and nitrogen respectively, now are
\[ r_m = 2\alpha_{Me}^O F_{O_2} (1 - \theta_c^O - \theta_c^N) m_O + 2\alpha_{Me}^O F_{N_2} (1 - \theta_c^O - \theta_c^N) m_N + 2\alpha_{MeN}^O F_{O_2} \theta_c^N m_O + (F_{Me} m_{Me} + F_{MeO} (m_{Me} + D^O m_O) + F_{MeN} (m_{Me} + D^N m_N)) \frac{A_t}{A_C} \]  

6.9

\[ x_O = \frac{2\alpha_{Me}^O F_{O_2} (1 - \theta_c^O - \theta_c^N) + 2\alpha_{MeN}^O F_{O_2} \theta_c^N + D^O F_{MeO} \frac{A_t}{A_C}}{(F_{MeO} + F_{MeN} + F_{Me}) \frac{A_t}{A_C}} \]  

6.10

\[ x_N = \frac{2\alpha_{Me}^N F_{N_2} (1 - \theta_c^O - \theta_c^N) + D^N F_{MeN} \frac{A_t}{A_C}}{(F_{MeO} + F_{MeN} + F_{Me}) \frac{A_t}{A_C}} \]  

6.11

The results of the simulation of the stoichiometry are depicted in figure 6.5 by the continuous curves. If the stoichiometry was governed by thermodynamics only, a complete oxidation of the film would be expected as long as sufficient oxygen is available, since the formation of an oxide is energetically more favorable as already discussed above and shown by the dashed curves. This case would be represented by \( \alpha_{MeN}^O = 1 \), i.e. whenever an oxygen molecule arrives at an already formed nitride, it should fully replace the nitrogen. The opposite case would be \( \alpha_{MeN}^O = 0 \), where no replacement is possible and the stoichiometry would be governed by the arrival rates of oxygen and nitrogen at the film. Neither of these two scenario fits to the composition data determined by RBS. The best agreement between measured and simulated data is found for \( \alpha_{MeN}^O \approx 0.1 \). This indicates that the stoichiometry of the films is determined by a combination of kinetics and energetics. For such small value of \( \alpha_{MeN}^O \), we conclude that kinetics dominate the reaction process though the energetics are also not negligible.

In figure 6.8 the continuous line depicts the simulation of the measured mass deposition rate (data points). The deposition rate is by a factor of three higher for the nitride than for the oxide since the binding energy, among other factors that affect the yield (equation 2.3), is much lower for the nitride. For example the diatomic bond strength between zirconium and oxygen compared to that zirconium and nitrogen is 1.91 against 1.40 eV, respectively [80]. For sputtering in a mixed nitrogen and oxygen atmosphere, the deposition rate is determined by the respective oxide and nitride target
coverages. This explains the increase in the mass deposition rate with increased nitrogen flow. There is therefore remarkably good agreement between the process simulations and experiment for both deposition rate and the film composition.

![Graph showing variation of mass deposition rate with oxygen and nitrogen flow](image)

Fig. 6.8. Variation of the mass deposition rate (data points), as a function of increasing oxygen and decreasing nitrogen for a sputter current of 900 mA. The continuous curve has been reproduced by simulation.

### 6.2.4 Structure investigations

The first X-ray diffraction pattern, shown in fig 6.9(a), was collected from a sample produced at 1.0 sccm O₂ and 2.5 sccm N₂, the chemical composition being close to ZrO₁.₇₅N₀.₁ as determined by RBS. The corresponding profile refinement was based on the experimentally known crystallographic parameters of pure phase ZrO₂ in the baddeleyite polymorph [100] and with the help of Fullprof program package [101]. The refinement of all parameters did not show any significant changes within the set of atomic positional and thermal parameters, thus only profile (pseudo Voigt function) and lattice parameters were eventually allowed to refine in order to acquire more reliable lattice constants. Fig. 6.9a shows that the whole pattern can be fully described using the ZrO₂ structure type, with slightly increased volume (see below). There are no additional reflections pointing towards a ZrO₂ superstructure or a new, structurally different phase.
For reasons of comparison, a fresh sample of pure ZrO$_2$ was made, too, and it is characterized by a lower crystallinity and a unit cell volume that is 1% smaller than the one of the oxynitride discussed before. The decrease in crystallinity of ZrO$_2$ is best described by the broadened half-width of the X-ray profile \( w = 0.78(1) \degree \) in contrast to the one of ZrO$_{1.75}$N$_{0.1}$ \( w = 0.53(1) \degree \); also, the background is higher for ZrO$_2$.

The second pattern, given in Fig. 6.9(b), corresponds to another sample made at 0.5 sccm O$_2$ and 3.0 sccm N$_2$, and the chemical composition corresponds to approx. ZrO$_{1.55}$N$_{0.2}$. The profile refinement went analogous to the preceding one and also yielded similar results, especially confirming the slightly increased volume of the unit cell and the sharper profile if compared to ZrO$_2$. However, there is one additional Bragg reflection at \( d = 2.96 \text{Å} \) which cannot be assigned to a known phase in Zr/O/N system. This \( d \)-value does not correspond to a reasonable metal-nonmetal interatomic distance, and it points to the formation of an unknown compound.

6.3 Conclusion

This chapter sought to examine the amount and the detailed lattice position of incorporated nitrogen as well as the formation mechanism of oxynitride films as oxygen is systematically replaced by nitrogen in the direct current reactive magnetron sputtering of zirconium target. The RBS results revealed nitrogen incorporation in the growing films above 64% of nitrogen flow. From thermochemistry predictions, this flow was relatively low since oxide formation is energetically more favorable. However, the RBS results were successfully reproduced by assuming a replacement coefficient of 0.1 for nitrogen by oxygen in a metal–nitrogen bond, in the extended Berg’s–Larsson model. This deviation from total nitrogen replacement by oxygen in the metal-nitrogen bond demonstrates a major role of kinetics in the reactively sputtered films. It is proposed that in the time scale involved between arrival of atoms, a formed metal – nitrogen bond and its subsequent burial by arriving atoms led to early nitrogen incorporation despite the oxygen’s high partial pressure and thermodynamic preference. We also simultaneously simulated the increased deposition rate. The increased rate was attributed to the increased target nitridation since binding energy is less for the nitride than for the oxide. The powder X-ray diffraction analyses indicate that, within the crystalline phase, nitrogen
FIG. 6.9. Rietveld refinement of a sample produced at (a) 1.0 sccm O$_2$ and 2.5 sccm N$_2$ and (b) 0.5 sccm O$_2$ and 3.0 sccm N$_2$ flows. The figures show measured (circles) and calculated (line) profiles, the position of the Bragg peaks, and the difference between observed and calculated intensities.
atoms occupy oxygen sites, therefore resulting in an almost unchanged ZrO$_2$ structure with a sevenfold metal-nonmetal coordination and interatomic distances around 2.04 – 2.27Å; the analytical data furthermore confirm the expected anionic (oxygen) voids upon replacing an O$^{2-}$ by an N$^{3-}$ anion in order to assure Zr tetravalency. The studies did not directly reveal the reason for increased density and the refractive index. However, the increased film crystallinity could have led to the increase in the films density, which was observed at no significant change in film stoichiometry. For the increased crystallinity some authors have attributed that to ‘catalytic effect’ of the impinging nitrogen atoms on the surface of the growing crystals. Transitory bonding of N atoms can reduce or saturate active sites increasing the surface mobility of the adatoms, and its subsequent evaporation and replacement by O atoms allow a continuous growth in the vertical direction leading to a highly oriented columnar structured film. Such a growing mechanism has been observed in nano-composite materials like ZrN/SiN$_x$ films where the driving force is the segregation of Si atoms [102,103]. And similarly the increased density can possibly account for the increase in the refractive index. These results and analyses lead to a significant understanding of some of the interesting properties observed from the reactively sputtered oxynitride films.
Chapter 7

Summary and Outlook

7.1 Summary

This work sought to address some of the fundamental processes encountered in reactive direct current magnetron sputtering that control film formation and structure. We had a particular focus on transition metal oxide and oxynitrides due to their interesting use as optical functional coatings. The understanding of these processes during preparation would lead to easier material characterization for the ever-increasing demand in industry and technology. Initially two illustrative cases in preparation and characterization of the metal oxide films upon varying the oxygen flow were presented. Through a number of analytical techniques, tantalum oxide (TaOx) samples prepared on glass and silicon at different oxygen flow rates and at constant current of 300 mA and pressure of 0.8 Pa were analyzed. To maintain constant current with increased oxygen flow, the cathode voltage increased quite rapidly to stabilize at 6 sccm oxygen flow. This flow as deduced from the variation of the mass deposition rate also marked complete target oxidation. The deposition rate was low in the oxidic mode due to the lower sputter yield of the oxide as a result of higher binding energy compared to the metal. Tantalum deposition showed no hysteresis effect, an obvious advantage due to the instabilities accompanying such an effect. Between 0 and 2 sccm oxygen lows the density decreased abruptly as oxygen was incorporated in the growing films. From the RBS analysis, films prepared up to 2 sccm were found to be understoichiometric. Stoichiometric films could be realized above 2 sccm oxygen flow within measurements errors. Films were also generally smooth and amorphous at all flows. They showed decreased compressive stress with increasing oxygen flow and the stress remained constant in the oxidic mode.

On the other hand, oxide film from the neighbouring hafnium metal showed, beside the similar general behaviour of the three sputter regions, quite distinct target
behaviour and film properties. There was a pronounced hysteresis effect only comparable to that of zirconium as reported elsewhere. The target showed quite an early oxidation at only 1.7 sccm oxygen flow accompanied with step like increases in both voltage and oxygen partial pressures. The deposition rate was quite low at only 0.1 nms⁻¹ in the oxidic mode. Remarkably, density decreased and stabilized at almost bulk hafnium oxide value upon reaching oxidized target state. Films between 0 and 1.7 sccm oxygen flows were smooth, amorphous and understoichiometric. In the oxidic regime films showed increased roughness possibly due to the crystalline nature as determined through X-ray diffraction measurements. Pictures from atomic force microscopy confirmed these changes in surface morphology. The deposition stress decreased with increasing oxygen flow and showed an abrupt increase upon target oxidation.

The deposition of these two oxides at exactly similar conditions provided a window for a need for further analysis to explain some of the fundamental differences observed in both discharge characteristics and films properties. In particular the increase in cathode voltages, which was different from the reported decrease upon target oxidation for some oxides and the differences in the magnitude between the different oxides required some plausible explanation. The resulting films’ structures, which could not be explained by the known growth laws required also to be accounted for. The increase in cathode voltage was attributed to decreased secondary electron emission yield and a procedure for the computation of these yields was provided, which forms first attempts beside the work of Ellmer et al. (who used similar approach) in quantifying the same for a number of transition metal oxides. Group IV oxides show a higher yield in comparison to V and VI oxides and hence a lower change in cathode voltage.

Through considering other similarly deposited transition metal oxide reports from groups IV, V and VI done in our research group, a model to account for the structure formation was advanced. The model attributes the film structure formation for reactively DC magnetron sputtered films at room temperature to sputtered oxygen ions bombarding the growing film. Due to a high activation barrier for oxygen ion formation in oxides of groups V and VI, only a low flux oxygen ion flux accelerated by very high cathode voltage is incident on the growing film. The high voltage is due to the lower secondary electron emission yield for these oxides as shown by the calculations. This energetic
bombardment of the growing film results in the amorphous structure. Further evidence for this energetic bombardment is derived from the evolution of the deposition stress and the occurrence of backspitting for these oxides. The high energy leads to stress relaxation through thermal spikes and erosion of the growing film. On the other hand, the low barrier characterizing oxides of group IV for oxygen ion formation implies a large incident flux of these ions. The ions are accelerated by moderate target voltages, which were correlated to higher secondary emission yields for group IV compared to groups V and VI. The ions therefore obtain moderate energies, which evidently lead to increased compressive stress and not high enough to cause backspitting. Beside testing out for hydroxides to rule out chemical influences on the resulting structure, the deposition stress and occurrence of backspitting provided unequivocal evidences for the concept of energetic particle bombardment and its effects on the properties of growing films especially film formation as discussed. This finding could be exploited for development and improvements of routes towards optical coatings with tailored properties where elevated substrate temperatures are a limitation.

Lastly in this work, the film formation mechanisms that lead to the remarkable properties observed in the growth of zirconium oxynitride films were also addressed. Through composition analysis the amount of nitrogen incorporation was analyzed. The exact nitrogen lattice position was examined through measurement and simulation of data obtained by X-ray diffraction on powder samples. A thermodynamic approach was used in trying to analyze the data. Though reactive sputtering is a non-equilibrium process, the thermochemistry analysis provided a vector along which the system may tend to. The deviation of the thermochemistry prediction from the measured data was corrected by use of process simulations, which accounts for those factors that make the system freeze in a non-equilibrium position. The composition results obtained by Rutherford backscattering were successfully reproduced by assuming a replacement coefficient of 0.1 of nitrogen by oxygen in a metal-nitrogen bond. Thermodynamics predicts total replacement and the low replacement coefficient therefore underlines the importance of kinetics in such reactions. A replacement coefficient of 0.1 has also been reported in the growth of titanium oxynitride [104]. The powder X-ray diffraction analyses showed that within the crystalline phase nitrogen may have occupied the site of oxygen resulting therefore in the
unchanged structure. The increased deposition rate was accounted for in terms of target coverage by oxide and nitride. The increased target nitride coverage for increased nitrogen flow led to increased rate due to higher sputter yield for nitride in comparison to oxide. Another interesting conclusion is on separation of target activities to those of the substrate. Whereas in oxide films deposition the target state also influenced film properties there is no such correlation in the oxynitride preparation. In deposition of the oxynitrvides there is delayed incorporation of nitrogen in the growing film despite increased target nitridation. As already mentioned this is deduced from the films growth rate (target dependent) and film composition (substrate reactions).

7.2 Outlook

Despite the great amount of literature that abounds for sputtering, it is evident from this work that a number of issues still remain unclear or largely not addressed at all. For example, as noted by other researchers and as addressed by this work the quantification of secondary electron emission yields for given deposition condition should lead to better simulations of reactive sputtering processes. It is hoped that the procedure can be further tested with other materials of experimentally known yields so as to generalize it for wide applications. The effect of sputtered ions on plasma (hence voltage) and therefore their contribution to electron sputter yield needs to be further addressed. However it has been pointed out that the ions undergo neutralization through some electron stripping processes.

From the analysis on structure formation and related evidence as obtained from the deposition stress and the occurrence of backspattering, the effects of energetic particle bombardment needs to be investigated more closely. It would thus be necessary to quantify of the flux and energy of the various species that may be found in sputter atmosphere and thus shed more light on the proposed mechanisms. An energy mass analyzer can help in deducing some of these quantities.

The analysis of the deposition stress was used as far as a pointer to the effects of energetic particle bombardment. Yet an atomistic understanding of the evolution of deposition stress in reactive sputtering has not been specifically addressed. Limited data exists on the same and more thorough work to identify treads and reasons is definitely
required. For example it would be interesting to know the roles of the heat of formation and bond strength in stress development for reactively sputtered films.

Remarkable film growth conditions and properties were observed upon partial substitution of oxygen as the reactive gas with nitrogen. This has opened an area of research that has also promising findings. It can for example be considered that this kind of sputtering has provided a situation where the film shows completely different properties to the existing target conditions. How this exactly takes place needs further work. In trying to simulate the composition of the films grown under such conditions, certain fit parameters like the replacement coefficient of nitrogen by oxygen in a formed metal-nitrogen bond was assumed and the value seems quite low in comparison to the thermodynamic expectation. A microscopic understanding of such values as parameters in the modeling is important. Other outstanding issues include: the role of nitrogen in such sputtering atmosphere i.e. does it inhibit or assist in occurrence of some film properties? Could nitrides also provide a source of energetic nitrogen ions that could result in different film properties?

A number of expensive sputter techniques like pulsed processes, radio and medium frequencies have been put forward to solve problems posed by direct current magnetron sputtering. These are for example arcing and low deposition rates as already mentioned elsewhere. Yet inexpensive alternatives as illustrated with nitrogen substitution can yield similar or even better results. Therefore other related systems like carbide and hydride sputtering or cosputtering should be investigated.
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Lebenslauf

**Persönliches**
Geburtsdatum / -ort 26.03.1967 / Kiambu
Nationalität Kenianisch
Familienstand Verheiratet

**Schulausbildung und Studium**
Schulausbildung
1974-1980 Kiairia primary school
1981-1984 Gathiru-ini secondary school
1985-1986 Njumbi high school

Schulabschluss 11/1986 Abitur (3 principals & a subsidiary)

Studium 05/1987 Immatrskulation an der Kenyatta Universität (Kenia) in den Studiengang: ‘Bachelor of Education Science’ mit Hauptfach Physik und Nebenfach Mathematik

1. Studienabschluss 08/1990 Bachelor of Education Science (Hons.) (note: Second class Hons.– Upper Division)

2. Studienabschluss 09/1997- Festkörperphysik an der Kenyatta Uni. (Master)
03/2000 Thema: ‘Multiple Thermal Switching Effect on the Stability of Vanadium Dioxide Films’ (Master of Science - M.Sc)

Deutschsprachkurs 04/2000- Goethe Institut Bremen (DSH prüfung – bestanden)
09/2000 Promotion seit 10/2000 Beginn der Doktorarbeit am I.Physikalischen Institut 1A der RWTH Aachen

**Berufserfahrung**
Lehrer 09/1990- Mombasa National Polytechnic (Physik und Mathematik)

Aachen, den 15.03.2004
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