DIFFUSION OF OXYGEN IN NANOSCALE-THIN TRANSITION METAL FILMS

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Diffusion of oxygen in nanoscale-thin transition metal films

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DISSERTATION

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*To my parents, who always supported me to follow my own path,
and to my grandmas, my examples of strength, independence and perseverance.*

List of Publications

This thesis is based on the following publications:

- Chapter 3: C. R. Stilhano Vilas Boas, A. A. Zameshin, J. M. Sturm, and F. Bijkerk, "The influence of oxygen on the neutralization of slow helium ions scattered from transition metals and aluminum surfaces" *Surf. Sci.* 700, 121680 (2020)
- Chapter 4: C. R. Stilhano Vilas Boas, J. M. Sturm, and F. Bijkerk, "Oxidation of metal thin films by atomic oxygen: A low energy ion scattering study" *J. Appl. Phys.* 126, 155301 (2019)
- Chapter 5: C. R. Stilhano Vilas Boas, W. T. E. van den Beld, J. M. Sturm, and F. Bijkerk, "Oxidation kinetics of transition metals exposed to molecular and atomic oxygen" *Submitted to Acta Materialia*
- Chapter 6: C. R. Stilhano Vilas Boas, J. M. Sturm, I. Milov, P. Phadke and F. Bijkerk, "Room temperature oxygen exchange and diffusion in nanometer-thick ZrO_2 and MoO_3 films" *Appl. Surf. Sci.* 550, 149384 (2021)

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1. A. A. Zameshin, A. E. Yakshin, J. M. Sturm, C. R. Stilhano Vilas Boas, and F. Bijkerk, "Limits of surface analysis of thin film compounds using Low Energy Ion Scattering" *arXiv:1809.01918 [cond-mat.mtrl-sci]* (2018)
2. P. Phadke, C. R. Stilhano Vilas Boas, J. M. Sturm, R. W. E. van de Kruijs, and F. Bijkerk, "Near-threshold, steady state interaction of oxygen ions with transition metals: Sputtering and radiation enhanced diffusion" *Appl. Surf. Sci.* 518, 146143 (2020)

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Introduction

In the modern world of nanoscale thin film systems, transition metal and metal oxide thin films are of paramount interest for a broad range of applications. These range from solid oxide fuel cells [1–3] to electronics [4–7], soft X-ray optics [8–13], and many other applications [14–16]. In all of these cases, the state of oxidation of the films is largely determining the performance of the devices. Given the continuous downscaling of device dimensions and, consequently, the film thickness, the role of the oxidation process calls for a detailed understanding and poses new challenges regarding both synthesis and improvement of the lifetime of devices. One of the main concerns during the life cycle of thin films is the proper control and maintenance of composition, as for both metallic and oxide films small changes in the composition of surface and near-surface regions may lead to dramatic differences in properties [17–21]. For thin metallic films, the growth of a nanometer-thick surface oxide might lead to detrimental changes in conductance in semiconductor devices [22] or reflectivity for extreme UV radiation by short-wavelength optics [10]. For oxides, changes in stoichiometry may directly influence the layer properties with respect to oxygen transport [2, 7, 9], an essential property for films applied in solid oxide fuel cells, or as insulating layers in microelectronics. In this scenario, the understanding of nanoscale oxidation and oxygen diffusion processes is a crucial topic, as the interaction between oxygen and thin films can act both as threat (decreasing the quality of metal films) or benefit (providing proper stoichiometry of oxides) in the design and lifetime improvement of technologically relevant systems.

Even though interaction of oxygen with thin films is a topic widely addressed in the literature [23–25], the fundamental knowledge on key physical aspects that dictate species migration and the relation between material properties and diffusion kinetics at low temperatures (< 500 K) still lacks. The research presented in this thesis aims to bridge this gap in the understanding of the interaction between oxygen and transition metal and transition metal oxide thin films. Furthermore, a deeper understanding on processes relevant for important techniques for oxidation and diffusion characterization in thin films is developed.

1.1 Oxidation of thin films

The majority of people associate the word “oxidation” uniquely to the reaction between oxygen and metal, and this association typically comes along with the image of “rusty” objects, such as represented by the degraded stranded boat shown in the left-hand image of Figure 1.1.

However, in chemical terminology, oxidation has a broader definition. Oxidation is defined as the change in valence state of an atom or ion such that it becomes more positively charged, as simplistically represented by Equation 1.1 :

with a hypothetical metal (Me) losing its n valence electrons [26]. Therefore, the step in an electrochemical reaction in which there is a loss of electrons from one chemical specie is classified as oxidation. Under this definition, not only the reaction between metal and oxygen, but also between metal or semiconductor and sulphur, nitrides or halides constitutes an oxidation process. As mentioned, however, the research

brought by this thesis focuses on the reaction between surfaces and oxygen.

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Figure 1.1: Oxidation under environmental conditions: stranded boat left for years under oceanic environment (left); 30 nm molybdenum thin film deposited on SiO₂ stored in a sample box for several months (right). From macro to nanoscale, the scaling does not alter the process.

Going back to Figure 1.1, these pictures represent two distinct classifications applied in the realm of oxidation science: corrosion and oxidation per se. **Corrosion** refers to the aggressive degradative process of oxidation given in solutions. In this process, elements like oxygen or acids dissolved in water react with metallic surfaces, leading to the formation of compounds and/or metallic ions, which typically detach from the material surface leading to the loss of mass by the metal [27]. In other words, corrosion is the destruction of a material by electrochemical reaction in a liquid environment. Typical examples of corrosive reactions are given by Equations 1.2 and 1.3, which respectively demonstrate the reaction between zinc and hydrogen in any acidic solution, and iron and oxygen in water:

Figure 1.2: Representation of Zn oxidation in acidic solution.

Equation 1.2 results in the formation of hydrogen gas and dissolved zinc ions (as schematized in Figure 1.2), and in Equation 1.3 the product Fe(OH)₃ is the rust observed in the ship of Figure 1.1. While corrosion is an extensively studied topic for applications such as engineering alloys and bulk metallic structures [28–31], the intersection between corrosion analysis and thin films has only been initiated more recently. Most of this work lies in the development of micro and nanometric films for protective coatings on various surfaces [9, 32, 33].

However, for the field of (nano)electronics, photovoltaics and lithography systems, where devices typically are only operated in dry gaseous atmosphere, such phenomenon is not an issue.

When processes are referred to as only *oxidation*, on the other hand, the reaction takes place in gaseous atmosphere and results in the growth of an oxide film on the metal surface. An example of this particular oxidation process is given by the right picture of Figure 1.1, which displays a thin molybdenum film stored in a sample box for several months. The contact between air and metal surface induced the growth of an oxide film, which is perceived by the gradient of colours in the sample (thin Mo films are grey metallic (reflective), while molybdenum oxides can display colours from light yellow to dark blue, depending on the oxide film thickness and oxidation state [34]). In this case, the oxide growth was induced by the interaction of the Mo surface and a mixture of components present in air, the most probable components to induce oxide growth being water vapour and oxygen. When water vapour is present in the oxidizing atmosphere, the oxidation is classified as “wet” and, evidently, “dry” oxidation refers to an environment with negligible H_2O content, typically a pure O_2 atmosphere. Defining the composition of the gaseous environment is an important sub-level of oxidation classification. The propensity for metal oxide formation in dry O_2 and aqueous environments is markedly different, as the latter typically leads to the formation of thicker oxide layers, even at lower temperatures [35–37]. One of the stronger hypothesis for the increase in oxide formation in the presence of water is connected to the water acting as a catalyst for O_2 dissociation, increasing the concentration of atomic oxygen species adsorbed at the metal surface [36]. The molecule dissociation and consequent formation of atomic oxygen species is a critical step in oxidation. This comes from the fact that oxide formation is necessarily a consequence of the reaction between the atomic species of metal and oxygen. As straightforward as this last affirmation may sound, elucidating all the factors controlling the initial stages of oxide formation and how external conditions may influence on the kinetics of oxide growth is not a simple task, and it is a topic that still requires (much) research.

Using the simplest case of an oxygen molecule impinging on a metal surface, we may characterize the initial phases of oxide formation as five (overlapping) stages [38]:

- (1) Oxygen **molecule impingement** from the gas phase onto the metal surface;
- (2) **Physical adsorption** of the impinging molecule onto the metal surface;
- (3) **Dissociative chemisorption** of the adsorbed oxygen molecules into atomic oxygen species;
- (4) **Place exchange** of the oxygen and the parent metal atoms to form a monolayer of oxide;
- (5) **Transport** of metal or oxygen atoms through the formed oxide and continuation of oxide formation.

All steps of oxide formation may be directly or indirectly influenced by environmental conditions, and consequently, significant modifications of the kinetics of oxide formation may occur. The classical way of changing oxidation kinetics is by

modifying the exposure temperature. Changes in temperature may, at the same time, change dissociation of oxidative species and the transport of ions through the grown oxide (phases 3 to 5) [26]. However, several reports in literature demonstrate that surface processes such as electron [39] or photon incidence [40, 41], or exposure of films to plasma [42] also influence the growth rate and final properties of the formed oxide, even though the in-depth temperature of the systems may not significantly change under such conditions.

In Chapters 4, 5 and 6 we explore the hypothesis of change in oxide growth kinetics at low temperatures by changes in step 3 – dissociative chemisorption. To that end, we mimic the increase in dissociative processes by directly exposing the samples to atomic oxygen species, and verify its influence on the oxidation of thin transition metal films (Chapters 4 and 5) and oxygen diffusion in transition metal oxide films (Chapter 6).

1.2 Kinetics of oxide growth

Still applying the model example of an oxygen molecule impinging on a metal surface, oxide formation can be simply written as:

Thermodynamically, the oxide will be formed when the oxygen chemical potential in the environment is greater than the oxygen partial pressure in equilibrium with the oxide. This equilibrium oxygen pressure is determined from the standard free energy of formation of the oxide as defined by Equation 1.5:

$$\Delta G^o = R T \ln p(O_2) \quad (1.5)$$

A standard way of verifying the tendency of oxide formation at a certain pressure and temperature is by means of Ellingham diagrams [43, 44]. However, one of limitations of these diagrams is that the plots do not take into account the kinetics of the oxidation reaction – going from surface reactions to in-depth oxide growth. Therefore, factors like a possible kinetic barrier that prevent oxide formation, the time required for oxide growth, together with how environmental conditions influence the growth rate are not considered by this approach. Furthermore, if formation of more than one oxide is possible (e.g. in an alloy), the diagrams cannot a priori tell us which oxide will preferentially form in a given environment. A kinetic analysis, on the other hand, provides such information. By understanding the kinetics of oxide growth one can estimate the lifetime of a metal to be used in a particular component at a specific temperature and environment, which is crucial for the engineering and design of devices.

Considering diffusion kinetics, fundamental analysis of metal oxidation can be dated back to the early 1900s. In their first publications, Tammann [45] and also Pilling and Bedworth [46] adopted a reasonable empirical approach which states that the diffusion rate of atoms at a time t , through an existing oxide film should be

inversely proportional to the oxide thickness (x). This approach went in accordance with Fick's first law for the diffusion of uncharged particles, and is defined as:

$$\frac{dx(t)}{dt} = \frac{k_p}{x(t)} \quad (1.6)$$

being k_p a proportionality constant defined by:

$$k_p = R D [C(0) - C(x)] \quad (1.7)$$

with D the diffusion coefficient, R the volume of oxide formed for each atom which diffuses through the film. Considering metal atoms as the diffusing species, $C(0)$ and $C(x)$ represent the concentrations of diffusing species near the metal-oxide and oxide-oxygen interface, respectively. Assuming a fixed-boundary concentration with a constant diffusion coefficient, and considering the initial oxide film thickness zero, Equation 1.6 is integrated to the well-known parabolic-growth law:

$$x^2 = 2k_p t \quad (1.8)$$

One key assumption of this approach, however, is that the oxide growth is generated by the diffusion of uncharged particles. Wagner was the first to propose that during oxide growth, the diffusing species are **charged particles**: ions (metal and oxygen) and electrons, with the flux of species governed by both the concentration gradient and an internally formed electric field [26, 47]. To guarantee the charge neutrality of the system, Wagner also proposed the local equilibrium between species, that is, the oxide growth would be governed by a number of local chemical reactions at each point in the film, each local reaction having a specific chemical potential for each reacting specie. This assumption culminated in the dependence of chemical potentials on oxide thickness, which led the developed diffusion equation impossible to be analytically solved. Details of this intricate equation development are clearly described in Ref. [26]. In short, the only condition in which it was possible to solve Wagner's equation was for conditions where the chemical parameters could be approximated to a constant value throughout the oxide, which reduced the complex formula to the previously developed parabolic-growth law.

Nevertheless, the concepts of charged particles diffusion and internal electric field introduced by Wagner turned out to be a groundbreaking statement in the development of oxidation kinetics theory, especially in the realm of thin film physics and low temperature processes.

1.2.1 Low temperature processes: the influence of the self-generated field

The parabolic-growth law (sometimes also referred to as Wagner's law, after the simplified conditions for Wagner's equations as described above) is generally sufficient to model oxide growth in the limit of high temperatures and thick oxide overlayers ($> 1 \mu\text{m}$). At high temperatures, the effect of gradient-driven oxidation surpasses any possible effect of internal electric fields (from Nernst-Einstein relation: $qaE \ll k_b T$ – with q the charge of ions, k_b the Boltzmann constant and

T the temperature), and a thick oxide can be approximated as a charge-neutral medium. Therefore, under such conditions, the species diffusion is simply modelled by a Fickian-type equation and, consequently, the parabolic-growth mode. However, this approximation is not valid for the limits of low temperatures and thin films. For these systems, the diffusion of ions by the available thermal energy is comparable or insignificant in relation to the internal electrical work, and especially for films lower than 100 nm, the system can no longer be taken as charge-neutral, as quantum effects might influence charge transfers in the system [48].

Cabrera and Mott [49] were the first to apply the concepts proposed by Wagner in a more elaborate way, setting the base for the development of the most accepted model for description of oxide growth in the limits of low temperature and thin films. The model of Cabrera and Mott expanded the idea of internal field generated by diffusion of charged particles, proposing that the interaction between adsorbed oxygen and the surface led to the formation of a contact potential, also termed the Mott-potential (V_M). This potential would be a consequence of the electron transfer from the metal Fermi level to the acceptor levels of adsorbed oxygen species by tunneling or thermionic emission [48, 50], with magnitude equal to the initial difference between the metal-vacuum work function (ϕ_0) and the oxygen O^- level (ϕ_L), as schematized in Figure 1.3 and described by Equation 4.4.

Figure 1.3: Schematics of an energy-level diagram for the metal-oxide-oxygen system: before (left) and during (right) oxidation.

The rise of the absolute value of V_M then results in the formation of an electric field, equal to $E_0 = -V_M/(x(t))$. This field lowers the energy barrier for ionic diffusion through the oxide film, enabling oxide growth. A logarithmic-type oxide film growth kinetics is typically followed in this case: a fast initial oxide film growth, followed by a transition to a slower regime and ending up with a limiting thickness, that can range from 0.5 to about 10 nm. An important contribution to the model was then developed by Fromhold and Cook [26, 48, 50], which introduced the coupled-currents approach, with still the general concept of CM theory remaining the same. The influence of the electric field on oxide growth kinetics in the low temperature regime is an unquestioned factor, having being applied for the

understanding of oxide growth kinetics of numerous systems [28, 51–56].

Despite the success of the CM model to describe the growth kinetics of metal oxidation at low temperatures, a general understanding of the factors that influence the driving forces of oxide growth and the limits to which the model is applicable were still somewhat obscure. In Chapters 4 and 5, the hypothesis of the influence of surface processes on oxide growth dynamics is respectively put forward and tested, with a detailed analysis demonstrating the main parameters that affect the field-driven oxide growth, and how metal and oxide properties can define the limits of model applicability.

1.2.2 Influence of self-generated field on oxygen diffusion in oxides

The electric field generated by adsorbed (electronegative) O species is not only important for oxide growth on metal thin films. In Chapter 6, we demonstrate how the action of highly electronegative species (such as atomic oxygen) can induce a similar field-induced diffusion in stoichiometric binary metal oxides.

The stages of oxygen-metal oxide interaction are quite similar to the ones observed for oxygen-metal interaction. Still following the model example with molecular oxygen, the molecule should *impinge*, *adsorb*, *dissociate* and follow to *transport* through the oxide lattice. The transport phase is initiated by oxygen exchange at the surface, and is followed by diffusion to sub-surface regions (along grain boundaries or bulk [57, 58]).

However, the understanding of the kinetics of oxygen diffusion in oxides at low temperatures is yet scarce. This lack of knowledge is mainly related to the typically low reactivity of stoichiometric stable binary oxide surfaces. With that, low temperatures typically do not provide the energy necessary to surpass the activation barrier of molecular dissociation, impeding the transport of species through the oxide lattice [59, 60]. However, as previously mentioned, in several applications metal oxides might be exposed to processes which change surface dissociation activity (such as exposure to ultraviolet light [61, 62] or energetic electrons [63, 64]) and, consequently, influence the kinetics of oxygen uptake and diffusion. By using principles similar to the ones developed by Cabrera and Mott [49], in Chapter 6 we identify the determining factors for the diffusion of oxygen in oxides at low temperatures, and demonstrate the critical effect of atomic oxygen in such processes. To the best of our knowledge, Chapter 6 shows the first experimental verification of oxygen diffusion in binary oxides at room temperature by means of isotope tracing analysis. Such verification was only possible due to the dedicated surface analysis cluster applied in this study.

1.3 Outline of the thesis

The proper analysis of oxide growth and diffusion first requires the preparation of a clean, uncontaminated surface before a well-defined quantity of adsorbate is brought into its contact, and a precise method for characterization is applied. These requirements are met in the Atomic layer Growth and Analysis (AG/A) cluster,

which was applied to obtain the results on which this thesis is based. In Chapter 2, details of the AG/A cluster, together with the principles behind the characterization techniques and methodology applied in the thesis are described in detail.

A key aspect of the work developed in this thesis was the use of Low Energy Ion Scattering (LEIS) for the characterization of oxide growth and oxygen exchange in oxides. To perform a robust analysis with LEIS, however, the neutralization efficiency of an ion scattered from a specific surface should be properly understood. The work presented in Chapter 3 is dedicated to the understanding of how oxide formation affects ion neutralization in the LEIS regime. To that end, the charge exchange of He^+ on metal and metal oxide samples of Mo, Hf, Ru, and Al (as well-studied reference) were investigated. The work described in this chapter demonstrates that quantitative surface characterization of transition metal compounds by LEIS requires proper choice of reference samples and highlights the importance of investigation of ion-surface charge-exchange mechanisms. This understanding enabled the determination of a proper procedure for quantitative characterization of transition metal compounds by LEIS, applied for acquiring of data for the studies presented in Chapters 4 and 6

In Chapter 4, a method for non-destructive determination of metal oxide film growth is established: LEIS static depth profiling (DP). By combining LEIS static DP and LEIS isotope tracing, a complete picture of the oxidation kinetics was obtained, and the mechanisms driving oxide growth on Ru, Ta, Zr and Mo thin films upon exposure to atomic oxygen at room temperature were determined. The evolution of oxide growth measured with LEIS static DP technique demonstrated a direct influence of the metal work function on oxide growth, manifesting a Cabrera-Mott oxidation mechanism. With the LEIS isotope exchange method, the reaction front of oxidation was determined as the oxygen/oxide interface, with the dominant diffusing species being metal interstitials or oxygen vacancies. It was also demonstrated that, at the analyzed conditions, the initial stages of oxidation are not influenced by the film structure.

Following this study on atomic oxygen exposure at room temperature, Chapter 5 contains a more thorough analysis of the oxidation of transition metal films (Hf, Ta, Mo and Ru) at temperatures ranging from 298 K to 473 K, upon the exposure to two different species: molecular oxygen and atomic oxygen. Using in-situ ellipsometry and in-vacuum X-ray photoelectron spectroscopy (XPS), the dynamics of oxide growth and the final stoichiometry after each exposure condition for the four metals were verified, and the particularities identified in each oxide growth mechanics explored. The analysis enabled the identification of two key factors for oxide growth at low temperatures: (i) the strong dependence of surface potential on reactive oxygen coverage; (ii) the interrelation between exposure conditions and crystalline oxide formation.

Chapter 6 comes back to LEIS isotope exchange analysis to verify the interaction between atomic oxygen and thin film oxides of zirconium (ZrO_2) and molybdenum (MoO_3), with various thicknesses and crystalline structures at room temperature. The developed analysis suggests that the formed isotope profiles are a consequence of the electric field formed upon chemisorption of reactive oxygen species in the oxide surface and associated accumulation of charged species near the surface (upward

1

band bending). This process induces penetration and increases diffusivity of oxygen in the oxides. Using modelling, the kinetic parameters were extracted and it was suggested how external processes (i.e. application of external field or increase in oxide defect density) may influence on the oxide diffusion in each system.

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2

Experimental

2.1 Thin film synthesis

All samples studied within this thesis were synthesized at the XUV Optics laboratory at the University of Twente. The details of systems and experimental procedures are described below.

2.2 Atomic layer Growth and Analysis (AG/A) cluster

The “real” surface of a solid under atmospheric pressure is far from the ideal system desirable for analysis of the intrinsic materials properties: all kinds of adsorbed particles – from strongly chemisorbed to weakly physisorbed – will be present at the surface. These contaminants might modify surface properties and consequently interfere in the interpretation of results in gas-solid interaction analysis. Therefore, when studying oxygen-solid reactions, the control of the sample surface state is often crucial for accurate data interpretation [1]. In addition, the employed low energy ion scattering (LEIS) requires a surface free of (hydrocarbon) contamination for proper analysis of the metal and oxygen surface concentration. Therefore, the use of a system which enables the synthesis, exposure and characterization in a controlled environment ensures the consistency of experiments and analysis. The AG/A cluster is an in-house designed ultra-high vacuum system (base pressure $< 10^{-9}$ mbar), which allows in-vacuum transfers between deposition, LEIS, X-ray spectroscopy (XPS), and oxygen exposure and analysis chamber (OEAC) with negligible surface contamination. A representation of the system is shown in Figure 2.1.

Figure 2.1: Schematics of the AG/A setup.

The deposition system in AG/A consists of a cylindrical UHV chamber with six magnetron sources located in symmetrical pairs. For the deposition of metal films, DC magnetron sputtering with argon as a working gas was applied. Oxides were deposited by reactive DC magnetron sputtering of the respective metallic target with a mixture of oxygen and argon, of which the proportion between both species

was established in order to guarantee the formation of stoichiometric oxides. A semi-automated script controls deposition parameters (introduction of sputter gas, positioning of samples, opening/closure of shutters and magnetron power), while sample transfer from the chamber to other parts of the cluster is performed manually (transfer time < 10 min).

2.2.1 Oxygen Exposure and Analysis Chamber (OEAC)

The Oxygen Exposure and Analysis Chamber (OEAC) consists of a complete system for the controlled exposure of samples to oxygen in both molecular and atomic state. Figure 2.2 shows in detail the configuration of the chamber. The author was involved from the design to full operation of the system. The OEAC is equipped with an annealing stage, for use with VG Scienta XL25 sample holder with built-in resistive heater, a Specs MPC-ECR mini plasma source and an ELG-2A-6373 Kimball Physics electron gun (not used for the work in this thesis). A Woollam M-2000 ellipsometer provides the possibility of in-situ characterization of samples during experiments. The sample stage can be adjusted in height to provide a correct alignment with respect to the light beam of the ellipsometer.

Figure 2.2: Oxygen Exposure and Analysis chamber (left) and detail of internal configuration (right).

A key component of this system is the Mini plasma source, which enables the generation of neutral atomic oxygen species. In this device, the plasma is physically confined inside the discharge chamber, not being in direct contact with the sample. For the plasma generation, the oxygen gas flow is set to the aimed value (1.4 sccm), resulting in a background O_2 pressure in the vacuum chamber of 1×10^{-4} mbar and a discharge current of 20 mA is applied. The formed plasma consists of dissociated molecular oxygen into various excited and neutral states. These generated species are directed towards the open end of the plasma chamber, which is closed with an alumina grid. The grid prevents ions from leaving the source, and a flow of neutral

atomic species with near thermal energy is directed towards the sample surface. The efficiency of the filtering of charged species (O ions and/or electrons) was verified by the analysis of sample currents between exposures to molecular (plasma off) and atomic (plasma on) oxygen. The detected current of charged species was five orders of magnitude lower than the specified flux of neutral O radicals at the applied experimental conditions, which is in the order of 1×10^{15} atoms/(cm²s) according to specifications of the supplier. The negligible charge current proves the suitability of this source as exposure facility for neutral atomic oxygen exposures.

For molecular oxygen exposures, same oxygen gas flow and pressure were used, with the plasma source switched off.

2.3 Ellipsometry

2.3.1 Ellipsometry setup

The spectroscopic ellipsometry (SE) measurements were made using a Woollam M-2000 spectroscopic ellipsometer mounted directly on flanges of the OEAC fitted with quartz viewports. The ellipsometer is equipped with a Xe light source, producing a beam footprint of ~ 8 mm length and ~ 4 mm width, adjusted to the middle of the sample. The angles of incidence and reflection of the light are 75° relative to the surface normal. The changes in value of the ellipsometric phase and amplitude parameters, Δ and Ψ , were measured in-situ in both static (before and after exposures) and dynamic (during exposures) mode. The static measurements were acquired at wavelength range of 245.8 – 1688.1 nm, with a step size of 0.8 nm. The dynamic data were acquired at time intervals of 2.48 s.

2.3.2 Ellipsometric modelling for oxide thickness analysis

Ellipsometry or spectroscopic ellipsometry (SE) is a well-known characterization technique based on the measurement of changes in polarization of light with known initial polarisation upon interaction with thin layers (few nm to μm thick) [2]. A schematic representation of an ellipsometry measurement as implemented in our equipment is shown in Figure 2.3 b. The polarization state of the incident light can be decomposed into two oscillatory components: π - (parallel) and σ - (perpendicular to the plane of incidence). The reflection coefficients of these components (r_σ and r_π) describe the complex reflectance ratio (ρ) of a sample, which can be translated into the so-called ellipsometry angles amplitude (Ψ) and phase (Δ) [2, 3]. This relation is expressed by Equation 2.1:

$$\rho = \frac{r_\pi}{r_\sigma} = \tan \Psi \cdot e^{i\Delta} \quad (2.1)$$

The SE analysis provides the values of Ψ and Δ for the measured system. However, these parameters cannot be directly converted into sample properties and a model analysis must be performed for the determination of characteristics such as layer thicknesses and optical constants. There are several approaches to constructing an ellipsometric model [2, 4–6]. For the analysis shown in this thesis, the applied method consisted of a multi-step approach with support characterization techniques

to minimize the number of variables during the model construction, and CompleteEASE software (Developed by J. A. Woollam Co., Ltd) was applied for model development.

Figure 2.3: a) Schematics of the model applied in ellipsometry. b) General principle of ellipsometry (adapted from Ref. [2]).

The first step for a proper characterization of thin layers via ellipsometry consisted of the substrate choice. Thermally oxidized Si with a ~ 300 nm thermal SiO₂ layer was chosen as substrate for all ellipsometry-related experiments. This substrate choice was based on three factors: the well-known optical properties of SiO₂/Si, allowing to apply an existing model for these layers; a higher precision on monitoring thickness changes of thin films deposited on a thicker underlayer [7]; the interface stability of metal/SiO₂ upon deposition and temperature increase, which decreases the uncertainties related to intermixed interfaces upon modelling [7, 8].

The second step for making an ellipsometry model relied on depositing single-layers of metal and stoichiometric oxide of three different thicknesses. These were then evaluated in-situ by ellipsometry and ex-situ by X-Ray reflectivity (immediately after removing from vacuum). The values of thickness obtained via XRR were used as input parameters in the ellipsometric model, and optical constants for each material were determined. For oxide layers, a Cauchy-type function was used to describe the refractive index n while the extinction coefficient k was set to zero over the entire concerned wavelength range or above UV range, depending on each oxide optical properties [9]. In the standard Cauchy layer, the software assumes an exponential decay shape for this k function [10]. For metals, a B-spline model was applied, using the parameters from the software database as starting reference. To guarantee a realistic model for the grown oxide film and overcome possible data misinterpretation induced by substoichiometric components, an extra layer of substoichiometric oxide was added between the stoichiometric oxide and the metal. The placement of this layer was based on Angle resolved X-ray Photoelectron Spectroscopy (AR-XPS) analysis (see Chapter 5). This extra layer was modelled by the effective-medium approach (EMA) using Maxwell-Garnett formulation, with the modelled stoichiometric oxide as matrix and modelled metal as “void” material [11]. It should be noted that this approach does not necessarily

provide a proper description of the optical properties of substoichiometric oxide, but serves as first order approximation.

Finally, these single-layer models were combined in the four-layered model schematized in the left of Figure 2.3. For all measurements performed in this thesis, the substrate and pristine metal layer were evaluated before oxygen exposure, increasing the reliability in fitting of the four-layer model. The quality of the ellipsometry numerical analysis was evaluated via the MSE (mean-squared error) between the experimental and calculated data. The MSE is directly calculated by CompleteEASE software, and it is defined as:

$$MSE = \sqrt{\frac{1}{3n - m} \sum_{i=1}^n \left[(N_{Ei} - N_{Gi})^2 + (C_{Ei} - C_{Gi})^2 + (S_{Ei} - S_{Gi})^2 \right]} \times 1000 \quad (2.2)$$

In Equation 2.2, n is the number of wavelengths, m is the number of variable parameters in the model, and $N = \cos(2\Psi)$, $C = \sin(2\Psi)\cos(\Delta)$ and $S = \sin(2\Psi)\sin(\Delta)$. The subscripts E and G correspond to measured and model generated data respectively. The lower is the value of MSE, the more accurately the simulating model describes the measured optical response of the sample. As the typical precision and accuracy of the measured ellipsometric data in terms of N , C and S is ~ 0.001 , a multiplicative factor of “1000” is included in the MSE definition [10]. This implies that an ideal model fit should have an MSE of ~ 1 . The static measurements kept a MSE of $12 < MSE < 25$, while the dynamic measurements had $15 < MSE < 40$. The higher values of MSE were related to oxides that showed higher degree of substoichiometry during growth (evaluated by X-Ray Photoelectron Spectroscopy).

2.4 Low energy ion scattering (LEIS)

2.4.1 LEIS setup

Low Energy Ion Scattering (LEIS) measurements in this thesis were performed using an IonTof GmbH Qtac¹⁰⁰ instrument. The system is equipped with an electron impact source, working with noble gas ions (He^+ , Ne^+ or Ar^+) at incident and scattering angles corresponding to 0° (normal to the surface of the sample) and 145° . The collection of scattered ions was performed by a double toroidal analyser (DTA) with azimuthal acceptance angle of 360° and acceptance angle $\delta\theta$ 2° around the scattering angle. The advantage of this DTA is the provided high sensitivity of the analysis, a key characteristic for this modern LEIS instrument. Whenever sample sputtering was performed, a separate ion gun at an angle of 59° with respect to the surface normal was used, with 500 eV Ar^+ ions.

In this thesis, all LEIS measurements were performed with He^+ gas, with energies ranging from 1 to 6 keV and currents of 1 to 4 nA. The spectra were collected for 60 - 240 seconds from a surface area of 1 mm^2 .

2.4.2 LEIS for characterization of oxide growth and oxygen diffusion

The accurate determination of thickness and composition is important for many applications, but can be complex for oxide thin films. Techniques such as Rutherford backscattering spectrometry (RBS) or secondary ion mass spectroscopy (SIMS) are insufficiently precise for measuring the formed oxide thickness due to limited resolution [12, 13]. Other techniques, such as Angle-resolved X-ray spectroscopy (AR-XPS), X-ray reflectivity (XRR), or ellipsometry provide more precise thickness determination [14, 15]. Nevertheless, these methods have certain limitations for characterizing details of the kinetics of oxide growth, as they are not suitable for the tracing of marker isotopes. In addition, the analysis of results requires complex modelling calculations for some of these methods.

Figure 2.4: Demonstration of LEIS signal evolution upon IEDP for a thin Zr^{16}O_2 film exposed to ^{18}O .

In this context, LEIS appears as a valuable tool for oxide characterization, since it provides a relatively fast and straightforward way to measure the atomic composition of the topmost layer - interesting for tracing isotopic species - and the sub-surface atomic distribution - valuable for oxide growth characterization. In this thesis, we cover these two different ways of applying LEIS: static depth profiling (static-DP) for sub-surface analysis, and sputter depth profiling (sputter-DP) in-depth analysis.

LEIS characterization is primarily based on the energy loss that a projectile (ion) of mass m_1 and primary energy E_0 suffers upon the collision to a target (atom) of mass m_2 . By considering the conservation of energy and momentum upon collision, the relation between final energy E_f and primary energy can be expressed according to Equation 2.3:

$$E_f = \left[\frac{\cos \theta + \sqrt{\left(\frac{m_2}{m_1}\right)^2 - \sin^2 \theta}}{1 + \frac{m_2}{m_1}} \right]^2 \cdot E_0 \quad (2.3)$$

where θ is the angle of the scattered ion [16]. With E_0 , m_1 and θ fixed for a specific experiment, the energy of the collected scattered ions thus represents a mass spectrum of the target atoms in the outer surface of the sample. Since LEIS combines identification of atomic mass (rather than chemical specie) with high surface sensitivity, this method is suitable for determining oxygen concentrations in Isotope Exchange Depth Profile (IEDP) analysis [13]. IEDP consists of the combination of oxide exposure to the isotope ^{18}O , followed by in-depth analysis by sputter depth profiling with an ion beam technique (LEIS in this case). Each sputter step is followed by the acquisition of a LEIS spectrum, resulting in a signal evolution as exemplified by Figure 2.4.

Figure 2.4 clearly shows the difference in position of peaks generated from the collision between He^+ and ^{16}O , ^{18}O or Zr atoms. In LEIS spectra, the integral area of each peak (S_i) will be proportional to the surface concentration of the respective element (N_i). Herewith, a simple way to perform quantitative analysis in LEIS is based on the proportionality between the integral areas for a measured surface and a reference sample [16]. For a multicomponent sample with $j_{\max}$ elements, the surface atomic fraction f of element i is calculated via Equation 2.4:

$$f_i^{\text{surf}} = \left[\sum_{j=1}^{j_{\max}} \frac{S_j}{S_i} \frac{S_i^{\text{ref}}}{S_j^{\text{ref}}} \frac{N_j^{\text{ref}}}{N_i^{\text{ref}}} \right]^{-1} \quad (2.4)$$

where S_i is the integral of the peak for element i in the measured sample, S_i^{ref} and N_i^{ref} are the integral area and surface atomic density of element i at the chosen reference surface.

However, this approach is only valid if the neutralization efficiency of an ion scattered from a specific surface atom does not depend on the surrounding species, that is, no matrix effect due to the different elements is present [17]. In Chapter 3 we explore the neutralization differences in He^+ ions scattered from metal and oxide surfaces. From this study we concluded that an oxide sample should be applied as reference for the correct quantitative analysis of isotopic concentration in oxides.

For the evaluation of oxides present in this thesis, S_x^{ref} (with $x = ^{18}\text{O}$, ^{16}O or metal) was obtained from stoichiometric polycrystalline metal oxide samples, with appropriate corrections of ^{18}O signal due to changes in sensitivity factor [18]. Values of N_{ref} were assumed to be equal to atomic bulk concentrations in the respective oxide. In Chapters 4 and 6 the use of LEIS sputter-DP in IEDP is explored, and the advantages of using a high-sensitivity technique for such analysis are highlighted.

Apart from outermost layer, in many cases sub-surface analysis is also provided by LEIS via the method of static depth profiling. Static-DP is based on the background (tail) signal in a LEIS spectrum, and is applicable for the determination of thickness of oxides grown on top of their respective metallic films [19]. The tail in

LEIS is formed by primary ions that penetrated into the solid, backscattered on a subsurface atom, and are emitted from the target in an ionized state into the direction of the analyser. Upon penetrating the solid, the projectile (ion or neutral at this stage) loses energy due to (inelastic) collision processes [16, 20]. This energy loss is described by:

$$\Delta E = \int \mathbf{S}(E, x) dx \quad (2.5)$$

with $\mathbf{S}$ the stopping power of ions by the target and x the travelled distance by the projectile.

Figure 2.5: a) Scattering configuration for a thin oxide on top of its respective metal. b) Demonstration of LEIS signal for a thin molybdenum oxide film on top of a molybdenum film.

Figure 2.5 can be used as a guide for the application of Equation 2.5 in calculating the top oxide thickness on a metal substrate. The scattering configuration for a thin oxide on top of the respective metal is schematized in Figure 2.5a. In the spectra of Figure 2.5b, E_{Me} is the energy corresponding to binary collisions between He^+ and the metal atoms present in the outermost layer. This peak is followed by an adjacent energy distribution at the low energy side, i.e. the tail spectra. This tail is formed by ions scattered from metal atoms in both oxide and metal. The change in atomic metal concentration between layers is translated in a change of intensities observed in the tail: the lower intensity part closer to the surface corresponds to the atomic density of metal atoms in the oxide, while the more intense part following corresponds to the atomic density in the metal. The effects of intermixing and interface roughness, together with straggling due to the stochastic nature of ion stopping, will result in a smooth intensity transition between regions with different compositions [21]. Therefore, the better way of modelling the interface is through an error function, as stated in Equation 4.2. Assuming the inflection

point of the fitted error function as an approximate limit between layers, and taking $\mathbf{S}$ as a constant dependent on the incident ion energy, the integration of Equation 2.5 becomes:

$$E_{Me} - E_i = \mathbf{S} \cdot d \left(\frac{1}{\cos \alpha} - \frac{1}{\cos(\alpha + \theta)} \right) \quad (2.6)$$

where d represents the oxide thickness, α and θ the incident and scattering angles, and E_i is the energy where the complementary error function inflection point is located, as shown in Figure 2.5 spectra. For the geometry of the LEIS system applied in this thesis ($\alpha = 0^\circ$ $\theta = 145^\circ$), Equation 2.6 is simplified to Equation 4.1, applied in Chapter 4 for determining the thickness of the grown oxide on metal upon atomic oxygen exposure. It is important to note that due to the stopping of ions by the target, the static-DP can provide information on thicknesses of $\lesssim 10$ nm, depending on the used primary energy and stopping power of the material under investigation. Therefore, when the characterization of thicker samples is needed, other techniques should be applied.

2.5 Further characterization techniques

Three other analytical techniques were applied in this thesis: X-Ray Photoelectron Spectroscopy (XPS), X-Ray Reflectivity (XRR) and X-Ray Diffractometry (XRD).

XPS was used to verify the chemical state of both reactively deposited oxides and oxides grown by oxygen exposure. In Chapter 5 this technique is particularly important for the verification of changes in oxide states formed upon exposure of metal films to different temperatures and oxygen species. In Chapter 3 we also apply XPS for measuring the valence band states of metals and oxides. All XPS analysis presented in this thesis were made using a Thermo Theta Probe spectrometer with a monochromatic Al-K α source.

Measurements of XRR and XRD were respectively performed for thickness and structure verification of samples. Both analysis were made with an Empyrean Cu-K diffractometer (Cu-K α radiation, 0.154 nm), manufactured by Malvern Panalytical. The XRD analysis was performed using in-plane grazing incidence (GIXRD) geometry at a fixed incident angle (higher than the critical angle).

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3

Influence of oxygen on the neutralization of He^+

Low energy ion scattering (LEIS) was employed for the analysis of thin films of Mo, Ru, Hf, Al and their oxides. Measurements with different He^+ energies showed that the characteristic velocities for neutralization of the transition metal atoms change when the metal binds with oxygen. However, such behaviour was not observed for aluminium. We suggest that the increased neutralization in oxidized Ru, Hf and Mo originates from the presence of the O 2s band. This band is in resonance with the He 1s level, which allows for a quasi-resonant neutralization mechanism (qRN). On the other hand, a decrease of the strong Auger neutralization for metallic Al upon oxidation may compensate for the increase in neutralization by qRN, leading to similar neutralization behaviour of Al in both states. We also demonstrate the dependence of characteristic velocity on oxygen content and discuss how this effect can be used to select proper reference samples for quantitative surface analysis by LEIS.

3.1 Introduction

The characterization of oxide surfaces has been a subject of considerable research effort for a long time. The control of surface composition is often crucial to achieving the optimal properties of oxide layers in the many areas in which these compounds can be applied, ranging from electrochemistry [1, 2] to catalysis [3, 4] and microelectronics [5]. In this context, Low Energy Ion Scattering (LEIS) appears as a valuable tool for quantitative analysis, since it provides relatively fast and straightforward way to measure the atomic composition of the topmost layer of materials [6]. This extremely low information depth arises from the strong neutralization of noble gas ions at the applied energy range (typically from 1 to 8 keV), and is unparalleled by other surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS) [7, 8] and secondary ion mass spectrometry (SIMS) [9–11], which are commonly applied in oxide characterization.

Quantification of surface composition by LEIS is usually done by comparing measured peak intensities of every element against peak intensities of reference samples, which can be either pure elements or their known compounds [6, 12]. However, this approach is only valid if the neutralization efficiency of an ion scattered from a specific surface atom does not depend on the surrounding species, that is, no matrix effect due to the different elements is present [13]. In the LEIS regime, many cases have been reported where matrix effects do not play a role in ion-surface interactions [6]. However, several studies have shown that neutralization processes can depend on the chemical environment for a range of compounds [14–17]. A matrix effect was suspected for NiO [18], but the conclusive proof would require characteristic velocity measurements, which were not performed. Bruckner et al. [19] verified the influence of surface oxygen on the reionization of He^+ scattered on sub-surface Ta and Zn, showing a significant dependence of the obtained yield on the presence of oxygen. These facts indicate that there is still a lack of knowledge on the role of oxygen on charge exchange in surface processes as studied by LEIS.

Recent characteristic velocity measurements on He^+ neutralization by elemental Ru and Ru in RuO_2 films were performed in our group [20], and He^+ neutralization by Ta in Ta_2O_5 were performed by Bruckner et al. [21]. These measurements provided a direct evidence of a matrix effect caused by oxygen. The present work aims to provide a deeper understanding of the role of oxygen in low energy ion neutralization, verifying the limitations of LEIS measurements and the reliability of obtained data for surface quantification of metal oxides. To that end, we investigated the charge exchange of He^+ on metal and metal oxide samples of transition metals Mo, Hf and Ru, and Al as well-studied reference material. The measurements with different He^+ energies show how oxide formation affects ion neutralization and may lead to misinterpretation of data when comparative analyses are performed. We further investigate ways to overcome these drawbacks and obtain a reliable quantitative analysis. This work shows that quantitative surface characterization of transition metal compounds by low energy ion scattering needs proper choice of reference samples and highlights the importance of investigation of ion-surface charge-exchange mechanisms.

3.2 Experimental

The experiments were performed in a home-designed ultra-high vacuum system at a base pressure of $\leq 1 \times 10^{-9}$ mbar, which allows for in-vacuum transfers between deposition, LEIS and XPS chambers with negligible accumulation of surface contamination. Films of typically 20 nm Mo, Hf, Ru, Al and respective oxides were deposited onto natively oxidized super-polished Si substrates by DC magnetron sputtering at room temperature. The working gas for metal deposition was argon, with an average pressure of 5×10^{-4} mbar. Oxides were obtained by reactively sputtering the respective metallic target with a mixture of oxygen and argon, for which the proportion between O_2 and Ar flow was adjusted in order to guarantee the formation of stoichiometric oxides.

To verify the chemical composition and measure the valence band states of the deposited films, XPS measurements were performed with a Thermo Theta Probe spectrometer using Al- $K\alpha$ radiation. LEIS measurements were performed in an ION-TOF GmbH Qtac¹⁰⁰ high sensitivity LEIS spectrometer. The system is equipped with a double toroidal electrostatic analyzer (DTA) and an electron impact source with ion incidence angle normal to the surface of the sample and scattering angle of 145° . The characteristic velocity for neutralization was measured by the analysis of deposited samples with a He^+ ion beam, with energies ranging from 1 up to 6 keV. The respective beam current was measured with a Faraday cup before each spectrum was acquired. Whenever sample sputtering was performed, Ar^+ ions with 500 eV energy and an average 100 nA current were applied at an angle of 59° with respect to the surface normal.

3.3 Results and discussion

3.3.1 Characteristic velocity calculation

In order to study He^+ neutralization of metal oxides, we applied an established method for the study of matrix effects in LEIS [14, 15, 22]. This method is based on the determination of the characteristic velocity of He^+ neutralization during scattering from surface atoms of given materials (v_c), a measure of the neutralization efficiency. In LEIS, the measured signal S_i (in counts per ion dose) from an element i is dependent on the fraction of scattered ions ($\mathbb{P}_i^+$, commonly referred to as ion fraction), the differential scattering cross section ($d\sigma_i$)/ $d\Omega$ of the element at the applied ion energy, the atomic surface concentration of the element N_i , ξ an instrumental factor including detector solid angle, detector efficiency and analyser transmission, and the surface roughness correction factor R , as expressed in Equation 3.1:

$$S_i = \frac{1}{e} \xi R \mathbb{P}_i^+ \frac{d\sigma_i}{d\Omega} N_i \quad (3.1)$$

where e is the electron charge. Different models for the ion fraction have been reported in literature over the years [6, 23–25]. In this work, we apply the Hagstrum model [25], in which the electron density is considered homogeneous and the neutralization rate is assumed to depend only on the distance between ion and surface.

According to this model, the ion fraction $\mathbb{P}_i^+$ can be written as:

$$\mathbb{P}_i^+ = \exp\left(-v_c \frac{1}{v}\right) \quad (3.2)$$

where $\frac{1}{v}$ represents inverse ion velocity, calculated as $\frac{1}{v_{0\perp}} + \frac{1}{v_{f\perp}}$, with $v_{0\perp}$ and $v_{f\perp}$ the surface normal components of the incoming and scattered ion velocities. By substituting Equation 3.2 in Equation 3.1, a linear relationship between the logarithm of LEIS signal divided by the cross section and the characteristic velocity is obtained [6, 14, 23]:

$$\ln\left(\frac{S_i}{d\sigma_i/d\Omega}\right) = -v_c \left(\frac{1}{v}\right) + \ln(C \times N_i) \quad (3.3)$$

with $C = \xi R/e$. In Equation 3.3, v_c serves as a slope and $\ln(C \times N_i)$ as a vertical offset of the line. Therefore, v_c and N_i of an element can be determined by plotting the $S_i/(d\sigma_i/d\Omega)$, measured at different energies, as a function of the inverse velocity. If no matrix effect is observed, for the same element at surfaces with different concentrations or composition, the plotted lines will present a fixed slope (v_c), but different vertical offsets.

3.3.2 LEIS measurements

Figure 3.1 displays measured LEIS spectra for Mo and MoO_3 films obtained with different He^+ beam energies.

Figure 3.1: Raw LEIS spectra for (a) Mo and (b) MoO_3 measured with different incoming He^+ energies

Figure 3.2 shows the inverse velocity plots for scattering on Mo, Ru, Hf and Al in elemental and oxide form, and O on the analyzed oxide surfaces. Table 3.1 and Table 3.2 show the characteristic velocities (v_c) of each system, extracted with the help of Equation 3.3. The data points presented for each set were obtained from measurements on (at least) three different samples.

Figure 3.2: Dependence of logarithmic normalized LEIS signal on the inverse velocity of He^+ ions, following Equation 3.3, for (a) Mo, (b) Ru, (c) Hf and (d) Al in metallic and oxide surfaces and (e) O in oxide surfaces. The least square fitted lines are shown for each set, together with the error corridor (shadowed area along the lines). The linear slope is v_c and the vertical offset is $\ln(C \times N_i)$. S_i is obtained in counts/nC and $\frac{d\sigma}{d\Omega} \delta\Omega$ (differential cross-section multiplied by analyser acceptance angle $\delta\Omega$ of 2°) in $\text{\AA}^2$.

The energy range on Figure 3.2 corresponds to those energies for which consistent measurements and a reliable fit of the binary collision peak were obtained. For

the metals, before each measurement, the surface was sputter cleaned until signal saturation of the metal peak, to exclude a possible influence of trace amounts of oxygen on the measurement results. In this work, the differential cross section was obtained by using the universal ZBL potential [26].

For clarification purposes, the characteristic velocity of He^+ neutralization by metal atoms in elemental form will be referred as v_c^{Me} (“Me” as a placeholder for the referred metal), and by metal atoms in the oxide surface as $v_c^{Me,Ox}$ (“Ox” as a placeholder for the referred oxide). The characteristic velocity of He^+ neutralization by oxygen in an oxide surfaces will be referred as $v_c^{O,Ox}$. It is clear from Table 3.1 that Mo, Ru and Hf exhibit differences in He^+ neutralization efficiency between metal and oxide surfaces. On the other hand, Al shows similar neutralization efficiency for both. On both Figure 3.2e and Table 3.2 it is possible to note the large scatter of data points between different oxide surfaces and, consequently, calculated v_c^O values. This scatter comes from the lower intensity of the oxygen peaks, a consequence of the lower elemental sensitivity factor of oxygen [27]. However, it is possible to note an oscillatory behaviour in Figure 3.2e, which is consistent between all four datasets. This behaviour strongly resembles the oscillatory behaviour of (quasi-)resonant charge transfer (qRCT) [15], a neutralization mechanism further described in Section 3.3.3. This observation directly contradicts the previous work of Tellez et al. [27], where the inverse velocity curves for both oxygen isotopes 16 and 18 are described by linear trends. Since no similarly strong oscillations can be assigned to the data from metals (Figures 3.2a-d), we can exclude the possibility of these oscillations being an artefact of our measurements.

Table 3.1: Characteristic velocities of He^+ neutralization by metal atoms extracted from the slope of least square fitted lines of data shown in Figures 3.2a-d

Element	$v_c^{Me}, 10^5 \text{ m/s}$	$v_c^{Me,Ox}, 10^5 \text{ m/s}$
Mo	0.65 ± 0.15	2.75 ± 0.12
Ru	0.71 ± 0.12	2.65 ± 0.12
Hf	1.60 ± 0.12	3.48 ± 0.12
Al	2.11 ± 0.11	2.18 ± 0.16

Table 3.2: Characteristic velocities of He^+ neutralization by oxygen atoms extracted from the slope of least square fitted lines of data shown in Figure 3.2e

Material	$v_c^{Me,Ox}, 10^5 \text{ m/s}$
MoO_3	0.55 ± 0.20
RuO_2	0.54 ± 0.16
HfO_2	1.15 ± 0.15
Al_2O_3	0.75 ± 0.25

To verify possible effects of sputtering and composition change on the characteristic velocities, characteristic velocity plots were also made based on sputter depth profiles. For each He^+ energy a sputter depth profile was made on a fresh spot of the sample. The data from those sputter depth profiles were then combined to

yield the characteristic velocity plots as a function of sputter ion fluence, and hence as a function of oxygen concentration. This approach was chosen due to the low stability of a surface at an intermediate oxidation state, which might have led to composition variation during the time when sequential measurements with different primary energies were made. This experiment was performed on two metals: Mo and Al, which were chosen as two cases where changes in characteristic velocity are present and absent, correspondingly. Sputter effects on oxide samples were verified by performing the described analysis on 20 nm reactively deposited oxides, with each sputter step removing an average of 0.3 to 0.5 nm of oxide. These samples served as a control group. The effect of composition change of oxygen versus metal was studied by analyzing samples of few nanometer oxide (2-3 nm) deposited on metal. For those samples, sputter depth profile was performed all the way through the oxide layer, with each sputter step removing an average of 0.3 to 0.5 nm of oxide, until saturation of the metal signal was obtained. An example of signal evolution at a specific primary energy and the inverse velocity plot obtained for each sputter step is shown in Figure 3.3a-h for all analyzed samples.

Figure 3.5 shows the obtained characteristic velocity as a function of sputtering fluence for both metal and oxygen atoms on each of the above mentioned samples. The inverse velocity plots related to oxygen signal are shown in Figures 3.4a-d.

Figures 3.3b and d and Figure 3.5a show that during the transition from Mo oxide to elemental Mo, v_c^{Mo} evolves in a non-monotonous way from a value similar to the one obtained for a thick deposited oxide to the one obtained for a deposited metal. At fluencies between 2.5 and $4 (\times 10^{16} cm^{-2})$, it is observed that v_c^{Mo} reaches lower values than the expected for elemental surfaces. This fact might be a consequence of the compositional changes upon sputtering, which implies in higher data scattering and imprecision of obtained v_c^{Mo} . On the other hand, sputtering does not influence the neutralization of samples that consist of bulk deposited MoO_3 . It should be noted that MoO_3 is particularly sensitive to reduction by preferential sputtering of oxygen. This explains the strong increase in Mo surface signal upon sputtering observed in Figure 3.3a. However, this apparent change in composition does not influence the value of v_c^{Mo, MoO_3} throughout the sputtering. For Al, the neutralization efficiency is constant throughout all sputter steps, both on thin oxide on metal and thick oxide films.

Lower elemental sensitivity factor of oxygen lowers the quality of the data presented in Figure 3.5b. Furthermore, due to preferential sputtering, the oxygen peak rapidly vanishes when approaching the metallic surface. Since each depth profile is performed at a different position on the sample, this fast change serves as additional source of uncertainty when combining measurements with the same fluence together. For these reasons, the interpretation of the data related to neutralization efficiency of O atoms with decrease of its surface concentration is not straightforward. Nevertheless, the obtained data indicates that the neutralization efficiency of oxygen is not systematically different between different thick deposited oxide surfaces. Further comments on the characteristic velocities of oxygen related to the transition from oxide to elemental Al and Mo are provided in Section 3.3.3.

Figure 3.3: Examples of LEIS spectra obtained during sputter depth profile at a specific primary energy (left) and the corresponding inverse velocity plots (right) for measurements with various primary energies at each sputter step. (a) MoO₃ analyzed with 3 keV He⁺ and (b) corresponding inverse velocity plots; (c) 2 nm MoO₃ on Mo analyzed with 3.2 keV He⁺ and (d) corresponding inverse velocity plots; (e) Al₂O₃ analyzed with 3 keV He⁺ and (f) inverse velocity plots; and (g) 2 nm Al₂O₃ on Al analyzed with 2.8 keV He⁺ and (h) inverse velocity plots. Each sputter step corresponds to a typical fluence of approximately 5×10^{15} ions/cm² of 0.5 keV Ar⁺, which removes an average of 0.3 to 0.5 nm of metal oxide. The grey arrow in the graphs indicates increasing sputter fluence.

Figure 3.4: Inverse velocity plots for oxygen atom related to data presented in Figure 3.3. (a) MoO₃; (b) MoO₃ on Mo; (c) Al₂O₃; (d) Al₂O₃ on Al. Each sputter step corresponds to a typical fluence of approximately 5×10^{15} ions/cm² of 0.5 keV Ar⁺, which removes an average of 0.3 to 0.5 nm of metal oxide. The grey arrow in the graphs indicates increasing sputter fluence.

Figure 3.5: Characteristic velocity against sputter fluence obtained for different systems, (a) metal atom (b) oxygen atom.

To recognize the origin of the (not) observed differences between neutralization of He^+ by metal atoms on oxide and metallic surfaces, charge-transfer processes between the projectile and the sample surface (target) must be explored.

3.3.3 Determination of neutralization mechanisms

In LEIS, the mechanisms of charge transfer between a target and a projectile can be divided into two main groups: resonant processes and Auger processes [28]. Auger processes are two-electron processes in which one electron is transferred to an unoccupied level of the projectile, and the energy of the system is conserved by the creation of surface excitations (electron-hole pair or plasmons) [29, 30]. Considering that in the LEIS regime the ion velocity is much smaller than the Fermi velocity of the metal electrons, Auger ionization processes are neglected in this study [30, 31]. In Auger neutralization (AN), one electron from the surface is transferred to a bound state (often the ground state) of the projectile, creating surface excitations. AN along the trajectory is possible at any primary projectile energy [32].

Resonant processes are single electron mechanisms in which electron tunnelling from a projectile to a target or vice versa takes place when the projectile energy level and a state or continuum of states of the solid are degenerate in energy. However, one must be aware that when a projectile is adjacent to a sample surface, the electronic levels of the projectile are modified with respect to the static levels at infinite distance: the projectile levels shift (and broaden) during the collision, a consequence of the interaction of the projectile states with the valence and core electrons of the target [6, 33]. In this context, the promotion of the He levels is important, as this may lead to an energy alignment not observed when the atom and target are in an unperturbed state [34, 35]. In the LEIS regime, resonant processes are classified according to the pair of energy levels of target and projectile between which the charge transfer takes place: collision-induced neutralization or reionization between the promoted ground state of the projectile (He 1s, in the present case) and lowest occupied states of target conduction band (metals) or valence band (non-metals) (CIN/CIR, also known as resonant neutralization/reionization in close collision); resonant neutralization from the highest occupied states of conduction band of a target to an excited state of a projectile (C-RN); (quasi-)resonant charge transfer between bound levels of a target and the ground state of the projectile (qRCT); and (quasi-)resonant neutralization from the valence band to the ground state of the projectile (VB-qRN) [6, 16, 20, 35–38].

The sum of all mechanisms present in the projectile-target interaction will determine the observed ion fraction related to a specific LEIS signal. For incident ion energy higher than the reionization threshold, we can describe the ion fraction from a single scattering ($\mathbb{P}^+$) by [35]:

$$\mathbb{P}^+ = P_{in}^+ \cdot (1 - P_{RN}) \cdot P_{out}^+ + (1 - P_{in}^+) \cdot P_{RI} \cdot P_{out}^+ \quad (3.4)$$

where P_{in}^+/P_{out}^+ is the probability of incident ions surviving AN in the way in/out; P_{RI} the reionization probability by resonant processes: CIR and, when present, reionization by qRCT. P_{RN} is the neutralization probability by resonant processes: CIN and, when present, C-RN, qRCT and VB-qRN. Therefore, the first term de-

scribes ions that remained charged along the entire trajectory and the second one describes ions that were initially neutralized, then reionized and survived AN on the way out.

CIN and CIR appear when the projectile energy exceeds a threshold, leading the projectile to be sufficiently close to the target. This proximity will promote the projectile ground state to align with the bottom of the target band (conduction or valence), enabling charge exchange [6, 14, 35, 39]. The presence of this process is clear due to the appearance of an angle in the slope of the energy dependence of the ion yield, as collision-induced neutralization is stronger than reionization [15, 40]. The chosen measurement range for the present experiments is above the reionization threshold (E_{th}) for the studied metals [38]. Therefore, the influence of such mechanism is expected to be constant for each ion-target combination.

As previously stated, C-RN occurs when an excited state of the projectile and conduction band of the target are in resonance. As explained in detail in the work of Cortenraad et al. [14], this phenomenon is expected for materials with work function values below 3.5 eV [14, 15]. Considering the work function values of both metallic and oxidized surfaces of the analyzed materials [41], such effect is not expected in this study.

The qRCT process is active for materials with an atomic level nearly resonant with the unperturbed He-1s level [6, 42, 43]. If the mismatch between these interacting levels is small, the transition rates for neutralization and reionization of qRCT will be similar. The charge state of the scattered He will oscillate between He^0 and He^+ as a function of interaction time with the target atom, which depends on the incident ion energy. Therefore, qRCT is the only mechanism to have an oscillatory ion velocity dependence [15, 44]. However, when He 1s is (quasi-) resonant with a band of energy states, or has a large mismatch with the interacting level, quasi-resonant neutralization (qRN) becomes much stronger than reionization, which leads to damping of the oscillations [43, 45]. These neutralization phenomena are then classified as VB-qRN and CIN. As previously mentioned, the latter occurs at very small distances between target nucleus and the projectile, at which the ground level of the projectile is promoted to energy high enough to become resonant with the valence band. On the other hand, VB-qRN occurs when the valence band is wide enough to become resonant with the ground state of the projectile even without strong level promotion, an effect first demonstrated for He neutralization by graphitic carbon [16]. Zameshin et al. [20] observed the presence of VB-qRN for carbides and borides, in particular a continuous change in characteristic velocity of Ru as a function of the amount of B it in the film. In the mentioned study, the wide valence band with low lying energy states (as low as 20 eV below Fermi level) for Ru-B and Ru-C films leads to VB-qRN, which was not observed in elemental Ru, as the lowest lying states of the metal are found at 7.5 eV. The difference in energy levels resulted in changes of neutralization efficiency, i.e. matrix effects for the compound surfaces. In the same paper, it was hypothesized that qRN-related matrix effects of a similar mechanism would appear in metal oxides, with a proof-of-principle experiment of Ru from an oxidized surface showing differences in characteristic velocities of Ru from a pristine surface. The resonance was considered to happen between He 1s and the O 2s levels present in the oxide [20].

To verify the energy distribution within the materials, XPS valence band analysis was performed. For this, a thin oxide (2 - 4 nm) on top of the corresponding elemental metal was analyzed by XPS. This thin oxide film was obtained by exposing the deposited metal to atomic oxygen at room temperature. With this method, a stoichiometric oxide with a known thickness is grown by controlling the oxygen exposure time [46]. Subsequently, the oxide was completely sputtered and the metallic surface was analyzed under the same conditions. Figure 3.6 displays the XPS valence band analysis for metallic and oxidized surfaces of the investigated elements. For HfO_2 , the valence band features are overwhelmed by the Hf 4f core levels that are present in this energy range. It is important to note that values obtained by XPS are relative to the Fermi level, while energy levels for He (ions) are usually referred from vacuum level. Assuming a typical value of work function of 4 eV, He 1s (with ionization energy of 24.6 eV) will be in resonance with a band as long as it presents energies close to 20.6 eV [20].

Figure 3.6: XPS valence band measurements of metal and oxide of (a) Mo (b) Ru and (c) Hf and (d) Al

In Figure 3.6 it is possible to note the contribution of the underlying metal layer to valence band spectra of the oxide thin films. This contribution is noted by the absence of a band gap in the spectra, while Al_2O_3 and MoO_3 are well-known dielectric materials with band gaps of values close to 6 eV [47, 48]. For RuO_2 no clear band gap of the oxide is expected, considering the metallic character of the oxide [49]. A contribution of the metal underlayer to the signal is also expected, as the thicknesses of the top oxide layer (about 1 nm) is smaller than the probing

depth of XPS, which typically lies between 3 and 10 nm [50–52].

It is noted that elemental Mo and Ru present the lowest lying valence band states between 5 and 7 eV, while for elemental Al electron emission is observed in two energy regions: one up to about 12 eV and another following from near 15 to 25 eV. In this case, the detected electrons of the second region do not correspond to primary electrons, but to electrons that are detected after undergoing inelastic scattering events in the solid, therefore presenting a lower kinetic energy [50]. These features are classified as bulk plasmons, and should not be taken into account as part of the valence band structure of aluminum [50, 52]. Therefore, for elemental Al, the lowest lying state is found around 12 eV. For the oxides of Mo, Ru and Al, a wide band in the region between 20 and to 25 eV is present, with respective peak position and full width at half maximum of 24.25 and 4 eV for Al_2O_3 , 21.4 and 3.8 eV for MoO_3 , and 21.2 and 3.5 eV for RuO_2 . This region corresponds to the O 2s band, also named the low valence band (LVB) region of oxides [50, 52–54].

As previously mentioned, a band will be resonant with He 1s if it lies in energies around 20 eV below Fermi level [20]. With this, considering the above mentioned observations and description of neutralization mechanisms, AN and CIN are expected to be the responsible for neutralization in the all analyzed samples, while oxides should present an extra effect related to the O 2s band. However, it is expected that the LVB region (O 2s) would lead to a neutralization phenomenon with characteristics that lie between the qRCT observed in lanthanides and the VB-qRN observed for graphitic carbon and borides [16, 17, 20, 45]. The contrast with VB-qRN comes from the fact that, in the present case, the resonance does not originate from an continuous valence band, but from an isolated band close in energy to He 1s. On the other hand, oscillations would not be expected as this isolated band relates to s-levels, which present wider radial distribution function of electron probability comparatively to the d-levels that lead to qRCT in lanthanides [15]. As reported by Tsuneyuki et al. [45], the width of the surface band strongly influences the final charge-transfer probability, with wide bands being responsible for more effective neutralization. This phenomenon occurs due to the diffusion of the hole (generated by the electron transfer from the band to the projectile) in the target band, impeding the oscillatory charge exchange process to continue. This aspect justifies the absence of oscillations in the inverse velocity plots for the oxides on Figure 3.2a-d. With this, we classify the neutralization phenomenon relative to O 2s as a quasi-resonant neutralization (q-RN).

It is known from literature that for transition metals like Pd [55] and Ag [56], AN appears as the dominant neutralization mechanism, with resonant processes being negligible. Therefore, the appearance of the O 2s band leads to an extra (non-local) neutralization process of He^+ for Ru, Hf and Mo. Considering Equation 3.4, the presence of two neutralization mechanisms of significant contribution results in a lower ion fraction and consequently higher characteristic velocity values [6] for the metals when bonded to oxygen. For HfO_2 , this neutralization appears to be even stronger, considering that HfO_2 shows the highest v_c values of all oxide surfaces, both for scattering on metal and oxygen atoms (Table 3.1 and Table 3.2). Unfortunately, the overlapping between Hf 4f and O 2s levels does not allow further investigation of this feature. However, the question still remains on why a similar

characteristic velocity is observed for Al in both metallic and oxide surfaces, considering a similar O 2s energy level as in the transition metals and the absence of resonant energy levels for Al metal.

Several studies have been developed presenting theoretical and experimental analysis of He^+ /Al neutralization on both metal and oxide surfaces [34, 35, 57–61]. In these studies, it is disclosed that both Auger and collision induced processes are important for the neutralization of ions by Al metal. However, for the scattering on aluminium oxide, a suppression of the Auger neutralization was found [13, 29, 32]. Therefore, the ion survival probability on the incoming and outgoing trajectories due to this mechanism is close to unity. In this case, if no other neutralization mechanism would be present, the total He^+ ion fraction scattered from Al_2O_3 would be higher than the one scattered from Al, which is not observed in neither this study, nor in previous studies presented in literature [13, 23]. We put forward a hypothesis that the appearance of neutralization by resonance with O 2s band increases neutralization probability by Al in Al_2O_3 , compensating the decrease in neutralization by suppression of Auger processes with Al oxidation. This would lead to similarly high neutralization probability and consequent high v_c^{Al} in both metal and oxide surfaces. Furthermore, the differences in AN between oxidized and elemental Al may also justify the observed increase in v_c^{O} values at the transition from Al_2O_3 to Al surface (green triangles in Figure 3.5b). This transition involves a gradual increase in Al content and consequent appearance of the AN channel. The non-local characteristic of this neutralization mechanism, implies that it can contribute to the neutralization for scattering on O atoms, resulting in an increase of v_c^{O} . This is not observed for v_c^{O} at the transition from MoO_3 to Mo as the AN remains the same in both surfaces.

3.4 Conclusions

In this work, a detailed analysis of the He^+ neutralization efficiency was performed for ion scattering on metal and metal oxide films of Ru, Mo, Hf and Al. The obtained results reveal the presence of a matrix effect for transition metals in oxidized state, which is absent for aluminium. By using XPS valence band analysis, we demonstrate that the increased neutralization in oxidized transition metals may originate from the presence of the wide O 2s band. This band is in resonance with the He 1s level, providing an extra neutralization mechanism: quasi-resonant neutralization (qRN). On the other hand, we suggest that the suppression of Auger neutralization and appearance of qRN for aluminum counter-balance each other and result in the same neutralization efficiency of He^+ for both elemental Al and Al oxide.

We also demonstrate that sputtering of pure metal or pure oxide surfaces does not interfere in the neutralization of He^+ , even for MoO_3 , which was found to be sensitive for removal of oxygen by preferential sputtering. This points out that by choosing a correct reference sample, quantification by LEIS analysis is not limited by matrix effects in metal oxides observed in this work. As long as the strength of involved neutralization mechanisms does not change, it is possible to choose proper reference samples for LEIS quantification of metals and metal oxides. Based on this work, we propose the following rule of thumb: when the sample of interest contains

the atoms of a given metal in its metallic form, a reference sample of a pure elemental metal should be used. On the other hand, if the sample of interest contains an oxide of a given metal, a pure metal oxide should be used as a reference. This way, the presence or absence of additional qRN mechanism associated with metal oxide will not affect the results.

This study indicates that the combined action of different mechanisms might lead to misinterpretation of the existence of matrix effects. This shows that there is still insufficient theoretical knowledge for description of the interaction mechanisms between ions and surfaces at low energies, highlighting the importance of further investigation of the topic.

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4

Low Energy Ion Scattering for oxidation analysis

In this study, we combine Low Energy Ion Scattering (LEIS) static and sputter depth profiles for characterization of the oxidation kinetics on Zr, Mo, Ru and Ta films of various thicknesses, following exposure to atomic oxygen at room temperature ($\sim 20^\circ\text{C}$). A method for non-destructive determination of the oxide growth rate via LEIS static depth profiling (static DP) is presented in detail. This method shows high sensitivity to the oxide thickness formed, and the results are in agreement with those obtained by X-ray reflectometry (XRR) and sputter depth profiling (sputter DP). Sequential exposures of oxygen isotopes in combination with LEIS sputter DP are applied to elucidate the growth mechanism of the oxide films. The results indicate that the oxidation kinetics at the applied experimental conditions is directly influenced by the metal work function, characterizing a Cabrera-Mott growth type. The maximum thickness of the formed oxide and oxide growth rate are in the order: $\text{Zr} \approx \text{Ta} > \text{Mo} > \text{Ru}$. The combining of analysis by LEIS static DP and isotope tracing sputter DP is decisive in the characterization of oxidation kinetics in the room temperature regime.

4.1 Introduction

The oxidation of surfaces represents a complex reaction scenario in the field of thin films. Regarding transition metals and their oxides, the understanding of such phenomena is paramount due to their wide range of applications. For ultra-thin metallic films applied in micro-electronics, catalysis, or soft x-ray optics, small changes in the composition of surface and near-surface regions may lead to dramatic differences in properties [1–5]. Regarding applications of thin oxide films, such as protective layers against corrosion [6], insulating layers in microelectronic [7], and in catalytic devices [8, 9], control of synthesis conditions is often crucial to achieve optimal properties of oxide layers. Therefore, both for preventing oxidation of materials and for synthesis of oxide films, knowledge on fundamental oxygen-solid interaction processes is required. For the past years, this importance has been recognized and significant attempts have been made to study the initial oxidation of clean and well-prepared surfaces under ultra-high vacuum (UHV) conditions both experimentally [10, 11] and theoretically [12, 13].

Nevertheless, accurate thickness and composition measurements on such thin films are not trivial. Techniques such as Rutherford backscattering spectrometry (RBS) or Secondary Ion Mass Spectroscopy (SIMS) are insufficiently precise for measuring the formed oxide thickness, due to limited resolution [14, 15]. Angle-resolved X-ray spectroscopy (AR-XPS), X-ray reflectivity (XRR) or ellipsometry provide more precise thickness determination. However, these methods cannot be used for characterizing details of the kinetics of oxide growth, as they are not suitable for the tracing of marker isotopes. In this scenario, Low Energy Ion Scattering (LEIS) appears to be a unique tool for oxidation kinetics analysis. LEIS is a characterization technique known for its monolayer information depth [15–17]. Allied to this, its ability to differentiate atomic mass makes it a valuable tool for isotopic tracing experiments, especially for O-18 tracing in oxides [15, 18]. A feature gaining more attention in the past years is the non-destructive in-depth analysis of sample composition, the so-called LEIS static depth profile (LEIS static DP). LEIS static DP is based on the analysis of signals from (mostly He^+) projectiles scattered by sub-surface atoms that are reionised upon leaving the sample. This process produces a background signal, commonly called tail, that provides in-depth distribution of a material. This tail starts at energies just below the LEIS characteristic binary collision peak and extends down to a low-energy threshold. This threshold varies depending on the ion-target combination, allowing a maximum probed depth of 5–10 nm [16]. This technique is classified as static depth profiling as it provides in-depth information without damaging the sample, provided that low ion doses are applied [15, 17].

In this work we demonstrate that the change in background signal following oxygen exposure can also be applied for thickness determination of the oxide grown on the metal. Therefore, LEIS provides the opportunity to understand oxide growth mechanisms and kinetics by correlating the precise atomic identification of the outermost layer with the grown oxide thickness determined by static DP. Thereby, precise information regarding oxygen-solid interaction processes in nanoscaled systems can be acquired. We analyse the oxidation kinetics of ultra-thin transition metal films

of Ru, Ta, Zr and Mo by applying LEIS static DP and LEIS isotope tracing techniques. The films were deposited via DC-magnetron sputtering and transferred to analysis and oxidation chambers without any break of vacuum. The data obtained by static DP was correlated to traditional thickness-determination techniques, such as XRR and sputter depth profiling. Isotope tracing provided information on the diffusing species during oxide growth, corroborating the oxidation mechanism of the analyzed metals. We provide a detailed analysis of the oxidation mechanism and growth kinetics of metals exposed to atomic oxygen, highlighting the differences in behaviour compared to oxidation by molecular oxygen, as obtained in previous experiments reported in the literature. Our results clearly demonstrate that the use of LEIS was critical in the understanding of important aspects previously neglected in experimental oxidation kinetics analysis.

4.2 Experimental set-up and methods

The experiments were performed in a home-designed ultrahigh vacuum system at a base pressure of $\leq 1 \times 10^{-9}$ mbar, which allows in-vacuum transfers between deposition (magnetron sputtering), characterization (LEIS) and oxygen exposure chambers with negligible surface contamination. Films of Zr, Ta, Mo and Ru were deposited onto natively oxidized super-polished Si substrates by DC magnetron sputtering at room temperature, using Ar as working gas with a deposition pressure of 5×10^{-4} mbar and growth rate of typically 0.05 nm/s. The films were exposed at room temperature to neutral atomic oxygen species (^{16}O or ^{18}O) generated by a Specs MPS-ECR mini plasma source. The exposure time ranged from 1 to 240 minutes, at an atomic oxygen flow in the order of 10^{15} atoms/cm²/s (partial pressure of $\times 10^{-4}$ mbar – background O_2), exposing the entire sample.

The evolution of oxide thickness with exposure time was obtained by LEIS static depth profiling (static DP), with details described in Section 4.2.1. LEIS measurements were performed in an ION-TOF GmbH Qtac¹⁰⁰ high sensitivity LEIS spectrometer, described in details elsewhere [19]. A He^+ ion beam at 3 keV energy and 2.5–3.5 nA current, measured before each spectra acquisition in a Faraday cup, was chosen for characterization. During the measurement, the beam is rastered over a 1×1 mm² area, with typical ion dose density of 2×10^{14} He^+ ions/cm², and total spectrum acquisition time of 3 minutes. Using these analysis parameters, the dose density is low enough to stay below the so-called quasi-static limit [20, 21], for which artifacts due to ion-induced sputtering and intermixing are negligible, since the probability that a detected ion interacted with a sample site damaged by other ions from the same measurement is negligible. For the isotope tracing experiments, the metals were consecutively exposed to atomic ^{16}O and ^{18}O (isotopic enrichment 98%) and analyzed by LEIS sputter depth profiling (sputter DP). In this analysis mode, each sputter step is followed by the acquisition of a LEIS spectrum under the same analysis conditions as previously described. Sputtering was done with a sputter gun attached to the LEIS chamber, positioned at 59° with respect to the sample's surface normal, applying a 0.5 keV Ar^+ beam at a 100 nA average current. The sputtered area was fixed at (2×2) mm². The sputtered depth was calculated by verifying the necessary ion dose (at the specified energy and current)

to sputter through a reference oxide sample with known thickness (determined by X-ray reflectometry).

To verify the accuracy of the oxide thickness determination via static DP, as well as the composition of the formed oxides, ex-situ X-ray reflectometry (XRR) was performed. The XRR measurements were obtained from a PANalytical Empyrean X-ray diffractometer (Cu-K α radiation, 0.154 nm).

4.2.1 Methodology of oxide thickness determination by LEIS static depth profiling

Static depth profiling is based on the analysis of the background (tail) signal in a LEIS spectrum. In LEIS, a sample is bombarded by noble gas ions with energies between 0.5 and 10 keV. In this energy regime, the projectiles are scattered from surface atoms almost exclusively by binary collisions, forming a characteristic Gaussian-shaped peak centred at an energy unique to each element [16]. If the referent element is present within the sample, a background (or tail) at the low energy side of its binary collision peak will emerge. The tail is formed by primary ions that penetrated into the solid, backscattered on a sub-surface atom and are emitted from the target in an ionized state into the direction of the analyser. Due to the low energy applied in LEIS, noble gas ions are neutralized on penetrating the sample [16, 19, 22, 23]. The formation of a tail will be determined by the finite probability of these scattered neutrals to be reionized upon leaving the sample, namely the reionization probability [16, 24, 25]. This feature depends on the energy of the backscattered particle (i.e. its velocity) and surface atomic composition of the sample. Figure 4.1 shows examples of spectra obtained with 3 keV He⁺ for both molybdenum and molybdenum oxide of different thicknesses. Only ions scattered from Mo can form the Mo related tail, as ions scattered from light elements lose more energy. Therefore, the ion yield energy in a LEIS tail signal depends both on the reionization probability and the distribution of the respective atoms inside the film [16, 19]. Due to the stopping of particles by the target, these backscattered ions will present an energy loss with respect to the energy of the surface peak. On average, the longer the path travelled by the particle through the solid, the larger the energy loss will be. This feature allows the energy scale of the spectra to be translated into a depth scale [17]. For the geometry of our experiment, the depth x from which a projectile is backscattered is found by the relation stated in Equation 4.1 [26, 27]:

$$x = \frac{E_p - E_x}{2.2 \cdot S} \quad (4.1)$$

where E_p is the energy of the relative binary collision peak, E_x a specific energy in the tail signal, S the stopping of ions by the target and the constant 2.2 is derived from the instrument geometry [23, 26, 28].

Assuming the reionization probability to be constant for a given surface, the intensity of the tail can be applied for determining the in-depth distribution of atoms, as, for example, in determining the interface transition between two materials of different compositions [10, 17, 24, 26]. The interface between two layers

is not expected to be sharp due to intermixing and interface roughness. In addition, straggling effects due to the stochastic nature of ion stopping will result in a smooth intensity transition between regions with different composition. Therefore, the interface can be modelled as an error function described in Equation 4.2 [26]:

$$c = \frac{1}{2} \left(1 - \operatorname{erf} \left(\frac{x - d}{\sqrt{2}\sigma} \right) \right) \quad (4.2)$$

where c is the atom fraction at a given depth x , d is the depth of the error function inflection point and σ is the width of the corresponding error function.

Figure 4.1: Demonstration of LEIS signals for 3, 4, 10 and 20 nm of molybdenum (top) and molybdenum oxide (bottom) deposited on a Si(100) substrate. E_{Me} represents the surface peak energy of the Mo metal and E_i the energy of the fitted error function inflection point (see Equation 4.2).

However, one must be aware that the height and width obtained by a fit according to Equation 4.2 are known to be affected by matrix and straggling effects, respectively. The straggling is a result of the statistical fluctuation of the energy-loss processes that particles are subjected to as they travel through matter [29]. The matrix effect appears from changes in neutralization according to changes in the composition of the material [16, 19, 30]. The position of the inflection point is the only variable minimally affected by artifacts [26]. Assuming the inflection point as an approximate limit between layers, its energy value can be applied as E_x in Equation 4.1 for determining the thickness of a sample. Examples of fitted inflection points are schematized in Figure 4.1 for Mo and MoO_3 . It is important

to note that in the case of Mo and MoO_3 , for thicknesses higher than 10 nm, the tail shape becomes constant. The limit for thickness detection emerges from the applied ion energy and stopping power of the target, this analysis can be typically applied for layer of thicknesses up to 10 nm [22, 27].

Figure 4.2: Demonstration of LEIS signal evolution with increasing of atomic O exposure time for Mo and parameters extracted from data for oxide thickness calculation.

Table 4.1: Values for metal surface peak energy (E_{Me}) and stopping power (S) applied for oxide thickness calculations. The stopping power values were obtained by SRIM software [30].

System	S [eV/nm]	E_{Me} [eV]
ZrO_2/Zr	68.7	2470
$\text{Ta}_2\text{O}_5/\text{Ta}$	65.4	2680
MoO_3/Mo	62.3	2490
RuO_2/Ru	69.8	2515

Analogously, the same procedure can be applied for determining the thickness of an oxide growing on a metal layer. Figure 4.2 shows an example of spectra evolution with oxide growth on a Mo film, where E_{Me} is the surface peak energy of the Mo metal. It is observed that, following oxygen exposure, there is a decrease of the background intensity just below E_{Me} . This change can be interpreted as a decrease of metal concentration, a consequence of oxide formation. Therefore, an error function can be fitted in this region and the grown oxide thickness extracted.

It should be noted that the metal concentration increases from oxide to metal, so the concentration will present an inverse profile compared to a metal film on a substrate with lighter atoms. Therefore, the complementary error function is applied in the fitting. With this, the energy value of the complementary error function inflection point, as schematized in Figure 4.2 by E_i , is applied in Equation 4.1, and the grown oxide thickness on a metal is calculated. There may be a very slight difference in surface peak areas of Mo and O for the different O exposure times shown in Figure 4.2. This is possibly related to hydrogen contamination during or after atomic O exposure. However, this does not influence the determination of the error function inflection point and metal surface peak position.

For the calculations performed in this paper, the stopping power was assumed to be equal to that of the bulk oxide form of each metal, as obtained from SRIM software [30]. The metal surface peak and inflection point energies were obtained by respectively fitting a Gaussian and a complementary error function in the respective spectrum regions with ION-TOF SurfaceLab 6 software. The values of the constants E_{Me} and S applied to calculations are listed in Table 4.1.

4.3 Results and discussion

Figure 4.3 shows the oxide thickness as a function of the exposure time obtained by static DP, XRR and LEIS sputter DP for 20 nm deposited metal films. Before exposure, the samples were analyzed with LEIS, confirming no prior oxygen adsorption. The error margin in the static DP arises from the uncertainty in stopping power that is inherent to the software calculation (3.5 percent of the obtained stopping for incident He^+ on targets) [30], the fitting of the error function to the spectrum and standard errors. Errors in sputter DP are also derived from standard errors.

After 240 min of exposure to atomic oxygen, the samples were removed from the vacuum system and directly analyzed by XRR. The layer thicknesses and associated errors were determined by fitting the obtained spectra with GenX software [31]. In GenX, a layered model of the structure is applied for simulating the reflection spectrum. For these samples, a pre-defined model was composed of the Si substrate and a SiO_2 layer of fixed thicknesses and densities, covered by the metal and a corresponding stoichiometric oxide layer. The free parameters applied in the GenX fitting were thickness and roughness of metal and oxide. Considering the oxide growth process [4, 13, 32–34] and to minimize the differences between simulations and experimental data, an intermediate higher density oxide layer, which can be considered as a substoichiometric oxide, had to be added to the model, resulting in structures as shown schematically in Figure 4.4 with the corresponding thicknesses specified in Table 4.1. Figure 4.3 plots the sum of both stoichiometric and high density oxide layers for XRR values.

Figure 4.3: Oxide thicknesses derived from static DP versus atomic oxygen exposure time for Ru (blue circles), Mo (yellow squares), Ta (green triangles) and Zr (red hexagons), from 1 to 240 min exposure (partial pressure of 1×10^{-4} mbar – background O_2). Reference measurement by XRR (black symbols at 240 min) and sputter profiles (open symbols) are given. The lines refer to the theoretically fitted growth curves based on the Cabrera-Mott inverse logarithm law. The shadowed area along the fits correspond to the fitting error.

Figure 4.4: Model applied for XRR spectra simulation on GenX software.

Table 4.2: LEIS static DP and XRR obtained oxide thicknesses for saturated samples (240 min exposure to atomic O). XRR values are obtained by a fit according to the model schematized in Figure 4.4.

System	Static DP [nm]	XRR	
		Stoich. Ox. [nm]	High Den. Ox. [nm]
Zr	5.1 ± 0.2	4.6 ± 0.2	0.9 ± 0.2
Ta	5.0 ± 0.2	3.6 ± 0.3	1.7 ± 0.3
Mo	3.6 ± 0.2	3.3 ± 0.3	0.6 ± 0.3
Ru	1.5 ± 0.1	1.3 ± 0.1	0.2 ± 0.1

It is important to note that the tail analysis by LEIS does not allow for the identification of the two-layer oxide, as observed with XRR. This limitation comes

from straggling effects suffered by scattered particles [28]. As mentioned in Section 4.2.1, the stochastic nature of the stopping of ions by the target will lead to a smooth intensity transition between regions of different composition, which does not allow a deconvolution of possible in-depth regions of oxide with different stoichiometry. However, the agreement between the total oxide thickness obtained by XRR, the oxygen-containing thickness obtained by sputter depth profiling and the results obtained by static DP validate the use of LEIS for determining metal film oxidation in a fast and non-destructive manner. This is particularly important for the analysis of nanometric films, in which small changes in the composition of surface and near-surface regions may lead to dramatic differences in properties from optical [1–3] to catalytic activity [34].

To further explore the application of the LEIS static DP technique, films of 3 nm Mo and 3 nm Zr were exposed to atomic oxygen and analyzed by the presented method. A reactively deposited 1.5 nm ZrO_2 film, with deposition parameters described in the work of Ribera et al. [35], deposited on 20 nm Zr also underwent the same experimental procedure. The resulting oxide growth profiles are shown in Figure 4.5.

Figure 4.5: LEIS static DP oxide thicknesses for 20 nm Zr; 1.5 nm sputter-deposited ZrO_2 on 20 nm Zr; 3 nm Zr; 20 nm Mo and 3 nm Mo, all exposed to atomic oxygen from 1 min up to 240 min (partial pressure of 1×10^{-4} mbar – background O_2). The dashed lines serve as guides to the eye.

In both Figures 4.3 and 4.5, the oxidation profiles derived from static DP show that all metals present a rapid initial oxide growth, followed by a decrease in rate with increasing exposure time, until a stable oxide thickness is reached (limiting oxide thickness). This oxidation behavior is in line with the theory initially derived by Cabrera and Mott [33] and further developed by Fromhold [36]. According to

this theory, the activation energy for diffusion is overcome by a surface-charge field, which arises as a result of an electrostatic potential, also termed the Mott-potential, between the Fermi level of the metal and the electron acceptor levels of adsorbed oxygen species [33, 36]. While the potential is constant, the formed field will be inversely proportional to the oxide thickness and, therefore, in the initial stages will have a high value. This strong electric field promotes positive metal ion diffusion to react with the adsorbed oxygen, forming a new metal oxide layer at the outer surface. For our exposure conditions at room temperature, the Nernst-Einstein relation ($qE_M a \ll kT$, with E_M the field, q the charge of ions, a the ionic jump distance (which is in the same order as the lattice parameter), k the Boltzmann constant and T the temperature) is not met. This means that diffusion of metal or oxygen ions by the available thermal energy is insignificant compared to the electrical work by the Mott-potential. Therefore the interpretation of oxide growth by the parabolic growth law is not applicable for our oxidation conditions [37, 38]. In Figure 4.3, superimposed on the experimental static-DP data points are the theoretically fitted growth curves based on the Cabrera-Mott inverse logarithm law [33, 39], which has the form:

$$\frac{1}{x} = A - B \ln(t) \quad (4.3)$$

where x is the oxide thickness, t is the exposure time and A and B are constants that contain material characteristics and temperature [33]. It is observed that the goodness of fit support the Cabrera-Mott mechanism of oxide growth for the analyzed regime.

To further elucidate the growth mechanism of the oxide films, isotope tracing LEIS sputter DP was applied. Figure 4.6 shows the relative concentrations of oxygen isotopes for 20 nm Zr, Ta and Mo consecutively exposed during 10 min to ^{16}O and 10 min to ^{18}O . These values are relative to the total concentration of oxygen found at the surface (i.e. the metal peak and possible other elements were not taken into account for quantification). This approach was followed in order to avoid misinterpretation related to preferential sputtering and a possible matrix effect present in transition metal oxides [25]. Ru tracer analysis was not possible due to rapid saturated oxide thickness (~ 1 min, Figure 4.3). The tracing of oxygen species shown in Figure 4.6 further confirmed the assumption of field-driven oxide formation. The profiles show that the exposure to ^{18}O leads to growth of additional oxide and possibly to an exchange of existing oxygen on the surface, a topic that will be further investigated in a following publication (Chapter 6). However, it is important to note that oxygen on the outermost layers of formed oxides correspond to the isotope specie to which the sample was last exposed to. Therefore, the predominant migrating defect type can be assumed to be oxygen vacancies or metal interstitials [33, 38].

One characteristic that should be noted is that the maximum oxide thicknesses achieved for exposures of thick metal films are considerably larger compared to those observed in natural oxidation; that is, the exposure of the metal to molecular oxygen at room temperature [3, 39, 40]. This can be explained by the absence of certain activated reaction steps for oxidation by atomic oxygen species. Oxida-

tion by molecular oxygen at room temperature is described by three main steps: physisorption, dissociative chemisorption and potential set up [40]. Dissociative chemisorption leads to the accumulation of electron-acceptor species on the surface, which induce the Mott-potential to arise and the consequent incorporation of oxygen in the metal [39, 41].

It has been shown both theoretically [41] and experimentally [39] that the concentration of oxygen species on a surface is determinant for the formation and maintenance of a Mott-field. In ambient O_2 , the potential set up may be kinetically hindered by the molecular dissociation step and the sticking probability of molecular oxygen on surfaces [40, 42, 43]. When atomic oxygen is used, these constraints do not exist. However, since these processes occur over a scale of just a few picoseconds, they are hardly observable through commonly available experimental techniques [43]. Simulations performed by Gibson et al. on Rh(111) indicated that atomic oxygen leads to the facile formation of a full-coverage and ordered (1×1) O monolayer, which induced O absorption into the bulk to proceed much more readily in comparison to oxidation by O_2 [44]. The exclusion of the dissociation step from the reaction pathway also leads to laterally uniform oxide growth, as defects and irregularities at atomic and nano scales, which act as active sites for molecular dissociation, do not interfere in the accumulation of oxygen at the surface [34, 40, 41, 45–47]. The results in Table 4.2 for XRR analysis of oxide-saturated films confirm the formation of an almost completely stoichiometric layer, including a small substoichiometric oxide interface. Therefore, direct use of atomic oxygen eliminates the dissociation step of O_2 as reaction barrier and maintains a high concentration of strong electron acceptors in the surface. In this way, oxide growth will only cease when the field generated by the Mott-potential is insufficient to act as driving force for ionic diffusion through the oxide. We now investigate whether the Mott-Cabrera theory [33] can be used to understand the differences in oxidation of the four analyzed metals. According to the theory, the Mott-potential is defined by Equation 4.4:

$$V_M = e^{-1} (\phi_0 - \phi_L) \quad (4.4)$$

where ϕ_0 is the metal work function, ϕ_L the difference between the vacuum potential and the Fermi level in the presence of adsorbed oxygen and e the elementary charge. The lower the metal work function, the more negative the formed potential will be, and the higher the generated field ($E_M = -V_M/L(t)$, where $L(t)$ is the grown oxide thickness as a function of time t). This field then lowers the energy barriers for initiation of ionic motion. With the oxide reaching a high $L(t)$ value, the field will no longer be effective in decreasing the diffusion barrier, causing the oxide thickening to stop.

Work function values for polycrystalline structures obtained from literature show the lowest values for Zr (4.0 eV) and Ta (4.0 eV), followed by Mo (4.3 eV) and Ru (4.7 eV). It is known that the value of the work function is dependent on the conditions of the surface (cleanliness, preferential plane), which is why measurements reported in the literature often cover a considerable range [48]. However, from the considered values, it is possible to correlate higher work function to a lower final oxide thickness as observed in this study.

Figure 4.6: In-depth concentration of oxygen isotopes relative to the total $^{16}\text{O} + ^{18}\text{O}$ surface oxygen concentration for (a) Mo exposed 10 min to ^{16}O and 10 min to ^{18}O , (b) Ta exposed 5 min to ^{16}O and 10 min to ^{18}O , and (c) Zr exposed during 10 min to ^{16}O and 10 min to ^{18}O . Samples were consecutively exposed to ^{16}O and ^{18}O with flow of 10^{15} atoms/cm²/s (partial pressure of 1×10^{-4} mbar – background O_2). The sputtered depth was calculated by verifying the necessary ion dose (at the specified energy and current) to sputter through a reference oxide sample with known thickness (determined by XRR). The gray dashed lines indicate the oxide thickness obtained by static DP.

In the case of oxidation by molecular oxygen, it is usually assumed that the cause of slow oxide film thickening is the formation of a closed oxide layer and consequent inhibition of electron transport from metal to adsorbed oxygen [5]. However, in our experiments it is seen that even when a closed layer of oxide is pre-deposited on the metal surface by reactive sputtering (1.5 nm ZrO_2 on 20 nm Zr in Figure 4.5), the exposure to atomic oxygen induces the continuation of oxide growth with a similar growth rate, until a similar saturation thickness is reached. This result indicates that when in Cabrera-Mott growth regime, it is not the formation of a closed oxide layer, but the lower concentration of atomic oxygen species on the surface that diminishes the field and leads to lower self-limited oxide growth. This decrease in concentration may come from oxide surfaces having both lower reactivity for O_2 bond dissociation and lower sticking probability of the molecule. This observation meets previous

studies where the influence of photon incidence [39, 41, 43], temperature and oxygen pressure [42] were verified for field-induced oxidation. Cai et al. [42] observed that the increase in O_2 surface concentration, by lowering of temperature or increase of partial pressure, lead to thickening of self-limited oxide on Al(111). For UV-assisted oxidation, the interaction of UV photons with O_2 or O_3 increases the molecule dissociation rate on oxide surfaces, and oxidation profiles analogous to the ones obtained in this paper are reached [39, 43]. These observations indicate that in cases where the presence of atomic oxygen species on the surface is not hindered by dissociation or adsorption, the obtained limiting oxide thickness will be directly related to the metal work function and, consequently, the formed Mott-field.

4.4 Conclusions

The use of atomic oxygen for room temperature oxidation of various transition metal films was studied by low energy ion scattering analysis. A methodology for determining the grown oxide thickness via LEIS static depth profiling has been presented in detail. This non-destructive method agreed well with results obtained by XRR and sputter-depth profiling. Exposures of 20 nm deposited metal films yielded a limiting oxide thickness of around 5 nm for Zr and Ta, while Mo and Ru formed an oxide thicknesses of ~ 3.5 nm and 1.5 nm, respectively.

With the use of isotope tracing coupled with LEIS sputter-depth profiling it was possible to verify that the reaction front is located on the oxygen/oxide surface in all analyzed samples, with the dominant diffusing species being the metal interstitials or oxygen vacancies. These findings indicate that the oxide formation observed on metals by atomic O exposure at room temperature is primarily driven by the value of the metal work function ($Zr \sim Ta < Mo < Ru$), which will determine the Mott-potential intensity. The use of LEIS in oxidation analysis was valuable in the understanding of oxidation kinetics and mechanisms in the room temperature regime.

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5

Oxidation kinetics of transition metals at low temperatures

In this work we analyse the oxidation of 30 nm polycrystalline transition metals films (Hf, Ta, Mo and Ru) at low temperatures (298 K to 473 K) upon the exposure to two different species: molecular oxygen and atomic oxygen. Using in-situ spectroscopic ellipsometry (SE) and in-vacuum X-ray photoelectron spectroscopy (XPS), we verify the oxide growth kinetics and the final stoichiometry after each exposure condition for the four metals, and explore the particularities present in each oxide growth mechanics. The temperature-dependent analysis enabled to experimentally obtain the dissociation energy of molecular oxygen at polycrystalline O covered surfaces. By applying the principles of coupled-currents and the Cabrera-Mott oxide growth mechanism, we extract values of the energy barrier for oxidation and the field formed in both oxygen molecule-metal and atom-metal interaction, exploring the differences between both exposure conditions. We demonstrate that in oxide growth at low temperatures two key points should be highlighted: (i) the strong dependence of surface potential on reactive oxygen coverage; (ii) the interrelation between exposure conditions and crystalline oxide formation. The obtained results and analysis contribute to the understanding of oxidation processes at low temperatures, advancing the knowledge required for the design and synthesis of thin metal and oxide films.

5.1 Introduction

Over the course of materials science development, metal oxidation kinetics have been an extensively studied topic both theoretically [1–6] and experimentally [7–13]. Due to the importance of preventing oxidation for applications such as engineering alloys and bulk metallic structures [14–17], much of these research efforts have focused on high-temperature oxidation and/or exposure at atmospheric pressure. This mostly follows from the fact that, for these applications, changes in the near-surface region (typically observed at low temperature oxidation) do not interfere in components performance. However, the downscaling of devices and consequent growth in metal and metal oxide thin-films use over the past decades has increased the awareness for low temperature oxide growth characterization [12, 18–21]. For thin metal films, the growth of a nanometre-thick surface oxide might lead to detrimental changes in properties, such as conductance [22] or reflectivity for extreme UV radiation [23], dramatically altering the performance of a device. On the other hand, controlled oxidation is a valuable asset in the synthesis of thin oxide films. In the field of solid oxide fuel cells, the oxidation states present in the oxide material and at the surface are closely related to its transport properties and surface exchange reactions [24]. For applications such as protective layers against corrosion [25] or as insulating layers in microelectronics [26], changes in the oxide film structure might directly influence the layer properties with respect to oxygen transport. Next to molecular oxygen exposure, metal films may also be exposed to atomic oxygen radical species, either deliberately (as part of an oxide film growth process) or unwanted (e.g. in plasma processes where oxygen containing gases are present as contaminant). In this context, the type of oxygen species to which the metal film is exposed to might also directly influence the growth rate and final properties of the formed oxide. Therefore, a thorough analysis, bringing mechanistic insights into the stages of molecular and atomic oxygen induced oxide growth, covering the differences in oxide composition and structure in the presence of activated oxygen species (such as atomic oxygen) at low temperatures is of great value.

In high-temperature oxidation, the transport of reactants (oxygen and metal) through the oxide layer is mainly accomplished by thermally activated diffusion, and the oxide growth process is in most cases well described by the parabolic rate law [17]. However, this theory is unable to explain the fast growth process observed at low temperatures. The most accepted model for description of low temperature oxidation was initially proposed by Cabrera and Mott [7] and further developed by Fromhold and Cook [27–29], and is usually referred to as the Cabrera-Mott (CM) model. The main principle of the CM model is based on the significant enhancement of ionic motion by a contact potential, also termed the Mott-potential (V_M). This potential is a consequence of the electron transfer from the metal Fermi level to the acceptor levels of adsorbed oxygen species by tunnelling or thermionic emission [27, 28]. The rise of V_M results in an electric field, which lowers the energy barrier for ionic diffusion through the oxide film, enabling oxide growth. Under the constraint that no net electric charge is transported through the oxide (coupled-currents approach [29]), the ion flux is equal to the difference between forward and reverse flux of electrons and this ion current is the rate-determining step of oxida-

tion. For temperatures where the Nernst-Einstein relation ($qV_M \ll k_bT$ – with q the charge of ions, k_b the Boltzmann constant and T the temperature) is not met, the diffusion of ions by the available thermal energy is insignificant compared to the electrical work by the Mott-potential. Since the rate of electron transport and field resulting from a constant Mott potential both decrease with increase of oxide thickness, the oxide growth ceases when the so-called limiting oxide thickness is reached.

Even though the CM model is widely employed to describe oxide film formation at low temperatures, the understanding of the factors that influence the formation, magnitude and preservation of the Mott potential – the critical value supporting oxide growth at low temperatures – is still somewhat fragmentary. Cai et al. demonstrated the dependence of V_M on pressure and temperature for aluminium exposed to molecular oxygen at temperatures from 223 K to 373 K [30, 31]. In another study of Al exposed to O_2 at temperatures between 373 K to 773 K by Jeurgens et al. [32], a change of V_M with temperature was not reported. However, the work demonstrated that at $T \geq 673$ K the limiting oxide growth behaviour is substituted by a continuous growth of oxide, hypothesized to be related to the transition from a potential-driven to a gradient-driven oxide growth. Lyapin et al. have reported a dependency of V_M with pressure for zirconium films exposed to O_2 at 298 K, and a transition similar to Al from potential to gradient-driven oxidation at $T \geq 573$ K [33]. In a complementary theoretical analysis by Sankaranarayanan and Ramanathan [34], it was indicated that the exposure of Zr to atomic oxygen can significantly increase values of V_M compared to molecular oxygen exposures. These studies provide concrete evidence on the influence of the oxidative environment on potential formation and consequent oxide growth for individual materials. However, to the best of our knowledge, a study that consistently verifies the influence of exposure factors to the formed potential, correlating the oxidation dynamics and driving mechanisms for different metals was not yet performed.

The present study focuses on the analysis of the growth kinetics, chemical composition and structure of a developing oxide in polycrystalline transition-metal films (Hf, Ta, Mo and Ru) exposed to molecular and atomic oxygen species in a low-temperature range (298 K to 473 K). The metal thin film deposition (magnetron sputtering), oxygen exposure (atomic and molecular species) and analysis (SE and XPS) were made without break of vacuum, enabling precise characterization of the oxide growth dynamics and final oxidation state without influence of surface contamination. With that, we were able to obtain quantitative information on critical physical processes that determine the oxide growth, such as the molecular oxygen dissociation energy and energy barrier of ionic motion. We verify the influence of exposure conditions (temperature and oxidative specie) to the derived value of the Mott-potential, correlating the observed results to the investigated metals properties. We further assess the particularities present for each metal oxidation condition, and explore the limits of the models adopted for describing the mechanisms that govern the oxide-film growth.

5.2 Experimental

The experiments were performed in a home-designed ultrahigh vacuum system with a base pressure of $\leq 1 \times 10^{-9}$ mbar, which allows in-vacuum transfers between deposition (magnetron sputtering), Oxygen Exposure and Analysis Chamber (OEAC) and X-ray spectroscopy (XPS) chamber with negligible surface contamination. The OEAC is equipped with an SE (Woollam M-2000), a Specs MPS-ECR mini plasma source and an annealing stage.

Films of 30 nm Hf, Ta, Mo and Ru were deposited onto substrates of thermally oxidized Si(100) (300 nm SiO₂ on Si, grown by dry oxidation at 1373 K) by DC magnetron sputtering at room temperature, using Ar as working gas with a deposition pressure of 5×10^{-4} mbar and growth rate of typically 0.05 nm/s. Oxide layers were grown at the OEAC as a function of exposure time (t) by heating the vacuum transferred samples to temperatures (T) of 298 K, 323 K, 373 K, 423 K or 473 K (± 5 K), and subsequent exposure to pure (99.999 vol%) molecular or neutral atomic oxygen at a partial pressure (p_{O_2}) of 1×10^{-4} mbar. Each exposure condition (combination of metal, oxidative specie and temperature) was applied to a freshly deposited metal film. The atomic species were generated by a Specs MPS-ECR mini plasma source, with atomic oxygen flux in the order of 10^{15} atoms/cm²/s. For the exposures, the sample was placed directly below the oxygen source, guaranteeing a homogeneous flow of species to the surface.

The evolution of oxide thickness was monitored by in-situ SE at an angle of incidence of 75° and a spectral range of 245.8 nm to 1688.1 nm. The oxide thickness was determined by a multi-layered model developed in CompleteEASE software (Developed by J. A. Woollam Co., Ltd). The procedure for model development is detailed in Section 5.2.1. After the end of exposure and cooling of the films, the grown oxides were in-vacuum transferred to a Thermo Theta Probe X-ray spectrometer, from which angle-resolved XPS (AR-XPS) measurements were acquired. The measurements were performed with monochromatic Al-K α (1486 eV) radiation and 400 μ m spot size, aligned at the centre of the sample. Angle resolved measurements were obtained for all samples, however, for brevity AR-XPS spectra reported in the present work are limited to a take-off angle of 34.25° (highest probing depth available). The collection and analysis of data was made by the use of Advantage software. The background of the spectra was subtracted according to Shirley model, and peak fitting was performed with a product of Gaussian and Lorentzian shapes. Quantification was based on Scofield sensitivity factors [35] and a model of uniform elemental distribution. Fits to XPS data were performed by first evaluating the spectra of as-deposited metals (also deposited and vacuum-transferred to XPS), in order to assess the metal peak position and asymmetry. The metal peak positions were fixed to the reference measurements for comparison of oxide composition between samples. Oxide peaks in the metal core levels of oxygen exposed samples were fit with a symmetric peak for oxides of Hf, Ta and Mo and an asymmetric peak for oxides of Ru [21, 36, 37]. Molybdenum and tantalum might exhibit multiple oxides with different stoichiometry within a small binding energy range [21, 36]. Therefore, when applicable, these oxide components were fit with a single peak with varying full-width half maximum (FWHM), and a larger FWHM was interpreted as a metal

containing stoichiometric and non-stoichiometric states [21].

The metals and grown oxides structures were verified by ex-situ X-ray diffraction (XRD), performed with a PANalytical Empyrean X-ray diffractometer (Cu-K α radiation, 0.154 nm), using in-plane grazing incidence XRD (GIXRD) geometry at a fixed incident angle (above the critical angle). The same diffractometer was used in X-ray reflectometry (XRR) mode for determination of reference metal and oxides thicknesses applied in the development of ellipsometry models.

5.2.1 Ellipsometry model development

For the analysis presented in this paper, the model development consisted of a multi-step approach with support characterization techniques to minimize the number of variables during the fitting. The base for the model consisted of characterization of single-layers of metal and stoichiometric oxide. The stoichiometric oxides were obtained by reactive direct current (DC) magnetron sputtering of the respective metallic target with a mixture of oxygen and argon. Three different thicknesses of these layers were deposited on SiO₂/Si substrates and evaluated in-situ by ellipsometry and ex-situ by X-Ray reflectivity (immediately after removing from vacuum). The values of thickness obtained via XRR were used as input parameters in the ellipsometric model, and optical constants for each material were determined.

For the substrate, an existing model (JAW for thermally oxidized Si) was applied. For oxide layers, a Cauchy-type function was used to describe the refractive index n while the extinction coefficient k was set to zero over the entire concerned wavelength range (for Hf oxide) or above UV range (for oxides of Ru, Ta and Mo) [38]. For the standard Cauchy layer, the software assumes an exponential decay shape for the k function. For metals, a B-spline model was applied, using the parameters from the software database as a starting reference. To guarantee a realistic model for the grown oxide film and overcome possible data misinterpretation induced by substoichiometric components, an extra layer of substoichiometric oxide was added between the stoichiometric oxide and the metal. The placement of this layer was based on AR-XPS analysis (see Section 5.3.2). This extra layer was modelled by the effective-medium approach (EMA) using Maxwell-Garnett formulation, with the modelled stoichiometric oxide as matrix and modelled metal as “void” material [39]. It should be noted that this approach does not necessarily provide a proper description of the optical properties of substoichiometric oxide, but serves as first order approximation. Finally, these single-layer models were combined for the fitting of oxide layers grown on metals. For all measurements, the substrate and pristine metal layer were evaluated before oxygen exposure, increasing the reliability in fitting of the multi-layered model.

5.3 Results and discussion

5.3.1 Oxide growth kinetics by ellipsometry

We begin our analysis by focusing on the general evolution of oxide growth as a function of oxidation time for Hf, Mo, Ta and Ru under exposure to molecular or atomic oxygen, presented in Figures 5.1a-h. It is important to observe the difference in the vertical scale – oxide thickness – between figures. The oxide thickness data was extracted by fitting obtained in-situ SE spectra following the procedure described in Section 5.2.1, with the plotted values corresponding to the sum of the two modelled oxide layers (stoichiometric and substoichiometric). A general trend of growth is shared among all metals, where it is interesting to note that some peculiarities are present in each combination of metal and oxidative specie.

According to the CM theory, at low temperatures, the oxide growth is expected to be initiated by a fast formation of a closed oxide layer (first phase of oxide growth). The formation of a stable film allows a voltage (V_M) to build up across the oxide, and consequent growth of oxide by a field-induced mechanism (second phase). With increasing oxide thickness the field will become too weak to assist diffusion and the oxide growth ceases [7, 29]. It is reasonable to assume that a monolayer of oxide has an average thickness of 0.3 nm [40]. As Mo exposed to O_2 at $T \leq 373$ K and Ru exposed to O_2 at $T = 323$ K show a maximum oxide thickness equal to or less than about 1 monolayer of oxide, we can conclude that the oxide formation under these conditions is restricted to the first phase of oxide growth, and therefore no CM-field is generated. The limiting oxide is considered to be reached when the oxide growth rate has reduced to about one “oxide” monolayer per 10^5 s ($\sim 10^{-15}$ m/s) [7, 32]. According to this rule, we observe a self-limiting behaviour of oxide film growth for: Hf from 298 K to 423 K for both species; Ta from 298 K to 423 K for O_2 , and from 298 K to 373 K for O; Mo from 298 K to 323 K for O; Ru from 298 K to 473 K for O_2 , and from 298 K to 423 K for O. For most of these cases, the increase in temperature leads to a higher oxide growth rate and limiting oxide thickness. However, for Ru exposed to O_2 , as mentioned, a considerable decrease in oxide thickness with the increase of temperature from 298 K to 323 K is observed. For $T > 323$ K, the increase in thickness and rate with increase of temperature is restored.

For the exposure conditions that do not present a self-limiting oxide growth (Hf at 473 K for both species; Ta at 473 K for O_2 , and from 423 K to 473 K for O; Mo at 473 K for O_2 , and from 373 K to 473 K for O; Ru at 473 K for O) there are also differences among its oxidation behaviour. Hf, Ta and Mo exposed to O_2 and Ru exposed to O at 473 K show a rapid initial oxide growth, followed by a decrease in rate with increasing exposure time. However, this second oxidation stage is continuous, and the setting of growth in a limiting oxide thickness is not observed. For Ta and Mo exposed to atomic oxygen at $T \geq 423$ K, the initial rate is slower than that obtained for lower temperatures. In these exposure systems, an almost linear oxide growth is set, and a saturating growth of oxide thickness is not observed. On the other hand, Hf exposed to O at $T = 473$ K presents a significantly higher growth rate during the entire oxidation process, reaching a much thicker oxide than the observed for the other metals after 300 min exposure.

Figure 5.1: Oxide thickness extracted from in-situ SE of metals exposed to molecular and atomic oxygen (partial pressure of 1×10^{-4} mbar – background O₂) at different temperatures. a) Hf + O₂ b) Hf + O; c) Ta + O₂, d) Ta + O; e) Mo + O₂, f) Mo + O; g) Ru + O₂, h) Ru + O. The fitted black dashed lines correspond to the theoretically growth curves based on the Cabrera-Mott inverse logarithm law (Equation 5.6). The shadowed area along the fits corresponds to the fitting error.

5.3.2 Analysis of oxide composition and structure

We now follow the analysis by individually assessing the composition of formed oxides. Figure 5.2 shows in-vacuum XPS analysis for example cases of samples exposed to atomic oxygen at 473 K, and Figures 5.6 to 5.9 show data for the 300 min exposed metals at all temperatures.

Except for the final oxide thickness, Hf films exposed to molecular and atomic oxygen present similar composition evolution as a function of temperature. As seen in Figure 5.6, Hf exposed to both species at $T \leq 373$ K shows the Hf 4f (HfO₂) peaks centred at energies slightly lower than 18.3 eV, the energy characteristic of stoichiometric HfO₂ [37, 41]. This can be interpreted as a slightly lower stoichiometry, as the increase in metal content leads to a shift of oxide peaks to lower energies. However, for the same samples, the higher angles of AR-XPS analysis (i.e. depth information more limited to the surface) show the formation of a stoichiometric oxide closer to the surface. This indicates metal interstices or oxygen vacancies as the dominant migrating species in oxide formation [18, 39]. The increase of temperature to 423 K and 473 K leads to the formation of homogeneously stoichiometric oxides from the surface up to the maximum analysis depth of XPS, with peaks centred at 18.3 eV.

Tantalum can be found in a continuum of oxidation states (Ta²⁺, Ta⁴⁺, Ta⁵⁺) [36] with the most stable, stoichiometric form (Ta⁵⁺) presenting a binding energy of 26.6 eV. Ta exposed to molecular oxygen up to 373 K shows oxide peaks centred at 26.6 eV of low intensity and high FWHM. Considering the small thickness of these oxide overlayers, the high FWHM can be related to a larger spread in binding energies due to a relatively high contribution from different binding energies at the layer surface and interface. As in the case of Hf, AR-XPS reveals a higher stoichiometry at depths closer to the surface, with an increase of intensity and decrease of FWHM for oxide peaks. The increase of exposure temperature to $T > 423$ K reduces the FWHM and leads to a slight peak shift to lower binding energy, which is maintained throughout all analysis angles. This indicates that the increase of temperature leads to a change in oxide stoichiometry. On the other hand, all atomic oxygen exposed samples present a constant FWHM (1.1 eV) and peak centred at ~ 26.6 eV from surface to maximum probed depth. Therefore, we can conclude that for atomic oxygen exposed tantalum, a stoichiometric oxide film is formed independently of the applied temperature.

As previously mentioned, molybdenum can also form oxides of multiple stoichiometries, with Mo⁴⁺ (229.5 eV) and Mo⁶⁺ (232.1 eV) the most stable forms [21]. The XPS spectra of molecular oxygen exposed samples show virtually no oxide peaks up to 353 K. However, O 1s peaks at energies corresponding to metal oxide compounds (529 - 531 eV) are observed. This is in agreement with the results obtained by in-situ SE, which indicate for these samples the formation of an oxide with thickness of less than 0.15 nm. For O₂-exposed samples at 423 K and 473 K, low intensity Mo⁴⁺ peaks are observed, which correspond to the formation of a thin MoO₂ layer. From 298 K to 423 K, the atomic oxygen exposed samples present a broad peak, centred at about 232.3 eV, indicating the formation of MoO₃ as dominant stoichiometry. For these samples, the AR-XPS indicates a slightly lower

FWHM near the surface. Contrary to Hf and Ta, the FWHM then increases with temperature, implying the increase of stoichiometry distribution for higher temperatures. At 473 K, the stoichiometry distribution is so evident that peaks relative to different oxidative states can be easily distinguished in the spectrum, which is kept throughout the oxide depth. For this sample, the most prominent peak corresponds to a well-defined peak at 231 eV, which is associated to the less stable Mo^{5+} state.

Figure 5.2: XPS measurement of metals exposed during 300 min to atomic oxygen at 473 K (partial pressure of 1×10^{-4} mbar – background O_2). The light grey line indicates measured data, coloured lines indicate fitted peaks for the specified chemical state. The pink line represents the sum of background and fitted components. a) Hf; b) Ta (the broad light pink peak at ~ 23 eV corresponds to O 2s and the light blue peaks correspond to suboxides); c) Mo; d) Ru (the light blue peaks at ~ 282.5 eV correspond to intrinsic plasmon features).

Ru is a well-known oxidation-resistant material at ambient conditions [23, 42]. The small shift between Ru^0 (280 eV) and Ru^{4+} (280.7 eV) can sometimes interfere in the identification of substoichiometric forms, due to the overlap between peaks from substoichiometric oxide and metal. However, the comparison between metallic Ru and Ru exposed to O_2 at 298 K, indicates a more pronounced shoulder on the high binding energy side of both peaks for the exposed sample, suggesting the

presence of oxidized Ru (peak centred at ~ 280.4 eV). On the other hand, the spectrum for O_2 exposure at 323 K presents really sharp Ru 3d core levels peaks. This suggests that, as also observed by in-situ SE, virtually no oxide is formed at the surface. The increase of temperature then leads to more pronounced RuO_2 peaks centred at 280.7 eV, indicating compositions close to stoichiometric for these exposure conditions. For atomic oxygen exposures, the RuO_2 features are clearly seen for all samples, and an intensity increase and a shift from 280.5 eV to 280.7 eV with increase of temperature is observed. Since Ru and RuO_2 overlayer are conducting, both have intrinsic plasmon probabilities contributing to the signal in the spectral range close to the Ru 3d core level [43]. These features are seen at ~ 282.5 eV for thicker oxides (O_2 exposed at $T \geq 423$ K and O exposed at $T \geq 323$ K).

Figure 5.3: XRD analysis of a) Hf, b) Ta and c) Mo exposed to different conditions. The dashed grey lines represent characteristic peak positions of crystalline metal (HCP Hf, tetragonal Ta and BCC Mo) and dashed-dot dark red lines characteristic peak positions of crystalline oxides (monoclinic HfO_2 , orthorhombic Ta_2O_5 and MoO_3).

Following the in-vacuum analysis, analysis of the crystalline structure of pristine and oxidized metals was made by ex-situ GIXRD. To minimize influence of atmospheric exposure and further oxide growth, the samples were analyzed immediately

after being removed from vacuum.

Figure 5.3 shows examples of XRD spectra of key cases. It was observed that only Hf, Ta and Mo exposed to atomic oxygen at 473 K formed crystalline oxides, as highlighted by the appearance of characteristic monoclinic HfO₂ and orthorhombic Ta₂O₅ and MoO₃ peaks in the spectra. The remaining metal-specie-temperature systems exhibited a final amorphous oxide. All of the amorphous oxide films had final thickness equal to or lower than about 6 nm. It is remarkable to note, however, that even though Mo exposed to atomic O at 423 K and 473 K present similar growth dynamics and final oxide thickness, only the sample exposed to the higher temperature shows the formation of crystalline oxide.

To facilitate an overview of all observed scenarios, Table 5.1 brings a summary of the main characteristics observed for the analyzed exposure systems. In the following sections, we will explore the entire process of oxide formation, correlating the obtained data and calculated parameters to properties of the studied metals.

Table 5.1: Summary of characteristics from oxide growth dynamics and final formed oxide on metals exposed to O₂ and O.

Oxide characteristic		O ₂ exposure	O exposure
Hf	Limiting oxide formation	CM growth for $T \leq 423$ K	CM growth for $T \leq 423$ K
	Stoichiometry	Stoichiometric at all T	Lower stoichiometry for $T \leq 373$ K
	Structure	Amorphous at all T	Crystalline at $T = 473$ K
Ta	Limiting oxide formation	CM growth for $T \leq 423$ K	CM growth for $T \leq 373$ K
	Stoichiometry	Lower stoichiometry for $T \leq 373$ K	Stoichiometric at all T
	Structure	Amorphous at all T	Crystalline at $T = 473$ K
Mo	Limiting oxide formation	Does not follow CM	CM growth for $T \leq 323$ K
	Stoichiometry	Substoichiometric when formed ($T \leq 423$ K surface-limited; $T = 473$ K continuous growth)	High substoichiometric for $T \geq 373$ K
	Structure	Amorphous when formed T	Crystalline at $T = 473$ K
Ru	Limiting oxide formation	CM growth for 298 K, 353 K $\leq T \leq 423$ K	CM growth for $T \leq 423$ K
	Stoichiometry	Lower stoichiometry for $T \leq 373$ K	Lower stoichiometry for $T \leq 373$ K
	Structure	Amorphous at all T	Amorphous at all T

5.3.3 First step of oxidation: molecular oxygen dissociation and surface-limited growth

We can use the advantage of real time SE monitoring to obtain more information about the very initial stages of oxide formation. For molecular oxygen exposure, the oxidation begins by the dissociation of molecules and atomic oxygen binding to surface atoms (dissociative chemisorption) [29, 44]. For molecular oxygen on transition-metal surfaces, two different pathways can be followed: trapping-mediated and direct chemisorption. The trapping-mediated mechanism involves a

two-step process [45]. The first step is the non-activated formation of a stable, molecular precursor, as stated in Equation 5.1:

where O_2^* represents a precursor with a stretched oxygen bond compared to a free molecule and Me the metal surface. Once trapped at the metal surface, the precursor can either desorb into the gas phase or proceed to dissociatively chemisorb, with the relative rates dictated by a surface temperature mediated kinetic competition [46–48]. If not desorbed, the second step is the activated transition of the precursor to the chemisorbed atomic oxygen state when the O-O bond is disrupted, and the O atoms approach closer to the metal surface [45]:

In the direct mechanism, the molecule proceeds directly to the process described by Equation 5.2, with no formation of intermediate precursors.

However, we should emphasize that at the applied oxygen pressure, the time needed for saturation of the metal surfaces with dissociatively chemisorbed oxygen atoms is expected to be much faster than the time resolution of the applied ellipsometry measurements (~ 2.52 s acquisition step). Previous studies have shown that the saturation of the O coverage on Ta surfaces occurs upon exposure to 10 L of O_2 [49]. Preliminary studies made in our research group have demonstrated the saturation of surface O coverage on a Ru surface with about 100 L of molecular oxygen. Therefore, based on the applied oxygen flux, we estimate that the metal surface should already be saturated within approximately 1 s of O_2 exposure. Therefore, we propose that the initial oxide growth rate as monitored by ellipsometry corresponds to the dissociation of molecular species on an oxygen saturated surface in conjunction with incorporation of oxygen atoms in sub-surface layers, following a mechanism represented by Equation 5.3:

As previously mentioned, we assume the oxide monolayer to have thickness of less than 0.3 nm, after which the limiting step of oxide formation might be substituted by the diffusion of ions through the formed oxide. In cases where the molecular dissociation of O_2 on an oxygen saturated surface acts as the limiting step for the initial phase of oxide formation, we propose that the energy barrier for this process can be derived from an Arrhenius analysis. With that, we can write a relation only for this initial oxide growth formation as described in Equation 5.4:

$$\left. \frac{dx}{dt} \right|_{x < 0.3nm} = A \exp \left(-\frac{E_a}{k_b T} \right) \quad (5.4)$$

with E_a the dissociation barrier of molecular oxygen and A a pre-exponential factor. Taking the natural logarithm of Equation 5.4, we obtain a linear relation between the initial rate and the inverse of temperature:

$$\ln \left(\frac{dx}{dt} \Big|_{x < 0.3nm} \right) = \ln(A) - \frac{E_a}{k_b} \left(\frac{1}{T} \right) \quad (5.5)$$

Hence, by plotting the logarithm of the initial rate of oxide growth as a function of $1/T$ for the oxidation, we can determine the energy needed for molecular oxygen dissociation at the analyzed surfaces.

Now we should evaluate for which set of exposure conditions this analysis is valid. Naturally, the metals should have been exposed to molecular oxygen. Furthermore, the processes involved in dissociation should be limiting and should not change along the analyzed temperature range. Hf and Ta do not show evidences of different processes acting on the initial stages of oxidation, as there is a clear oxide formation with rates scaling with temperature. However, the cases of Ru and Mo deserve each a more detailed discussion.

For Mo it is known that a low oxygen uptake and oxide growth is given upon thermal oxidation at low temperatures [50–53]. Previous studies have shown that such behaviour is related to the sharp decrease in adsorption and surface reactivity of the initially formed thin MoO_2 towards oxygen species [52]. However, before the formation of the first oxide monolayer, earlier studies on monocrystalline Mo surface have shown a similar dissociation and oxidative behaviour from room temperature up to about 573 K [51], indicating that the same dissociation mechanism might act in this temperature range. As our analysis was performed at temperatures below this range, we can assume a constant dissociation mechanism to be present and, therefore, the developed analysis can be applied to the performed exposure conditions.

For Ru, as previously mentioned, with the increase of temperature from 298 K to 323 K a decrease in limiting oxide thickness is observed. This can be attributed to a decrease in equilibrium oxygen coverage at 323 K (compared to 298 K), as also previously reported by Cai et al. for Al exposed to O_2 at temperatures ranging from 223 K to 373 K [30]. Similarly, a lower initial oxidation rate is observed with increase of temperature from 298 K to 323 K, which is also attributed to oxygen coverage being the limiting factor for oxide growth. Wheeler et al. [46] have demonstrated the existence of a trapping-mediated mechanism on O_2 -Ru reaction for molecules with low incident energy. In this study, an inverse dependence of the initial dissociative chemisorption probability with surface temperature was observed, related to the kinetic competition between oxygen desorption and dissociation at the Ru surface (a similar mechanism was also observed for Al surfaces by Hofmann et al. [54]). For Ru at T above 323 K (and for the cases of Hf and Ta), two possibilities are raised: i) the temperature-induced dissociation becomes more prominent than desorption, therefore the availability of oxygen is no longer a limiting factor; or ii) the mechanism changes from a trap-mediated to a direct chemisorption [46, 47]. Therefore, for Ru at $T \leq 323$ K, the limiting step for oxide formation will not be the oxygen dissociation itself, but the kinetic competition between oxygen desorption and dissociation; and/or there is a change in the predominant dissociative chemisorption mechanism. In either case, to guarantee that the analyzed temperature range is undergoing the same surface processes, it is reasonable to include only the exposures of Ru to O_2 at 373 K and 423 K in the proposed oxygen-dissociation analysis.

The conditions assumed to be consistent with the proposed analysis were then evaluated and the logarithm of the initial rate of oxide growth as a function of $1/T$ is plotted in Figure 5.4. Indeed a linear relationship between the terms is observed for all metals. The extracted values of the energy needed for molecular oxygen dissociation (E_a) in each metal surface obtained from this analysis are shown in Table 5.2.

Figure 5.4: Natural logarithm of the initial oxide growth rate for exposure to molecular oxygen as a function of the reciprocal of temperature for all analyzed metals. Only data for temperatures for which thermally activated dissociation of molecular oxygen is the limiting factor for oxide growth is included.

Table 5.2: Effective O_2 dissociation barrier for initial oxide growth (< 0.3 nm) for the analyzed polycrystalline metals.

	E_a [eV]
Hf	0.10 ± 0.004
Ta	0.11 ± 0.002
Mo	0.12 ± 0.005
Ru	0.13 ± 0.006

A small difference in dissociation barrier of molecular oxygen was found compared to typical differences obtained for theoretically calculated dissociation energies of O_2 on different clean metals (cf. refs. [45] and [47], it should be noted that theoretical calculations with similar methodology were not found for most of the metals studied in this work). This suggests that the effective energy barrier for dissociation of O_2 on a metal surface saturated with oxygen, in conjunction with the migration of oxygen to the sub-surface layer is less strongly dependent on reactivity

of the metal. Unfortunately, to our knowledge there is little theoretical background on expected activation energies for this stage of oxidation. However, a certain order of the calculated values ($\text{Hf} < \text{Ta} < \text{Mo} < \text{Ru}$) is still observed. It is known from literature that the oxygen adsorption, dissociation and formation of a chemical bond with the metal surface is a consequence of the electron donation from the metal surface into the antibonding orbitals of the oxygen molecule [47]. Looking at transition metals, the d-band filling increases and d-band centre becomes lower in energy and large in spatial extent in the direction from the top-left to the lower-right end of the periodic table, which results in a weaker covalent interaction and strong Pauli repulsion between metal surface and oxygen [55, 56]. Therefore, it is expected that the interaction with oxygen (and other adsorbents) should follow an order similar to that observed with our calculations. To the best of our knowledge, no previous quantitative analysis of molecular oxygen dissociation was performed for initially polycrystalline metallic surfaces as the ones analyzed in our experiments, at least after saturation of the surface with oxygen. However, the comparison with simulation [45, 56] and experimental data on monocrystalline metals [55] support the observed trends and differences in dissociation energy.

5.3.4 Second step of oxidation: oxide growth beyond few monolayers

Following the analysis of initial oxide formation, we now focus on the dynamics of oxide growth after the formation of the first oxide layer. As previously mentioned, the main mechanism driving low-temperature oxidation is reported to be the electric field-driven, described by CM-theory. However, the change in exposure conditions can interfere in the main parameters determining oxide growth and formed oxide properties. In the following sections, the predominant mechanism in each exposure condition was evaluated. A calculation of main parameters describing oxide growth kinetics, together with the correlation between the obtained results and exposure conditions (the combination of temperature, oxidative specie and metal of interest) was performed.

Limiting oxide growth and the influence of coverage on V_M

As previously mentioned, the self-limiting behaviour of oxide film growth observed for Hf (298 K to 423 K for both species), Ta (298 K to 423 K for O_2 and 298 K to 373 K for O), Mo (298 K to 323 K for O) and Ru (298 K to 473 K for O_2 , 298 K to 423 K for O) is consistent with the Cabrera-Mott model of electric field-driven oxide growth [7, 32]. According to CM, with the establishment of V_M , the growth rate of oxide thickness x follows the equation:

$$\left(\frac{dx}{dt}\right) = \Omega n \nu \exp\left(\frac{-U + qa \frac{V_M}{x(t)}}{k_b T}\right) \quad (5.6)$$

where Ω is the volume of oxide formed per cation, n is the number of cations per unit area which may jump through the rate-limiting energy barrier U , ν is the attempt frequency of the cation, q is the charge of the migrating cation, $2a$ is the distance between potential minima. The field responsible for decrease in the energy

supplied for ionic diffusion is re-written as the term $V_M/x(t)$, highlighting its dependence on oxide film thickness. In our previous study on low-temperature oxidation (Chapter 4), we have demonstrated that the reaction front of oxide formation in the analyzed transition metals correspond to the oxygen/oxide interface. This was further confirmed by the AR-XPS analysis performed in this study, which showed that for the cases that follow CM-type growth, a higher stoichiometry is found near the surface. This higher stoichiometry near the surface is characteristic of reactions where metal interstices (M_i^{z+}) or oxygen vacancies (V_O^{z+}) are the dominant migrating species.

Therefore, for the mentioned conditions and with known values of Ω , n , ν , q and a , V_M and U can be obtained by fitting the inverse logarithm law given by Equation 5.6 to the growth rate curves shown in Figure 5.1 [29, 30, 57]. The fitting results are shown as black dashed lines in Figure 5.1. As checked by XRD analysis, for the cited cases which follow a CM-type growth, the oxidation results in an amorphous oxide growing on a polycrystalline metal. Therefore, we assume an isotropic diffusion in the oxide film, with the rate-limiting barrier for cation motion located within the oxide. From this assumption, n and a are estimated based on the hopping from metal cations between interstices of the corresponding oxide. Considering their amorphous nature, the values for Ω , n and a were obtained based on bulk values of density and molar mass of the oxides. For the calculations performed in this paper, $\nu = 10^{12} \text{ s}^{-1}$ [7] and $q = ze \text{ C}$ (with the elementary charge $e = 1.6022 \times 10^{-19} \text{ C}$, and $z = 4$ for Ru and Hf, $z = 5$ for Ta and $z = 6$ for Mo). All the applied values for Ω , n , ν and $2a$ are shown in Table 5.3, together values of U obtained from the fittings for both molecular and atomic oxygen exposures. The values of V_M are shown in Figure 5.5 as a function of exposure temperature for both species.

Table 5.3: Fitted values for the rate-limiting energy barrier for cation motion (U), for dry thermal oxidation of metals under exposure to atomic and molecular oxygen at $p\text{O}_2 = 1 \times 10^{-4} \text{ mbar}$. The values of V_M are displayed in Figure 5.5 as a function of temperature. The corresponding constants applied for the volume of oxide formed per cation (Ω), number of cations per unit area (n), and distance between potential minima ($2a$) are also displayed. These were estimated based on bulk values of density and molar mass of the oxides and assuming the rate-limiting barrier for cation motion to be located in the oxide film.

Metal	Oxidative specie	$\Omega \text{ [nm}^{-3}\text{]}$	$n \text{ [nm}^{-2}\text{]}$	$2a \text{ [nm}^{-2}\text{]}$	$U \text{ [eV] (fitted)}$
Hf	O ₂	0.108	9.1	0.23	1.5± 0.2
	O				1.8± 0.3
Ta	O ₂	0.313	7.9	0.23	1.8± 0.2
	O				1.9± 0.3
Mo	O	0.204	7.3	0.23	1.9± 0.1
Ru	O ₂	0.095	9.9	0.22	1.8± 0.4
	O				2.0± 0.3

From the performed analysis, we noted the activation energy barrier to be independent of T and present similar values for metals exposed to molecular and atomic oxygen. This supports the obtained fitting results, as the activation energy for oxidation is related to the energy necessary for the ions to diffuse through the formed oxide and thus should be independent of oxidation conditions as long as in depth transport is rate limiting [32]. As in both molecular and atomic oxygen exposures amorphous oxides were formed, U values should not be dramatically different. This also suggests a similar atomic structure in the formed amorphous oxide films among the analyzed temperatures. On the other hand, the V_M formed across a metal oxide changed dramatically between the molecular and the atomic oxygen exposure, presenting also a slight variation with temperature, as seen in Figure 5.5.

Figure 5.5: Calculated Mott-potential (V_M) as a function of temperature for each metal-oxidative specie combination. a) Metals exposed to O_2 , b) metals exposed to O . The corresponding constants applied for the volume of oxide formed per cation (Ω), number of cations per unit area (n), and distance between potential minima ($2a$) are displayed in Table 5.3. The dotted lines serve as guides to the eyes.

We shall initially focus on the effect of temperature on potential for each oxidative specie. As seen in Figure 5.5a, for O_2 exposure the increase of T does not significantly affect V_M of Hf and Ta, only values for Ru are influenced. As discussed in Section 5.3.3, this variation seen in Ru might be due to enhanced desorption upon increase of T and thereby reduction of oxygen coverage. One should note that, as a closed oxide layer was probably not formed for 323 K, the data point might not represent a real value of V_M . However, it serves as an indication of the effect of coverage on the formed potential, indicating that at temperatures where dissociative chemisorption becomes again more prominent than desorption ($T \geq 373$ K), values of V_M are restored.

For direct atomic oxygen exposure, the change in temperature is critical only for Ta. It is important to observe that also for Ta, the increase in T induces a decrease in growth rate at the initial fast oxidation stage. Based on the analysis developed by Jeurgens et al. on Al oxidation [32], a decrease of the rate in the fast oxide growth stage and a reduction of V_M can be related to either of the following phenomena: (a) increase of oxygen desorption (reduction of coverage) or (b) low rate supply

of oxygen (due to low exposure pressure). For our experimental conditions, the atomic oxygen supply is in the order of 1 ML/s, making it improbable that the supply is the limiting factor for oxide growth. Furthermore, when exposing Ta to molecular oxygen, no effect evidenced the increase of desorption with the increase of temperature. As atomic oxygen presents an even higher sticking probability than O₂ [55], it is also unlikely that temperature induced desorption of atomic oxygen might increase in the analyzed temperature range. However, the increase of temperature might lead to an increased ionic diffusion, such that thermal diffusion induced by concentration gradients becomes significant compared to field assisted (self-limiting) oxide growth. With that, according to the coupled-currents approach, the potential starts to shift to the so-called “kinetic” potential V_K , which is weaker than the Mott potential V_M [27–29, 32]. Therefore, we propose that the reduction of coverage allied to increased influence of the concentration gradient leads to the observed growth behaviour, respectively resulting in decrease of oxide growth rate and surface potential.

Following this analysis, we can now discuss the difference in V_M between oxidative species for all metal cases. Being oxygen an acceptor-type molecule, electrons from the metal are transferred to the molecule upon contact with the metal surface [29, 55]. This process leads to the dissociation of molecular oxygen (following the energy trend calculated in Section 5.3.3) and formation of charged atomic species. For atomic oxygen, considering its high reactivity and no need of dissociation, immediate charge transfer is assumed upon contact with the metal surface. The reaction follows to place exchange between metal and charged atomic oxygen and formation of the first oxide monolayer. After this first monolayer is formed, a certain coverage of charged species should still exist on the surface for maintenance of V_M and oxide growth to be continued (one should be aware that, by then, the presence of oxide might influence charged species-surface interaction). As a simple analogy, the CM oxidation system can be viewed as a parallel-plate capacitor [32, 58]. In a capacitor, however, the applied voltage determines the charge accumulated on the plates, while in the CM oxidation model the amount of adsorbed atomic oxygen determines the charge concentration and consequent electric field.

The influence of reactive atomic species on the value of formed V_M is directly evidenced by the differences in V_M between atomic and molecular oxygen exposed metals. Previous studies have shown that atomic oxygen presents a higher sticking probability than molecular oxygen on both pristine metal and oxidized surfaces for the analyzed metals [42, 46, 55, 59–61]. Another point to be taken into account is that the probability of dissociative chemisorption of molecular oxygen decreases with increase of oxygen coverage [62]. With that, the probability of the existence (and maintenance) of a high atomic oxygen coverage and consequent surface charge density is superior upon direct atomic exposure. As previously mentioned, studies have suggested a dependence of Mott-potential on the oxygen coverage based on variation of temperature and/or pressure [30, 31, 33, 34]. The increase of V_M with coverage is further supported by analysis where processes such as ultraviolet [41, 63] or electron [64] irradiation were employed during O₂ exposure. In these studies, an increase in final oxide thickness (compared to pure O₂ exposure) was reported,

strongly indicating that the presence of processes that induce O_2 dissociation (and consequent atomic oxygen surface concentration) lead to higher surface potential values.

Finally, looking specifically into atomic oxygen exposure, we can correlate the values of V_M to metal properties. According to the CM theory, the Mott-potential can be defined by $V_M = e^{-1}(\phi_0 - \phi_L)$ [7], with ϕ_0 the metal work function and ϕ_L the difference between the vacuum potential and the Fermi level in the presence of adsorbed oxygen. It is important to emphasize that this calculation of V_M is valid in the limit where the electron transmission from metal to adsorbed oxygen is dominated by the tunnelling effect and cation diffusion is the limiting step in oxide formation [29]. With that, the lower the metal work function, the more negative the formed potential will be, and consequently the higher the generated field. Work function values for polycrystalline structures obtained from the literature show the lowest values for Hf (~ 4.0 eV) and Ta (~ 4.0 eV), followed by Mo (~ 4.3 eV) and Ru (~ 4.7 eV) [65]. One should be aware that the work function values are strongly dependent on surface properties, such as preferential plane and cleanliness. Therefore, values of work function reported in the literature often cover a considerable range.

However, it is generally possible to correlate a lower work function to a more negative value of potential and consequently larger final oxide thickness for exposures of metals to atomic oxygen. As discussed, this is not necessarily true for molecular oxygen exposures, where surface effects such as the competition between desorption and adsorption, together with coverage limitations directly influence the value of the Mott-potential. As an example, based only on electronic characteristics, it was expected that Ru, among the analyzed metals, would present the lowest oxide formation for both molecular and atomic oxygen exposure. However, Mo and Ta formed thinner oxide than Ru for molecular oxygen exposures at the analyzed T range. This difference can be related to the differences in catalytic ability of the initially formed oxide, as RuO_2 presents higher probability of O_2 dissociative chemisorption [60, 66], leading to the maintenance of chemisorbed O concentration and consequent thicker oxide formation. These observations indicate that in cases where the presence of atomic oxygen species on the surface is not hindered by desorption or limited by coverage, the formed Mott-field and consequent obtained limiting oxide thickness at low temperature oxidation can be directly related to the metal electronic properties.

Continuous oxide growth and crystalline oxide formation

Lastly, we should discuss the exposure conditions that do not present a self-limiting oxide growth: Hf at 473 K for both species; Ta at 473 K for O_2 , and from 423 K and 473 K for O; and Mo at 473 K for O_2 , and from 373 K to 473 K for O; Ru at 473 K for O. We hypothesize that at these conditions, three identified processes could potentially influence the maintenance of a continuous oxide growth within the timescale of the experiment: (i) increase in molecular dissociation (for molecular oxygen exposures); (ii) increase of ionic diffusion; (iii) contribution of electron transport by thermionic emission.

For molecular oxygen exposure of Hf, Ta and Mo at 473 K, a rapid initial oxide

growth followed by a decrease in rate with increasing exposure time is observed. However, this second oxidation stage is continuous, and the setting of growth in a limiting oxide thickness is not observed. This transition is observed for Hf, Ta and Mo at very thin oxide thicknesses, of about 0.7 nm, 0.6 nm and 0.2 nm respectively. This continuous growth could be induced by the increase of both molecular dissociation and ionic diffusion with temperature (with thermal diffusion induced by concentration gradients significant compared to field assisted oxide growth). As molecular oxygen dissociation and the chemical diffusion of metal cations are thermally activated processes, the increase in temperature could enhance both the concentration of atomic oxygen species at the metal surface and number of cations diffusing for oxide formation. Both processes acting together can lead to a continuous supply of oxygen and cations for oxide formation, resulting in a continuous oxide growth. However, the slow rate of the second oxidation stage and the fact that the oxide thicknesses for all cases are still much lower than those obtained by direct atomic oxygen exposure indicate that surface processes might still be a limiting factor in these oxide growth dynamics.

5 For Ta at 423 K and 473 K, and Mo from 373 K to 473 K, an almost linear oxide growth is set, without observing a limiting oxide thickness. For both materials, the initial growth rate also decreases with increase of T . As discussed in the previous section, we propose that in these cases, the increase of temperature leads to a higher ionic diffusion through the oxide and consequent reduction of atomic oxygen coverage. A similar phenomenon has been recently observed for Cu oxidation at low temperatures [12]. As discussed by Unutulmazsoy et al. [12] for Cu, the different oxidation kinetics for Ta and Mo can be attributed to the very fast diffusion of cations in the corresponding oxides, which is comparably higher than typically observed for binary oxides. Usually in the low T regime, the molecular dissociation seems to be a critical factor for further metal-oxygen reaction and oxide growth. However, the direct exposure to atomic oxygen enables the direct oxide formation and high consumption of oxygen from the surface, which is accentuated with ion diffusion induced by further T increase. For Mo, the increase in ionic diffusion is supported by the stabilization of different oxidation states with temperature increase, observed in the XPS analysis. For Ta, we believe such difference in oxidation states is not observed due to the higher reactivity of tantalum as compared with molybdenum [67].

This decrease in rate observed for Mo and Ta, however, is not observed for Ru and Hf exposed to atomic oxygen at 473 K. For these materials, a higher growth rate is observed during the entire oxidation. Both systems present a rapid initial oxide growth followed by a decrease in rate with increasing exposure time. However, Hf shows a significantly higher growth rate during the second stage compared to Ru, reaching a much thicker oxide than observed for the other metals after 300 min exposure. We hypothesize that the continuous growth observed for Ru and Hf at this exposure condition is a consequence of the increase of thermionic emission of electrons with T . Thermionic emission is a process considered to be strongly dependent on both metal properties and temperatures to which the system is exposed [28, 68]. Considering the electronic properties of Hf, Ru and their oxides, and the analyzed temperature range, the effect of thermionic emission is negligible

up to an oxide thickness of $\sim 2\text{--}3$ nm, and the tunnel current is dominant in the charge transfer processes during oxide growth [27, 28, 68]. However, for thicknesses above this value and at a significant temperature, the tunnel current will cease and thermionic emission becomes the main charge transfer process. It is important to note that, contrary to tunnelling, thermionic emission is independent of oxide thickness [28, 32, 68]. Therefore, even after the oxide reaches a thickness where the contribution of tunnelling is reduced, electron transport through the thickening film remains. Following the constraint of coupled currents between cations and electrons, the initial fast growth must be followed by a second stage of relatively slower, continuous oxide formation [29]. This transition between first fast and second slower stages is marked by a distinct drop in rate, a result of the breakdown of V_M by termination of tunnelling. For Hf at 473 K, this transition is observed at ~ 2 nm oxide. This relative ease of electron transmission at 473 K and consequent oxide growth might be related to the lower work function of Hf and the high number of traps present in metal oxide films synthesized at lower temperatures, a phenomenon reported to be especially significant for HfO_2 thin films [69–71]. Considering the higher work function of Ru, the thermionic release of electrons should be less intense and, therefore, the oxide growth not as steep as observed for Hf. We hypothesize that the influence of thermionic emission would also be present for the other oxides that show continuous oxide growth at 473 K, however, the previously cited effects (increase in molecular dissociation and ionic diffusion) might be more determinant for the growth in the other oxidation systems.

The final point to be discussed is the formation of crystalline oxides at 473 K for Hf, Ta and Mo exposed to atomic oxygen. Previous studies have demonstrated that for the oxide overgrowth on its metal substrate an amorphous phase is stable only up to a certain critical thickness [72, 73]. The theoretical analysis developed by Reichel et al. [72] has demonstrated that this transition thickness is dependent on thermodynamical properties (such as bulk Gibbs energies, surface and interfacial energies) of both the metal and overgrown oxide films, and was estimated to lay in the range of $\sim 1\text{--}3$ nm for oxides growing on densely packed monocrystalline metal surfaces. Therefore, the high reactivity and continuous oxide formation (induced by the phenomena discussed above) prompt the oxide growth past the thickness limit where the amorphous oxide overlayer is thermodynamically stable. However, we believe that temperature also plays a critical role in this phenomenon. This assumption is based on the observation that even though Mo exposed to atomic O at 423 K and 473 K present a similar final oxide thickness, only the sample exposed to the higher temperature shows the formation of crystalline oxide. For lower temperatures there may thus be a kinetic barrier that prevents formation of the more stable crystalline oxide phase. This interrelation between exposure conditions and crystalline oxide formation is an interesting phenomenon that will be further investigated in a future publication. However, preliminary experiments done in our research group have demonstrated that for HfO_2 growing on polycrystalline Hf, the crystallization of the oxide occurs at a thickness of approximately 5.5 nm. Furthermore, we observed that even after reaching of crystallization at 473 K, the oxide growth can be ceased by reducing the exposure temperature. This verification was done under a constant flow of atomic oxygen species. This is a strong indication

that, contrary to what was previously assumed [32], the oxide structure might not be the main factor leading to continuous oxide growth at low temperatures.

5.4 Key oxide formation characteristics for the analyzed metals

5.4.1 Hf

Hf samples present significant oxide formation for both molecular and atomic oxygen exposures, following a CM-type growth at $T \leq 423$ K for both species. No direct evidence of temperature influence on the V_M was observed, with values of -0.8 ± 0.2 V for molecular oxygen exposure and -5.3 ± 0.3 V for atomic oxygen exposure. This difference indicates the significant effect of reactive species coverage on potential formation and consequent oxide growth. At $T = 473$ K, atomic oxygen interaction led to increased continuous oxide growth rate, forming a crystalline HfO_2 layer of ~ 15 nm after 300 min exposure. We hypothesize that this intense oxide growth is due to the transition of a tunneling mediated electron transfer to thermionic emission, a phenomenon marked by a distinct drop in growth rate between first fast and second slower growth stages at ~ 2.0 nm oxide. This relative facility of electron transmission is associated to the low work function of Hf and higher probability of electron trap formation for HfO_2 synthesized at lower temperatures.

5.4.2 Ta

Ta films present a CM-type growth at $T \leq 423$ K for O_2 and $T \leq 373$ K for O exposures. The significance of coverage for oxide formation was manifested in two different ways: for molecular oxygen, this was evidenced by the formation of a low V_M (-0.6 ± 0.1 V); for atomic oxygen, by the decrease of V_M with increased temperature. The first is associated to the lower molecular dissociation at the formed Ta_2O_5 surface, while the second is related to the increase in ion diffusion induced by T increase. The increase in ion diffusion is indicated by the almost linear rate of oxide growth. With intense oxide growth, at 473 K its thickness surpasses the limit in which amorphous oxide is thermodynamically stable and, therefore, a crystalline oxide structure is formed.

5.4.3 Mo

Mo presents significant oxide formation only for molecular oxygen exposures at 473 K and direct atomic oxygen exposures. For molecular oxygen exposures, the formation of a MoO_2 monolayer hinders further formation of oxide. The low reactivity of MoO_2 decreases the molecular dissociation probability, which impedes building up a significant V_M . As a result, only an increase of temperature to 473 K provides enough input of energy for continuous dissociation and oxide growth. For atomic oxygen exposures, the impediment of the oxidation reaction is no longer present, and oxide growth follows according to the CM mechanism up to 323 K. For higher temperatures, as in the case of Ta, the increase in ionic diffusion leads to a continuous oxide formation. Even though a similar oxide thickness is achieved

for 423 K and 473 K, only the last temperature shows crystalline oxide formation (monoclinic Mo), indicating the critical influence of temperature in the structure stabilization of the formed oxide.

5.4.4 Ru

Upon both molecular and atomic oxygen exposure at temperatures below and equal than 473 K and 423 K respectively, Ru follows a field-driven oxide growth mechanism. The critical feature determining the maximum oxide thickness observed for this metal is the coverage of reactive atomic oxygen species. For molecular oxygen exposures, at $T < 323$ K, the kinetic competition between oxygen desorption and dissociation at the Ru surface leads to an increase in desorption with increasing temperature. Consequently, below 323 K, there is an inverse relation between temperature and V_M . The exposure to atomic oxygen (and consequent higher coverage of reactive species) leads to values of V_M almost five times higher than for molecular oxygen exposures (-2.9 ± 0.2 V for O exposure; -0.6 ± 0.1 V for O₂ exposure), resulting in faster oxide growth rates and formation of thicker oxide overlayers for all analyzed temperatures. For exposure to atomic oxygen at 473 K, we propose that the effect of thermionic emission induces the continuous oxide growth. However, at a lower rate than observed for Hf, considering the higher work function of Ru.

5.5 Conclusions

In this work the complete process of oxidation (from surface processes to film growth) was analyzed and described for polycrystalline Hf, Ta, Mo and Ru films. The reactions were studied at low temperatures (298 K to 473 K) upon the exposure to molecular oxygen and atomic oxygen.

Upon exposure to molecular oxygen, the surface O coverage rapidly saturates due to dissociative chemisorption. We observed that the initial growth rate up to an oxide thickness of ~ 0.3 nm can be described by an Arrhenius relation and we thus extracted the effective energy barriers for molecular dissociation and penetration of oxygen to the sub-surface layer. Small differences in dissociation barrier were found compared to typical differences obtained for the dissociation energies of O₂ on clean metals. However, the effective energy barrier still scaled in the order from more to less reactive metals as $\text{Hf} < \text{Ta} < \text{Mo} < \text{Ru}$.

Considering the formation of oxide films beyond monolayer thickness, temperature limits for which Cabrera-Mott type growth is followed and the influence of oxidation specie on the formed potential and oxide growth dynamics were evaluated. A key finding from our studies was the demonstration that the surface concentration of reactive atomic species is the determining factor in the oxidation process for all analyzed metals. For the conditions that followed Cabrera-Mott type growth, all formed oxides were amorphous. The calculated values of energy barrier of diffusion were similar for both molecular and atomic oxygen exposures, indicating a similar atomic structure in the formed amorphous oxide films among the analyzed temperatures. For molecular oxygen exposures, surface effects such as the competition between desorption and adsorption, together with coverage limitations directly

influence the formed Mott-potential (V_M) for $T < 473$ K. For atomic oxygen exposures, the high sticking and absence of a surface coverage limitation enable the correlation of lower work function (WF) to more negative values of the potential and consequently larger final oxide thickness, as determined by the Cabrera-Mott (CM) oxidation mechanism. The higher coverage derived upon O exposure was evident by the difference in potential and final oxide thickness formation. The values of V_M for O_2 exposure were higher than -1 V, with a small difference between the analyzed metals, while for atomic oxygen exposure the values scaled relative to WF decrease, from -2.9 eV (Ru) to -6.5 eV (Ta).

We also verified the interrelation between exposure conditions and crystalline oxide formation. Hf, Ta and Mo exposed to atomic oxygen at 473 K formed crystalline oxide structures, while Ru at the same exposure conditions remained amorphous. We hypothesize that the high reactivity and continuous oxide formation induced by increased ionic diffusion (Mo and Ta) and thermionic emission (Hf) prompt the oxide growth past the thickness limit where the amorphous oxide overlayer is thermodynamically stable. Nevertheless, temperature also has shown to present a critical role in oxide crystallization, as Mo exposed to atomic O at 423 K and 473 K present similar final oxide thickness, and only the sample exposed to the higher temperature showed the formation of crystalline oxide.

The present study shows a thorough analysis into the stages of molecular and atomic oxygen induced oxide growth, covering the differences in oxide composition and structure in the presence of activated oxygen species at low temperatures. The obtained results provide a general guideline for synthesis and control of oxide growth on polycrystalline transition metal oxide thin films at low temperatures. The overall picture shows that in cases where the presence of atomic oxygen species on the surface is not hindered by desorption or limited by coverage, the formed Mott-field and consequent obtained limiting oxide thickness at low temperature oxidation can be directly related to the metal electronic properties. We further hypothesize that this principle can be extended to other acceptor-type adsorbents, such as nitrogen: if radical species are directly in contact with the metal layer and enough coverage is present, a field assisted diffusion and compound growth process will be established. These results might have a significant impact, not only in the design of materials for a wide range of practical applications, but also for development of processes where reactive species are put in direct contact with thin layers (e.g. atomic layer growth or etching).

5.6 Appendix

Figures 5.6 to 5.9 show the in-vacuum XPS analysis for example cases of the 300 min exposed metals at all temperatures.

Figure 5.6: XPS measurement of Hf exposed during 300 min to molecular oxygen (left) and atomic oxygen (right). The light grey line indicates measured data, coloured lines indicate fitted peaks for the specified chemical state. The pink line represents the sum of background and fitted components.

Figure 5.7: XPS measurement of Ta exposed during 300 min to molecular oxygen (left) and atomic oxygen (right). The light grey line indicates measured data, coloured lines indicate fitted peaks for the specified chemical state. The broad light pink peak at ~23 eV corresponds to O 2s, and the light blue peaks correspond to suboxides. The pink line represents the sum of background and fitted components.

Figure 5.8: XPS measurement of Mo exposed during 300 min to molecular oxygen (left) and atomic oxygen (right). The light grey line indicates measured data, coloured lines indicate fitted peaks for the specified chemical state. The pink line represents the sum of background and fitted components.

Figure 5.9: XPS measurement of Ru exposed during 300 min to molecular oxygen (left) and atomic oxygen (right). The light grey line indicates measured data, coloured lines indicate fitted peaks for the specified chemical state. The light blue peaks at ~ 282.5 eV correspond to intrinsic plasmon features. The pink line represents the sum of background and fitted components.

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6

Oxygen diffusion in transition metal oxides at room temperature

The diffusion of oxygen in thin films of ZrO_2 and MoO_3 was investigated with atomic ^{18}O as a tracer using low energy ion scattering sputter depth profiling. 3 nm amorphous and 20 nm polycrystalline films were prepared by reactive magnetron sputtering and exposed to atomic oxygen species at room temperature. Exposure results in a fast diffusion of oxygen to a limited depth of ~ 1 nm and ~ 2.5 nm for ZrO_2 and MoO_3 , respectively, and surface exchange limited to a maximum of 65% to 75%. The influence of the crystalline structure of the films on exchange and diffusion was negligible. We propose that the transport of oxygen in oxides at room temperature is dominated by a field-induced drift, generated by the chemisorption of reactive oxygen species. The maximum penetration of oxygen is limited by the oxide space charge region, determined by the oxide electrical properties. We applied a drift-diffusion model to extract values of surface potential and kinetic parameters of oxygen exchange and diffusion. The developed experimental analysis and modelling suggest that the electric field and consequent distribution of charged species are the main factors governing exchange rates and species diffusion in an oxide thin film at room temperature.

6.1 Introduction

With the advance in nanometer-thick film synthesis, the application of transition metal oxides has exponentially grown. As thin films, they are employed in a wide range of functions, from electrodes in solid oxide fuel cells [1] and charge injection layers in organic electronics [2], to protective layers against corrosion and for increase of components lifetime [3]. In most of these applications, the interaction between the oxide surface and atmospheric species, such as oxygen, is present. The majority of studies in that context focused on molecular oxygen-oxide interaction at high temperatures ($T > 573$ K), in which it is commonly accepted that the chemisorption and incorporation of oxygen into the oxide lattice results in change of oxide properties [4–8]. However, little is known on the effect of atomic oxygen species interacting with oxide surfaces at moderate temperatures, i.e. close to 298 K (about room temperature) [9].

The aim of the present work is to understand the mechanisms governing the interaction of atomic oxygen with oxides at room temperature. The understanding of such interaction is critical considering applications where oxides are not directly exposed to high temperatures, but processes such as exposure to ultraviolet light [10, 11] or electron beam [12, 13] might induce the formation of atomic oxygen species at oxide surfaces. Transport of oxygen in an oxide lattice is initiated by oxygen exchange at the surface, followed by diffusion to sub-surface regions. The diffusion can be along grain boundaries (commonly assumed to be a faster diffusion pathway [14]) or bulk [15]. For molecular species in contact with binary oxides at room temperature, it is reported that the surface oxygen exchange is quenched, as the low temperature and the lack of high defect or dopant concentration prevents the reaching of the energy required to surpass the activation barrier of molecular dissociation [16, 17]. However, in case of exposure to atomic or radical species, the absence of the molecular dissociation step might enable the interaction to proceed to the lattice transport phase. This transport might affect the system in which an oxide is employed, for example by inducing changes in the oxide properties or by affecting layers that are supposed to be protected by the oxide (especially relevant when oxides are employed as diffusion barrier materials). Therefore, a better understanding of the nature of the interaction between atomic oxygen and oxide at low temperatures is of immediate importance for relevant technological applications of oxides.

One of the most powerful methods for studying oxygen transport processes is the so-called Isotope Exchange Depth Profile (IEDP). This technique consists of the combination of exposure of an oxide to the isotope ^{18}O , followed by in-depth analysis of the isotope profile by sputter depth profiling with an ion beam technique. Typically, secondary ion mass spectrometry (SIMS) is applied in IEDP analysis, as it provides a direct measure of oxygen transport kinetic parameters [18]. However, SIMS profiles lack precise information about the surface chemistry and oxygen exchange in thin films in the nanometer range, due to its large information depth (between 4 and 7 monolayers depth) [18]. In this context, the low-energy ion scattering (LEIS) technique provides the opportunity of correlating exchange kinetics with chemical processes at the topmost atomic layers of materials, giving an un-

precedented level of information on surface exchange and diffusion in oxides with isotopic discrimination [18, 19]. Therefore, the detailed analysis with LEIS-IEDP allows one to unambiguously discern between the mechanisms involved in lattice diffusion and surface exchange processes, together with determining the respective transport parameter characteristics of each mechanism [15, 18].

In the present study, we apply LEIS-IEDP to verify the interaction between atomic oxygen and thin film oxides of zirconium (ZrO_2) and molybdenum (MoO_3), with different thicknesses and crystalline structures. These materials were chosen to allow a comparison between a metal that only forms a single stable stoichiometric oxide (Zr) and a prototypical metal that can form various stable bulk oxidation states (Mo). Deposition by reactive magnetron sputtering, atomic O exposure and LEIS analysis were carried out in-vacuum, which enables to extract the precise time evolution of isotope surface exchange and in-depth diffusion without the interference of surface contaminants. Our analysis suggests that the formed isotope profiles are a consequence of the field formed upon chemisorption of reactive oxygen species at the oxide surface and associated accumulation of charged species near the surface (upward band bending). This process induces exchange and increases diffusivity of oxygen in the space charge region of the oxide. By applying a drift-diffusion model, we extract relevant kinetic parameters and suggest main factors that may influence oxygen diffusion.

6.2 Experimental

The experiments were performed in a home-designed ultrahigh vacuum system at a base pressure of $\leq 1 \times 10^{-9}$ mbar, which allows in-vacuum transfers between deposition (magnetron sputtering), characterization (LEIS and X-ray photoelectron spectroscopy (XPS)) and oxygen exposure chambers with negligible surface contamination. Films of 20 nm and 3 nm of ZrO_2 and MoO_3 were obtained by reactive direct current (DC) magnetron sputtering of the respective metallic target with a mixture of oxygen and argon. The samples were deposited on a $25 \times 25 \text{ mm}^2$ Si(100) substrate with a native oxide layer. The average deposition pressure was 5×10^{-4} mbar and the growth rate was typically 0.05 nm/s. The stoichiometry of deposited films was verified by XPS experiments with a Thermo Theta Probe spectrometer, using Al-K α radiation.

For a complete analysis of oxygen-oxide interaction, we performed three types of oxygen exposure: (i) exposure to molecular tracer oxygen ($^{18}\text{O}_2$) for testing of oxide surface stoichiometry; (ii) exposure to atomic ^{18}O (isotopic enrichment 98%) to perform isotope tracing analysis; (iii) exposure to atomic ^{16}O to check the reversibility of obtained isotopic profiles. All exposures were performed at room temperature with background O_2 partial pressure of 1×10^{-4} mbar. The atomic species were generated by a Specs MPS-ECR mini plasma source, with atomic oxygen flux in the order of 10^{15} atoms/ cm^2/s . The exposure time ranged between 10 s and 2400 s, and an IEDP analysis was performed after each exposure period. Isotope exchange depth profiles were obtained by performing LEIS sputter depth profiling on the exposed samples. In this analysis mode, each sputter step is followed by a LEIS analysis according to the acquisition parameters described below.

LEIS measurements were performed in an ION-TOF GmbH Qtac¹⁰⁰ high sensitivity LEIS spectrometer, described in detail elsewhere [20]. A He⁺ ion beam at 3 keV energy and 2.5–3.5 nA current, measured before each spectrum acquisition in a Faraday cup, was chosen for characterization. The typical ion fluence directed at the sample was 2×10^{14} He⁺ ions/cm², with a total acquisition time of 3 minutes. Using these analysis parameters, artifacts such as ion-induced sputtering and intermixing are negligible. Sputter depth profiling was done with a sputter gun attached to the LEIS chamber, positioned at 59° with respect to the sample surface normal, applying a 0.5 keV Ar⁺ beam at 100 nA average current. The sputtered area was fixed at 2×2 mm². The sputtered depth was calculated by verifying the necessary ion dose (at the specified energy) to sputter through a reference oxide sample with known thickness (determined by X-ray reflectometry).

The X-ray reflectometry measurements were performed using a PANalytical Empyrean X-ray diffractometer (Cu-K α radiation, 0.154 nm). The same equipment was applied in X-ray diffraction (XRD) mode, using in-plane grazing incidence XRD (GIXRD) geometry at a fixed incident angle (higher than the critical angle) to determine the structures of deposited films.

6.3 Results

6

To verify a possible influence of atomic arrangement on the process of oxygen-oxide interaction, the crystalline structure of the deposited films was characterized by X-ray diffraction. Figure 6.1 shows XRD measurements of reactively deposited thick and thin oxides. The main peak of 20 nm ZrO₂ is related to the monoclinic phase [21], and the three peaks of 20 nm MoO₃ correspond to the orthorhombic (α -MoO₃) phase [22]. Thin oxides with a thickness of 3 nm do not show any characteristic oxide peaks, being therefore amorphous. The broad features around a 2θ value of 50° are related to the Si(100) substrate and typically appear for thin oxide films.

It is known from literature that at room temperature the stoichiometric surfaces of ZrO₂ and MoO₃ are chemically inert to O₂ interactions [17, 23]. In order to verify the reactivity of the deposited oxide layers towards molecular oxygen, we exposed the films of 3 and 20 nm of ZrO₂ and MoO₃ to molecular isotopic oxygen (¹⁸O₂) for 25 min. Figure 6.2 shows as an example the obtained LEIS signals for the as deposited and ¹⁸O₂ exposed 3 nm films. Both spectra show characteristic surface peaks of ¹⁶O (indicated by the dashed line) and metal atoms (around 2500 eV) at the surface. The broad tail feature at the low energy side of the metal surface peak is related to scattering on sub-surface metal atoms [19]. The oxide films exposed to molecular isotopic oxygen exhibit no characteristic ¹⁸O peak (see dashed line labelled with ¹⁸O for the expected position from reference measurements). The LEIS signals from thick 20 nm films (not shown) exhibit similar behaviour. This analysis demonstrates that the as deposited surfaces can be considered as stoichiometric with a low defect concentration.

Figure 6.1: XRD measurements of reactively deposited oxide samples. Main peaks corresponding to monoclinic ZrO_2 and orthorhombic MoO_3 are indicated with dashed lines. The curves intensity are shifted for clarity.

On the contrary, exposure to atomic ^{18}O radical species leads to exchange of isotopic oxygen in metal oxide films. Figure 6.3 compares the LEIS signal from 20 nm MoO_3 before and after the exposure to isotopic atomic oxygen species. It is worth noting that the exposure does not significantly change the intensity of the metal peak, which is observed for all analyzed materials. With this, we can conclude that the observed ^{18}O peak corresponds to atoms that replaced ^{16}O in the topmost atomic layer, and not to additional oxygen species adsorbed on top of the surface metal atoms. This fact is in agreement with previous studies that revealed lattice exchange as the dominating diffusion mechanism in binary oxides [24].

Figure 6.2: LEIS measurements of as deposited (purple) and 25 min $^{18}\text{O}_2$ exposed (red) (a) 3 nm ZrO_2 and (b) 3 nm MoO_3 .

Figure 6.3: LEIS measurements of 20 nm MoO_3 as deposited (purple) and after exposure to atomic ^{18}O for 10 min (red).

Figure 6.4: Isotope profiles of samples exposed to ^{18}O after selected exposure time for (a) 3 nm ZrO_2 , (b) 20 nm ZrO_2 , (c) 3 nm MoO_3 and (d) 20 nm MoO_3 . The red lines represent the calculated diffusion profiles at the saturation exposure time (100 s for ZrO_2 and 450 s for MoO_3) using Equation 6.2 with parameters presented in Table 6.1.

Figure 6.5: Comparison between experimental (blue circles) and calculated evolution of surface ^{18}O concentration as a function of exposure time. (a) 3 nm ZrO_2 (b) 20 nm ZrO_2 (c) 3 nm MoO_3 (d) 20 nm MoO_3 . Both continuous (red) and dotted (grey) lines are obtained with values presented in Table 6.1. The red lines refer to calculations (discussed in Sections 6.4.1 and 6.4.2) considering complete surface coverage/exchange, while grey dotted lines refer to calculations with limiting surface exchange values.

Following this initial analysis, IEDP was performed for all samples. Figure 6.4 shows the obtained profiles of ^{18}O relative concentration for the different samples and exposure times as a function of sputtered depth, and Figure 6.5 shows the surface concentration evolution with exposure time. Here we represent the ^{18}O concentration by the ratio of the atomic fraction of this oxygen isotope to total oxygen (i.e., $^{18}\text{O}/(^{18}\text{O} + ^{16}\text{O})$). The atomic fractions were determined by using a pure metal oxide as reference in order to avoid the influence of matrix effects [25] and with appropriate corrections of the ^{18}O signal for differences in sensitivity factor compared to ^{16}O [26]. No significant difference in the obtained profiles is observed between thin amorphous and thick polycrystalline samples. A slight difference in final oxygen diffusion depth (~ 1 monolayer depth, or < 0.5 nm) observed between amorphous and polycrystalline films is within systematic uncertainty (estimated as 0.3 nm for ZrO_2 and 0.4 nm for MoO_3). One can see that in all cases the outermost surface and in-depth concentration of ^{18}O gradually increases with exposure time, until saturation is reached. After that, further exposure does not lead to considerable increase in isotope concentration. The saturation of surface exchange occurs at about 65% to 75% for all samples, while the maximum diffusion depth of

isotopes is ~ 1 nm for ZrO_2 and ~ 2.5 nm for MoO_3 . The saturation time is equal to ~ 100 s for ZrO_2 and 450 s for MoO_3 . No difference in preferential sputtering due to incorporation of ^{18}O was observed [27], as verified by comparing the evolution of total oxygen concentration between exposed and as deposited samples.

The reversibility of the transport profiles was checked by consecutive exposures to ^{16}O and ^{18}O . Initially, the as-deposited oxide films were exposed to ^{16}O atoms (for 2400 s). The film was subsequently exposed to ^{18}O atoms and analyzed by LEIS-IEDP. These samples presented the same isotopic evolution as presented in Figures 6.4a-d. After this, the same samples were again exposed to ^{16}O . The profiles were shown to be reversible (i.e. ^{18}O was replaced by ^{16}O) and not affected by the consecutive exposures. The performed experiments indicate that it is unlikely that the saturation and evolution of the surface exchange and in-depth concentration profiles are governed by a possible substoichiometry of the (surface layer) of the as-deposited films.

Since the observed diffusion depth of isotopic oxygen species is in the range of few nm, special attention should be paid to potential broadening or modification of sputter depth profiles by ion-induced intermixing, as recently pointed out in literature for complex mixed oxide materials [28]. Based on TRIM software, it can be expected that 0.5 keV Ar^+ ions incident at 59° with respect to the surface normal have a penetration depth in ZrO_2 and MoO_3 with a mean value of 1 nm and induce atomic recoil of up to 2 nm [29]. Theoretically, especially for the case of ZrO_2 , one might therefore argue that oxygen exchange is only taking place in the topmost surface atomic layer and that the detection of oxygen in-depth can be a result of sputter-induced effects. However, possible inaccuracies in the stopping powers for low energies, allied to the fact that dynamic changes in the target are not taken into account in these simulations, might lead to variations in calculated profiles that influence the analysis in the limit of ultrathin films. Therefore, in order to assess the effect of sputter-induced intermixing, we followed an experimental approach to compare the isotope profiles in Figure 6.4 with isotope exchange profiles for atomic O exposure of Mo and Zr metal films in Figure 4.6. This method was chosen as the isotope profiles in those experiments were obtained for O exposure times below the time required for obtaining a saturation oxide thickness on the metal film, guaranteeing that diffusion effects are present in the system. It is clear from this comparison that the in-depth decay of the ^{18}O concentration for isotope exchange in oxides films (Figure 6.4) looks quantitatively similar to the isotope profiles obtained for O exposure in non-saturated oxide films on metals (Figure 4.6). This fact serves as a strong indication that the profiles must result from actual diffusion of oxygen and cannot be solely explained by sputter-induced intermixing. In addition, the results in Figure 4.6 also show that the decay of the measured total O concentration at the metal oxide/metal interface is much faster than the decay of the isotopic O concentration within the metal oxide film. This provides additional evidence that the intermixing of oxygen by the ion sputter beam has a shallower depth range compared to isotope diffusion, which is probably related to preferential sputtering of oxygen with respect to the metal atom. Another observation to be taken from Figure 4.6 is that for the ZrO_2/Zr interface the oxygen decay is much steeper than for the MoO_3/Mo interface. Accounting for the expected oxide thickness determined

by Static DP (grey dashed lines in the figure) such difference might be related to the lower enthalpy of formation of ZrO_2 (-1097.4 kJ/mol of oxide formed) compared to MoO_3 (-745.1 kJ/mol of oxide formed) [30]. The more negative enthalpy of ZrO_2 implies in a lower probability of: i) oxygen preferential sputtering (due to the higher binding energy), and ii) extension of the oxide profile due to sputter-induced reactions. For MoO_3 , the preferential sputtering of oxygen is a more significant effect (as also observed and discussed in Chapter 3). Even though these effects do not interfere in the depth of isotope diffusion, they might affect the shape of the observed profile.

In all, the decoupling of sputter and diffusion effects on sputter depth profiling analysis is still a topic that requires further development. Ion-collision models should be improved in order that one can unambiguously discern between the effects of sputter-induced intermixing and diffusion of isotopic oxygen species in the limits of ultrathin films. However, assuming the analysis above mentioned, we conclude that even though the actual shape of the profile may be affected by ion-beam induced processes, the in-depth observation of ^{18}O must be related to the diffusion of O atoms. With that, we explore the physical reasons that may result in the isotopic profile in the analyzed oxides.

6.4 Discussion

Previous investigations of thin metal films exposure to atomic oxygen at room temperature showed that Mo and Zr form oxide films with a limited thickness of about 4 and 5.5 nm, respectively, after which further growth of oxide ceases [31]. As first explained by Cabrera and Mott [32], oxygen and/or metal transport across thin oxide films at low temperature is assisted by an electric field generated between adsorbed (electronegative) O species at the surface and the metal underneath. As the oxide film thickness grows, the electric field across the oxide decreases, until it becomes too low to induce diffusion. Since thermal diffusion is negligibly small at this temperature, the growth processes ceases. Therefore, at first glance it may seem surprising that oxygen diffusion at room temperature occurs in fully oxidized metal oxide films. However, for metal oxides, it is reported in literature that surface phenomena such as adsorption, can also lead to a generation of an electric field at the oxide surface [12, 33]. For n-type oxides, such as MoO_3 and ZrO_2 [34, 35], when an acceptor specie approaches the surface, the unfilled orbital of the specie extracts electrons from the oxide. The accumulation of negatively charged species at the oxide surface induces the formation of an electric field near the surface. The low free carrier density and poor screening length in the oxide impede the screening of the formed electric field, which leads to charge redistribution and creates a space charge region (SCR) near the oxide surface [12]. Upon the adsorption of acceptor species, electrons are depleted from the surface (accumulation of positive charges), which leads to an upward shift of the energy band edges at the oxide surface. For a donor specie, the opposite effect occurs and a downward band bending is observed. This phenomenon is analogous to the process described by Schottky and Mott on metal/semiconductor interfaces [12, 36].

We propose that the adsorption of atomic oxygen induces the formation of an

electric field and, consequently, the formation of an SCR at the near-surface region of both oxides studied. Since atomic oxygen is an acceptor specie, a negative field is generated (upward band bending). This field assists the diffusion of mobile oxygen, metal and/or vacancy species within the SCR, thereby explaining significant oxygen diffusion in the topmost few nanometer of the film. It was previously reported in literature [16, 37] that the interaction between molecular oxygen (at relatively high pressures) and ozone with n-type oxides at room temperature leads to an upward band bending. In the work by Nowotny [16], it is argued that oxygen rapidly chemisorbs to the surface, forming singly ionized molecular and atomic species, which slowly diffuse into the oxide. Lampimäki et al. [37] demonstrated with high-pressure XPS analysis that titanium and iron oxides when exposed to ozone generate a SCR – and a resulting electric field – of only few nanometer thickness. However, the process of isotope exchange was not explored in these studies. For our analysis, we take into consideration these previous studies and assume the experimentally observed isotopic diffusion depth to be related to the electric field within the oxide SCR. With that, we applied a drift-diffusion model to obtain values of band bending, charge defect density and kinetic parameters of diffusion for all analyzed cases.

6.4.1 Drift-diffusion model for RT isotopic exchange

As previously described, it is assumed that the formation of a SCR alters the concentration of mobile charged species with respect to the bulk concentration, while the associated electric field (E) assists their diffusion. According to literature, the kinetics of oxygen transport is limited by the migration of oxygen vacancies ($V_{\text{O}}^{\bullet}$) in a lattice [38]. Therefore, in the present case, the diffusion of isotopic oxygen within the oxide will be driven by the concentration gradient (i.e. as in a classical temperature-induced diffusion) assisted by the field-enhanced diffusion of charged species in the SCR, which enhances the diffusion of O species in general (regardless of its isotopic label). Using a description analogous to the one applied by De Souza [39], one possible pathway for the forward exchange reaction between oxide and atomic oxygen can be written in absolute terms as:

The atomic specie chemisorbs (subscript chem) to the oxide surface and reacts with an oxygen vacancy placed on the outermost layer of the oxide ($x = 0$), penetrating the film. The oxygen ion is then transferred through the space charge region ($0 < x < \lambda$), with thermal (T) and field-induced (E) mechanisms influencing the atomic motion. Finally, the oxygen will diffuse in the bulk of the oxide (considered here as the region beyond the space charge layer, $x = \text{bulk}$), where charge distribution is assumed to be neutral and only thermal processes are considered [40].

The transport equation that describes the entirety of the diffusion process is obtained by implementing a field-driven (drift) term to the Fickian-type diffusion equation, as described in Equation 6.2:

$$\frac{\delta C^*(x, t)}{\delta t} = D_e^* \nabla^2 C^*(x, t) - \mu \vec{E} \nabla C^*(x, t) \quad (6.2)$$

where C^* is the atomic fraction of diffusing oxygen specie, in this case tracer ^{18}O [41], referred in the text as “isotopic concentration” for simplicity, μ is the ionic mobility, t is the exposure time and x is the depth. The mobility μ can be approximated by the Nernst-Einstein’s relation $\mu = (qD_i^*)/(k_bT)$, where k_b is the Boltzmann constant, T is the absolute temperature and q is the charge on the diffusing specie ($-2e$ for oxygen, with e being the electronic charge) [42]. D_i^* represents the intrinsic diffusion coefficient of oxygen species in the oxide, i.e. without influence of charge effects. Therefore, D_i^* can be approximated to the thermal self-diffusion coefficient of oxygen in the oxide lattice at room temperature [43, 44]. The theoretical analysis developed by Yang et al. [45] suggests that, at low O_2 pressures, the oxygen self-diffusion coefficient at room temperature for single-crystal monoclinic ZrO_2 should be in the order of $10^{-30} \text{ m}^2\text{s}^{-1}$. A similar study was not found for MoO_3 . However, with similar values for defect formation and oxygen binding energies for ZrO_2 and MoO_3 presented in literature [46, 47], we assumed D_i^* of both oxides to be in the same order of magnitude. The coefficient D_e^* designates the field-enhanced diffusivity at the space charge region. This concept was initially pointed-out in our previous study on the diffusion of energetic oxygen ions in transition metals [43], where we applied the term “radiation induced diffusivity” to describe the coefficient influenced by the total concentration of vacancies/interstitials generated in the oxide. In the present case, we extend the previous analysis and determine values for D_e^* based on formalism demonstrated by Meyer et al. [38] and further developed by De Souza and Martin [48], in which the vacancy concentration within the SCR and, consequently, the derived field-enhanced diffusivity are correlated to the expected surface potential generated by the oxygen-oxide interaction:

$$D_e^* \approx D_i^* \exp \frac{q(\Phi_0 - \Phi_b)}{k_bT} \quad (6.3)$$

where Φ_0 and Φ_b respectively represent the electrostatic potential at the surface and in the bulk.

The electric field distribution $\vec{E}$ was obtained by solving Poisson’s equation. Considering that the charge density in the space charge layer is not influenced by the ion exchange (the charge density only refers to stoichiometry defects, and it is assumed that the exposure to atomic oxygen does not change the oxide stoichiometry, as also validated by our experiments), the time-independent form of Poisson’s equation can be used:

$$\nabla \vec{E} = \nabla^2 \Phi = -\frac{\rho(x)}{\varepsilon \cdot \varepsilon_0} \quad (6.4)$$

where $\rho(x)$ is the space charge density, ε_0 is the vacuum permittivity and ε is the relative permittivity of the oxide. In this study, we apply Schottky’s approximation to solve Poisson’s equation [12, 48, 49]. In this approximation, the charges are assumed to be homogeneously distributed in the SCR with a density of N_d , while the potential is set to a fixed value at the surface (Φ_0) and zero in the bulk (Φ_b). As previously mentioned, in our analysis we assume the experimentally observed maximum diffusion depth of isotopes to be equivalent to the thickness of the SCR.

Finally, the solution of Equation 6.2 requires an initial condition and two boundary conditions to be determined. The right boundary is set as $\nabla C^*|_{x \rightarrow \infty} = 0$ and for the left boundary we assume that the net injected flux of tracer species (j_{18}^{in}) obeys Fick's first law:

$$j_{18}^{in} = k_e^* (C_g^* - C^*(x=0, t)) \quad (6.5)$$

where k_e^* is the effective surface exchange coefficient [48, 50, 51], $C^*(x=0, t)$ is the surface tracer concentration at time t , and C_g^* is the isotope fraction in the gas. Values of ε were based on literature [52], while N_d and the surface potential Φ_0 were obtained from the best fit of the system of Equations 6.2 to 6.5 to experimental results [33, 52–55].

6.4.2 Model implementation and analysis of parameters

Based on the described model and mentioned assumptions, we applied a numerical finite difference method to solve the system of differential equations and obtain the values for N_d , Φ_0 and k_e^* with best fit to the observed diffusion profiles. Table 6.1 shows the best fit values of N_d , Φ_0 and k_e^* , and the corresponding values of SCR and D_e^* for all cases. Figure 6.4 and Figure 6.5 compare the experimental and calculated values for in-depth saturation profile and surface concentration evolution, respectively. It is seen in Figure 6.4 that the profiles calculated for 100 s exposure of ZrO_2 and 450 s exposure of MoO_3 are in agreement with the obtained experimental data. However, the model does not justify the experimentally observed saturation of the diffusion profiles (i.e. variation of oxygen concentration in depth). That is, for longer periods of exposure, the model predicts an increase of isotopic concentration within the SCR. Similarly, in Figure 6.5, the theoretical model also predicts a continued increase of oxygen exchange (close to unity) with exposure time, which is not confirmed experimentally.

The calculated results are sensitive to the set of parameters used. Therefore, we continue the discussion by exploring the validity of the assumptions taken for solving the system of equations, and the consequent parameters obtained by the fitting. For that, we compare the obtained results with data previously reported in literature. We also look into the possible reasons for the experimentally observed saturation of oxygen exchange and diffusion.

Table 6.1: Values describing experimental data with results presented in red on Figures 6.4 and 6.5.

	Input parameters SCR [nm]	N_d [m^{-3}]	Best fit parameters Φ_0 [eV]	k_e^* [ms^{-1}]	Calculated parameters D_e^* [m^2s^{-1}]
3 nm ZrO_2	1.2	4.1×10^{-26}	-0.28	4.5×10^{-12}	9.2×10^{-22}
20 nm ZrO_2	1.0	4.0×10^{-26}	-0.28	3.6×10^{-12}	5.5×10^{-22}
3 nm MoO_3	2.3	2.1×10^{-26}	-0.28	2.3×10^{-12}	9.2×10^{-22}
20 nm MoO_3	2.5	1.8×10^{-26}	-0.29	2.9×10^{-12}	1.2×10^{-21}

We begin with addressing the saturated maximum diffusion depth of isotopes and the obtained values of charged carrier concentration. One key point of our

analysis lies in the assumption that the maximum diffusion depth of isotopes is directly linked to the thickness of the SCR. From this assumption, we obtain values of N_d higher than typically reported values of bulk charge carrier concentration of undoped oxides [12]. An important observation, however, is that according to the generalized treatment of space charges at interfaces in crystalline solids, the concentration of charged species in the SCR might differ considerably from the bulk, especially when the surface is exposed to strongly oxidizing conditions or in the presence of surface potentials [48, 56, 57]. This initial assumption for maximum diffusion depth also influences the obtained values of Φ_0 and, consequently, D_e^* . However, the values of Φ_0 shown in Table 6.1 are in agreement with measurements of the shift in electronic states for different n-type oxides exposed to molecular oxygen and ozone at room temperature, reported ranging from 0.2 eV to 0.9 eV [16, 37]. Additionally, the comparison between the diffusion of oxygen observed in this study and previous analysis in literature [4, 23, 58, 59] provides a strong indication that the in-depth diffusion kinetics is mainly determined by the surface potential generated from the oxygen adsorption. If only thermal processes and concentration gradients would act as driving force for diffusion, we imagine that one of the two following scenarios would be detected: i) the oxygen diffusion would not surpass the outermost oxide layer in the analyzed time-frame (since the reported bulk diffusion constants of oxygen in the studied oxides are in the order of $10^{-30} \text{ m}^2\text{s}^{-1}$ at room temperature [45]); or ii) in case our deposited films had a much higher thermal/bulk diffusion constant than reported reference values, the profile would not saturate within a limited diffusion depth. Finally, it is interesting to note that the obtained values of D_e^* are similar to the estimated field-induced diffusion term described in our previous oxygen ion diffusion study [43]. This might be an indication that the space charge layer formation and field build-up on oxides is present whenever atomic species are in contact with the oxide surface, independent of the initial state of the oxygen specie to which the sample is exposed to. We would like to point out, however, that the assumed bulk-diffusivity directly influences the derived values of surface potential and diffusion constants. So the obtained values should be considered as realistic estimates. Furthermore, the comparable oxygen diffusion in both amorphous and crystalline oxides indicates a negligible influence of structure on the exchange and diffusion of oxygen at room temperature. With similar values of surface potential obtained for MoO_3 and ZrO_2 , the lower permittivity of ZrO_2 results in the formation of a thinner SCR. Such an effect was also observed in the comparison between SCR depths of Fe_2O_3 and TiO_2 [37]. This fact supports the hypothesis of the oxygen exchange and diffusion processes to be mainly dominated by the material electronic properties.

The limited surface exchange and diffusion profile observed in practice can be related to several causes. It is reported in literature [37] that space charge effects might also lead to a limited surface coverage of the adsorbed oxygen species, influencing the concentration of isotopic species available for exchange. Other sources for the limited saturation may be a limited isotopic purity (e.g. caused by exchange reactions between ^{18}O atoms with ^{16}O atoms on oxide materials in the plasma source) and the presence of oxygen atoms on the surface that do not participate in exchange reactions. Unfortunately, there is no possibility to probe experimentally

the isotopic purity of our atomic oxygen source. However, a restriction of the maximum surface isotope concentration to 80% in the calculation (grey dotted curves in Figure 6.5) for both oxides leads to a better agreement of surface exchange values between model and experimental data for higher exposure times. Nevertheless, this assumption is not enough to exactly reproduce the experimentally observed saturation of the exchange and diffusion profiles. This indicates a higher complexity of the dynamics of surface exchange and diffusion processes, not covered by the adopted model.

In view of the above discussion, we propose the oxygen-oxide interaction at room temperature to proceed as schematized in Figure 6.6: the atomic oxygen specie (^{18}O in the present case), when in contact with the oxide, becomes negatively charged and induces the formation of a depletion layer at the oxide surface and consequently a negative field (pointing in the direction from the substrate towards the surface). This field promotes the redistribution of positively charged species near the surface and consequently enhances inward diffusion of oxygen. Meanwhile, surface reactions between adsorbed oxygen (^{18}O) and oxygen on the surface (^{16}O) may occur, e.g. through exchange of O on coordinately unsaturated sites with O on regular lattice sites, or by reactions of O radicals with surface O atoms, resulting in O_2 desorption, thereby generating vacancy sites that promote O adsorption and, consequently, isotopic exchange. Therefore, the formed SCR represents a highly reactive region where isotope exchange is observed.

Figure 6.6: Schematic diagram of the effect of oxygen chemisorption on surface charge distribution for a n-type oxides. (a) Flat band model: before oxygen exposure. (b) Band model representing the effect of oxygen chemisorption on band bending, and consequent interaction of isotopic oxygen (^{18}O - purple) with oxygen in the oxide lattice (^{16}O - blue) and vacancies (red squares).

In the context of room temperature exposure of oxides to atomic oxygen, the exchange and diffusion are dominated by the field-induced drift, and contrary to

oxides exposed to molecular oxygen [16], the incorporation is fast, as the limiting step of molecular dissociation is not present. The depth and dynamics of exchange will be mainly dependent on the electronic properties of the oxide, with negligible influence of crystalline structure. This would justify the reversible near-surface behaviour for both thin and thick ZrO_2 and MoO_3 . Comparatively, in our previous study on the oxidation of thin metal films by atomic oxygen at room temperature (where non-oxidized metal was present below the formed oxide film) [31], we have identified the depth of the isotope diffusion to be greater than observed in the present analysis. This increased isotope diffusion might be attributed to the influence of the Cabrera-Mott field that drives oxide growth. Typical Cabrera-Mott fields are in the order of 10^9 V/m [60], which is about an order of magnitude larger than the fields expected in the space charge region of oxide films characterized in the present work. This phenomenon appears as an interesting fact to be further investigated regarding the role of the space charge in the kinetics of metal oxidation and oxygen transport in thin films.

6.5 Conclusions

Our study demonstrates room temperature oxygen exchange and diffusion in amorphous and polycrystalline films of zirconium (ZrO_2) and molybdenum (MoO_3). The results show that, for all analyzed oxide films, oxygen exchange and diffusion reach saturation in a few minutes (< 10 min). The isotopes were found at maximum depth of approximately 2.5 nm for MoO_3 and 1 nm for ZrO_2 . The surface exchange reached a maximum of 65% to 75% for all the analyzed samples. Our analysis suggests that, due to its acceptor nature, atomic oxygen becomes negatively charged when in contact with the oxide surface. The accumulation of negatively charged species at the oxide surface induces the formation of an electric field, and as a result a space charge region is formed. We found that these processes are determining factors for the diffusion of oxygen at low temperatures. The generated field is responsible for the increase in diffusion coefficient, whereas the saturation of exchange and diffusion are most likely related to the space-charge layer thickness and distribution of charged species in the analyzed thin films. The oxide structure, however, does not play a role in oxygen diffusion at the experimental conditions considered. By applying a drift-diffusion model, we obtained values of the surface potential, and exchange and diffusion coefficients for the films analyzed. All oxides presented similar values of the surface potential (~ 0.28 V), with effective diffusion and exchange coefficients varying from 5.5×10^{-22} to 9.1×10^{-21} m^2s^{-1} and from 2.3×10^{-12} to 4.5×10^{-12} ms^{-1} respectively. We discussed the implications of charge dynamics to the applied diffusion model, revealing that the existing models might be insufficient to completely describe the complex dynamics of oxygen transport in oxides at low temperatures.

This study indicates that the presence of molecular dissociation processes (such as exposure to ultraviolet light or electron beam), or application of an external electric field might lead to higher exchange rates and species diffusion in an oxide thin film. Furthermore, we demonstrate LEIS-IEDP as a robust method for determining surface exchange and diffusion under exposure conditions where interaction results

in fast near-surface processes.

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Valorization and Outlook

Thin transition metal and oxide films play a crucial role in the high-tech industry. This importance is mainly related to their varied relevant associated properties, e.g., the high catalytic activity of ruthenium (in both metal [1] and oxide [2] forms), the high dielectric constant of HfO_2 [3], the high thermal and chemical stability of ZrO_2 [4], among others. This extended range of properties makes them suitable for applications from insulating layers in micro-electronics [5] and protective layers in soft x-ray optics [6], to solid oxide fuel cells [7, 8] and catalytic devices [9, 10]. All these distinct applications, however, have one thing in common: the need for control and stability of the composition of thin films in order to maintain the properties for which a specific material is selected.

Accurate thickness and composition measurements on such thin films are not trivial. In this context, Low Energy Ion Scattering (LEIS) appears as a valuable tool for quantitative analysis of oxides, since it provides a relatively fast and non-destructive way to measure the atomic composition of the topmost layer of materials with sub-nanometer resolution [11]. In this thesis we have contributed to the advance of this important characterization technique by both: (i) demonstrating the influence of surface composition on low energy ion neutralization, proposing a rule for selection of reference samples for the correct quantitative analysis of compound surfaces (Chapter 3) and (ii) by validating its application as a non-destructive in-depth analysis of sample composition for oxide films on metal (Chapter 4). With that, LEIS poses itself as a fast, straightforward technique with now a robust method for characterization of surface oxide growth and composition – all characteristics that are valuable for the composition analysis of surfaces at an industrial level.

Regarding fundamental knowledge on oxygen-thin films interaction, the results and analysis developed in Chapters 4, 5 and 6, which demonstrate the key physical aspects that dictate species migration in metals and oxides at low temperatures, can be directly transposed to industrial applications. For instance, this knowledge can be used in the selection of top layers that better resist to oxidation at the aimed conditions, or for the development of strategies to tackle film degradation and increase device lifetime, contributing to their implementation. One of the highlights was the observation that at low temperatures, the surface coverage of atomic species plays a more important role in oxidation and oxygen diffusion resistance than the film crystal structure. Knowing this, the development of solutions that decrease oxygen accumulation, such as dosing of reactants or annealing to temperatures that increase oxygen desorption are suggested to contribute more to lifetime enhancement than the engineering of the thin film structure. Furthermore, this thesis brings a deeper understanding of the oxidation kinetics induced by oxygen radicals exposure. This

knowledge is directly related to techniques where films are exposed to O radicals or other highly reactive O species (such as O ions and ozone), or techniques where films are exposed to high energy photons or electrons in presence of O containing species. For example, as described in Chapter 4 and Chapter 5, the oxide growth behaviour upon direct exposure to atomic oxygen is the same as previously reported for metals oxidized by the method of photon-assisted oxidation. Therefore, the kinetics of oxide growth and metal properties that dictate oxide formation discussed in these chapters can be used to improve processes involving the photon-assisted oxidation method. This method is relevant for industrial production of high quality oxides [12], as it enables the selective enhancement of anion species at significantly lower synthesis temperatures compared to the typically applied thermal oxidation, and can be implemented both during oxide synthesis as well as a post-deposition step.

Though important knowledge has been developed in this thesis, the oxygen-metal/oxide interaction is an area with much space for further development. Some of the topics that require more investigation are, for example, (i) the formation of a space charge layer within the oxide film during oxidation and its influence on the oxide growth, as this process is usually disregarded in existing growth models; (ii) how the space charge layer formed in oxides evolves with temperature and improvement of equations to model it; (iii) the relation between oxide growth, oxide crystallinity and substrate structure; (iv) determining the evolution of surface potential with atomic oxygen coverage, identifying the lowest coverage necessary to initiate and maintain a field-driven diffusion mechanism; and (v) how these processes are extended to binary metallic or compound (sulfide, silicide) thin films, among others. With the continuous increase of nanometer-thick films applications, monolayer changes in composition (and hence properties) are becoming progressively relevant. Therefore, the continuous development of the understanding of nanoscale oxidation and oxygen diffusion is crucial for the improvement of the design and lifetime development of technologically relevant systems.

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Summary

This thesis aims to deepen the understanding on the interaction between oxygen and transition metal (TM) and transition metal oxide thin films, together with the development of knowledge related to the low energy ion scattering (LEIS) technique. To that end, topics from the influence of oxygen on the neutralization of slow ions and the use of reionized ions for thickness analysis, to the role of oxidative specie and temperature on oxygen-solid interaction are covered throughout the chapters. The work described in the thesis builds on an extensive experimental analysis, performed on thin films of TM (and their oxides) from groups IV to VIII of the periodic table, with various thicknesses and crystalline structures. The use of mathematical models enabled the determination of important parameters, such as ion neutralization efficiency on different surfaces, energy barriers of diffusion of metal cations through oxides during oxidation and oxygen diffusion constants in oxides, among others.

LEIS is well-known for being a high precision, non-destructive characterization technique, with a straightforward methodology for quantification of the atomic composition of surfaces. However, the quantification derived from LEIS analysis is directly related to the neutralization efficiency of the detected ions (typically He^+ or Ne^+) scattered from a specific surface. A detailed analysis regarding the charge exchange of He^+ on metal and metal oxide samples of Mo, Hf, Ru, and Al (as reference material) was performed in order to identify the neutralization mechanisms present on oxide and metal surfaces. It was verified that the presence of oxides modified the neutralization efficiency of TM surfaces, but not of Al. It is suggested that the increased neutralization in oxidized Ru, Hf and Mo originates from the presence of the O 2s band. This band is in resonance with the He 1s level, which allows for a quasi-resonant neutralization mechanism (qRN). On the other hand, a decrease of the strong Auger neutralization for metallic Al upon oxidation may compensate for the increase in neutralization by the qRN, leading to a similar neutralization behavior of Al in both states. These results enabled the determination of a proper procedure for quantitative characterization of transition metal compounds by LEIS. Further exploring the resources of LEIS analysis, a method for non-destructive determination of metal oxide film thickness was demonstrated, named LEIS static depth profiling (DP). This method is based on the analysis of reionized ions scattered from subsurface atoms, and was shown to be highly sensitive to the thickness of an oxide top layer. These developments of the LEIS technique provided the opportunity of correlating a precise surface atomic quantification with the grown oxide thickness, which was paramount for the precise composition analysis of surfaces during oxidation and oxygen diffusion processes explored in this thesis.

Following the advances of LEIS analysis, a thorough investigation of the oxidation of transition metal films (Zr/Hf, Ta, Mo and Ru) at temperatures ranging

from 298 K to 473 K, upon the exposure to molecular oxygen and atomic oxygen was performed. The in-vacuum analysis by LEIS static DP and isotope tracing, in-situ ellipsometry and X-ray photoelectron spectroscopy (XPS), provided a complete picture of the dynamics of oxide growth without interference of external contamination, which was critical for verifying important aspects previously neglected in experimental oxidation kinetics analysis. A key finding from our studies was the demonstration that the surface concentration of reactive atomic species is the determining growth factor in the oxidation process at low temperatures. At low temperatures, the oxide growth is enabled by the formation of an electric field, a consequence of a formed contact potential. However, the understanding of the factors influencing the formation, magnitude and preservation of this potential were still somewhat fragmentary. The results presented in this thesis provide concrete evidence on the influence of the oxidative environment on potential formation and consequent oxide growth for individual materials. We present a direct relation between atomic oxygen coverage, surface potential and oxide growth dynamics. For molecular oxygen exposures, surface effects such as the competition between desorption and adsorption, together with coverage limitations lead to the setting of a lower potential, a factor not observed for direct atomic oxygen exposures. In all cases, the initial metal crystalline structure did not play a significant role in oxide growth. The overall picture shows that in cases where the presence of atomic oxygen species on the surface is not hindered by desorption or limited by coverage, the oxidation kinetics at low temperature can be directly related to the metal electronic properties, e.g. a metal with a more negative work function will present the formation of a thicker oxide.

A similar mechanism was verified for the diffusion of oxygen in TM oxides (ZrO_2 and MoO_3). The direct exposure to atomic oxygen led to an unexpected oxygen diffusion at room temperature in fully oxidized metal oxide films. At this temperature, the oxygen interaction with the oxides resulted in a fast diffusion of oxygen (up to eight orders of magnitude higher than estimated value for bulk) to a limited depth, and again no influence of the crystalline structure of the films was observed. The developed analysis suggested that the formed isotope profiles are a consequence of the electric field formed upon chemisorption of reactive oxygen species on the oxide surface and associated accumulation of charged species near the surface (upward band bending), which was substantiated through comparison with band bending measurements reported in literature and calculations with a drift-diffusion model. This work shows the first experimental verification of oxygen diffusion in stoichiometric oxides at room temperature, detected by means of isotope tracing analysis. The analysis developed throughout this thesis allows for putting forward the hypothesis that these observations on field-induced diffusion can be extended to other acceptor-type adsorbents, such as nitrogen: if radical species are directly in contact with the metal or oxide layer and enough coverage is present, a field assisted diffusion will be established. These results contribute to the better characterization and understanding of oxygen-thin films interaction, and might have a significant impact, not only in the design of materials and synthesis of thin metal and oxide films for a wide range of practical applications, but also for development of processes where reactive species are put in direct contact with thin layers.

Samenvatting

Het doel van dit proefschrift is het verdiepen van de kennis op het gebied van interactie tussen zuurstof en dunne films van overgangsmetalen (OM) en hun oxides. Daarnaast beschrijft dit proefschrift ook de ontwikkeling van kennis op het gebied van lage-energie ionenverstrooiing (LEIS) die voor dit specifieke onderwerp relevant is. De hoofdstukken in dit proefschrift omvatten onderwerpen die reiken van de invloed van zuurstof op neutralisatie van langzame ionen en het gebruik van gereïoniseerde ionen voor dikteanalyse, tot de invloed van oxiderend molecule of atoom en temperatuur op de interactie tussen zuurstof en vaste stof. Het in dit proefschrift beschreven werk is gebaseerd op uitgebreide experimentele analyse van dunne films van OM (en hun oxides) uit de groepen IV tot VIII van het periodiek systeem, met verschillende diktes en kristallijne structuren. Met behulp van wiskundige modellen zijn belangrijke parameters, zoals neutralisatie van ionen op verschillende oppervlakken, energiebarrières voor diffusie van metaal-kationen door oxides en diffusieconstanten van zuurstof in oxides bepaald.

LEIS staat bekend als nauwkeurige, niet-destructieve techniek om de atomaire samenstelling van oppervlakken te bepalen. Echter, de kwantificatie van LEIS-resultaten is afhankelijk van de neutralisatie (of ionenfractie) van de gedetecteerde ionen (meestal He^+ of Ne^+) na verstrooiing op het te meten oppervlak. Een gedetailleerde analyse van de ladingsuitwisseling tussen He^+ en metalen en metaaloxides van de materialen Mo, Hf, Ru en Al (als referentiemateriaal) is uitgevoerd om de neutralisatiemechanismen op metalen en oxides te vergelijken. Hierbij is vastgesteld dat de aanwezigheid van zuurstof de neutralisatie op OM oppervlakken verandert, terwijl dit niet het geval is op een Al oppervlak. De veronderstelling is dat de toename van neutralisatie op oxides van Ru, Hf en Mo het gevolg is van de O 2s band, die in resonantie is met het He 1s energieniveau, waardoor een quasi-resonerend neutralisatieproces (qRN) op kan treden. Bij oxidatie van Al treedt er waarschijnlijk een afname op van de sterke Auger-neutralisatie door metallisch Al, die de toename van neutralisatie door qRN compenseert, zodat bij Al de neutralisatie niet afhangt van oxidatietoestand. Met behulp van deze resultaten kon een goede procedure bepaald worden voor kwantificatie van oppervlakteconcentraties op oxides van overgangsmetalen met behulp van LEIS. Daarnaast is aangetoond dat de methode bekend als LEIS statisch diepteprofiel, toegepast kan worden om op niet-destructieve wijze de dikte van metaaloxidefilms op metaal te bepalen. Deze methode is gebaseerd op de analyse van gereïoniseerde ionen die verstrooid zijn op atomen onder het oppervlak en is zeer gevoelig voor de dikte van de oxidefilm. Deze ontwikkelingen van de LEIS-techniek maakten het mogelijk om zowel de oppervlakteconcentratie op, als de dikte van oxidefilms te kunnen bepalen, wat belangrijk was voor de compositieanalyse zoals die gebruikt is bij het bestuderen van oxidatie- en zuurstofdiffusieprocessen in de rest van dit proefschrift.

Na de ontwikkeling van de LEIS-techniek, is er gedetailleerd onderzoek gedaan

naar de oxidatie van OM films (Zr/Hf, Ta, Mo en Ru) bij temperaturen tussen de 298 K en 473 K, bij blootstelling aan moleculair en atomair zuurstof. Dit onderzoek is uitgevoerd met in vacuo LEIS statische diepteprofielen en isotopenuitwisseling, Röntgen-foto-elektronspectroscopie (XPS) en in situ ellipsometrie. Op deze wijze kon een compleet beeld van de dynamica van oxidatieprocessen bepaald worden, zonder invloed van externe contaminatie, wat van belang was om aspecten van de oxidegroei te bestuderen die voorheen nog onvoldoende belicht waren. Eén van de belangrijkste uitkomsten van ons onderzoek, is de constatering dat de oppervlakteconcentratie van reactieve atomaire zuurstof de bepalende factor is voor oxidegroei bij lage temperatuur. Bij lage temperaturen wordt oxidegroei mogelijk gemaakt door de vorming van een elektrisch veld, resulterend uit een opgebouwde contactpotentiaal. De factoren die de vorming, grootte en instandhouding van deze potentiaal bepalen, zijn nader bestudeerd. De resultaten in dit proefschrift laten concreet bewijs zien dat de oxiderende atmosfeer bepalend is voor deze potentiaal en daarmee de oxidegroei voor een specifiek materiaal. We laten de relatie zien tussen atomaire zuurstofbedekking, oppervlaktepotentiaal en dynamica van de oxidegroei. Bij blootstelling aan moleculair zuurstof, zorgen effecten zoals het evenwicht tussen desorptie en adsorptie tot een limiet aan de bedekking en daarmee een lagere contactpotentiaal. Bij blootstelling aan atomair zuurstof speelt een dergelijke beperking in de praktijk geen rol. In alle gevallen is er geen significante invloed van de initiële kristallijne structuur van de metaalfilm gevonden. Samenvattend kan gesteld worden dat in gevallen waarin de bedekking van atomair zuurstof niet beperkt wordt door desorptie of andere factoren, de oxidatiekinetica bij lage temperaturen direct in verband kan worden gebracht met de elektronische eigenschappen van het bestudeerde metaal, in zoverre dat bij een metaal met een meer negatieve potentiaal (kleinere elektron-uittreearbeid) een dikker oxide gevormd wordt.

Een vergelijkbaar diffusiemechanisme is gevonden bij diffusie van zuurstof in OM oxides (ZrO_2 en MoO_3). Blootstelling van volledig geoxideerde films van deze materialen aan atomair zuurstof bij kamertemperatuur leidde, tegen de verwachting in, tot meetbare zuurstofdiffusie. De berekende diffusieconstante is tot acht keer hoger dan de geschatte diffusieconstante in bulk, terwijl diffusie beperkt blijft tot geringe diepte en er geen invloed van kristallijne structuur van het oxide waargenomen is. De ontwikkelde analyse van de resultaten suggereert dat de gevormde isotoopprofielen een gevolg zijn van het elektrische veld dat gevormd wordt door chemisorptie van reactieve zuurstofatomen op het oxideoppervlak. Dit heeft ladingsaccumulatie nabij het oppervlak tot gevolg (opwaartse bandbuiging), wat gerelateerd kon worden aan bandbuigingsmetingen uit de literatuur en berekeningen met een drift-diffusiemodel. Dit onderzoek toont voor het eerst experimenteel aan, gebruik makend van isotopenuitwisseling, dat zuurstofdiffusie bij kamertemperatuur op kan treden. Het vermoeden bestaat dat veldgeïnduceerde diffusie ook op kan treden bij andere adsorbaten van het acceptortype, zoals stikstof, mits radicalen in direct contact komen met het oppervlak en er voldoende bedekking opgebouwd kan worden. Deze resultaten dragen bij aan een beter begrip van de interactie tussen zuurstof en dunne oxidefilms, wat relevant is voor het ontwikkelen van materialen, de synthese van dunne metaal- en metaaloxidefilms voor een breed scala aan toepassingen en de ontwikkeling van processen waarbij reactieve atomen of moleculen in contact komen

met dunne films.

Sumário

Esta tese tem como objetivos aprofundar o conhecimento sobre o processo de interação entre oxigênio e filmes finos de metais de transição (MT) e óxidos de metais de transição, e o desenvolvimento dos conceitos relacionados à técnica de espalhamento ou reflexão de íons de baixa energia, ou *low energy ion scattering* - LEIS em inglês. Para alcançar estes objetivos, tópicos englobando desde a influência de oxigênio na neutralização de íons de baixa energia e o uso de íons reionizados para análise de espessura de óxidos, ao papel das espécies oxidativas e temperatura na interação entre oxigênio e sólido foram abordados ao longo dos capítulos. O trabalho descrito nesta tese é baseado em uma extensiva análise experimental, realizada em filmes finos de MT (e seus óxidos) dos grupos IV ao VIII da tabela periódica, filmes estes com várias espessuras e estruturas cristalinas. O uso de modelos matemáticos possibilitou o cálculo de importantes parâmetros, dentre eles a eficiência de neutralização de íons em diferentes superfícies, a barreira energética de difusão de cátions metálicos através de óxidos e constantes de difusão de oxigênio em óxidos.

LEIS é uma técnica não-destrutiva de caracterização amplamente conhecida por sua alta precisão e metodologia relativamente simples para quantificação da composição atômica de superfícies. No entanto, esta quantificação é diretamente relacionada à eficiência de neutralização dos íons detectados (geralmente He^+ ou Ne^+) após serem refletidos por uma superfície. Uma análise detalhada sobre o processo de troca de cargas entre He^+ e superfícies óxidas e metálicas de Mo, Hf, Ru e Al (usado como material de referência) foi realizada para a identificação dos mecanismos de neutralização presentes em superfícies óxidas e metálicas. Constatou-se que a presença de óxidos resulta na modificação da eficiência de neutralização em superfícies de MT, fato não observado em Al. Foi proposto que o aumento da neutralização observada em óxidos de Ru, Hf e Mo é causada pela banda O 2s presente em óxidos. Esta banda está em ressonância com o nível 1s do íon He, o que resulta no chamado mecanismo de neutralização quasi-ressonante (qRN). Em contrapartida, a diminuição da forte neutralização Auger do alumínio metal em consequência da oxidação contrabalança o aumento da neutralização por qRN, resultando em uma neutralização similar por Al em ambos estados. Estes resultados possibilitaram a determinação de um método robusto para caracterização quantitativa de compostos de metais de transição por LEIS. Aprofundando-se ainda mais nos recursos oferecidos pela técnica LEIS, um método não destrutivo para determinação da espessura de filmes óxidos foi demonstrado, denominado LEIS *static depth profiling* (DP). Esse método se baseia na análise de íons reionizados que são refletidos de átomos localizados em camadas do interior do sólido, e mostrou-se altamente sensível à espessura do óxido presente na superfície da amostra. Esses desenvolvimentos na técnica LEIS proporcionaram a possibilidade de associar uma quantificação precisa da composição atômica da superfície juntamente à caracterização da espessura do óxido formado, o que foi primordial para a precisa análise dos materiais durante o

processo de oxidação e difusão de oxigênio explorados nesta tese.

Subsequente aos avanços desenvolvidos na técnica LEIS, uma completa investigação da oxidação de filmes finos de metais de transição (Zr/Hf, Ta, Mo e Ru) em temperaturas indo de 298 K a 473 K, expostos a oxigênio atômico e molecular foi realizada. A análise em vácuo por meio das técnicas LEIS *static depth profiling* e rastreamento de isótopos, elipsometria e espectroscopia de fotoelétrons excitados por raios-X (XPS), ambas in-situ, proporcionaram o completo entendimento da dinâmica de formação de óxidos sem a interferência de contaminações externas, um fator crítico para verificação de aspectos previamente negligenciados em análises experimentais da cinética de oxidação. Um fator chave dos nossos estudos foi a demonstração de que a concentração de espécies atômicas reativas na superfície dos materiais é o fator determinante no processo de oxidação em baixas temperaturas. Em baixas temperaturas, o crescimento de óxido é proporcionado pela formação de um campo elétrico, consequente da formação de um potencial de contato. Porém, os conhecimentos presentes na literatura relacionados aos fatores que influenciam a formação, magnitude e preservação deste potencial ainda eram de certa forma incompletos. Os resultados presentes nesta tese trazem evidências concretas da influência do ambiente oxidativo na formação do potencial e consequente crescimento do óxido para cada um dos materiais analisados. Apresentamos uma relação direta entre a concentração de espécies atômicas na superfície, o potencial formado e a dinâmica de crescimento de óxido. Quando materiais são expostos a oxigênio molecular, efeitos de superfície como a competição entre dessorção e adsorção, combinados com a limitação de concentração na superfície resultam em um menor potencial, um fator não observado quando materiais foram diretamente expostos a oxigênio atômico. Em todos os casos analisados, a estrutura cristalina inicial do metal não teve um papel significativo no processo de crescimento de óxido. O quadro geral das análises indica que em casos nos quais a presença de oxigênio atômico não é limitada por dessorção ou concentração na superfície, a cinética de oxidação em baixas temperaturas pode ser diretamente relacionada às propriedades eletrônicas dos metais. Por exemplo, um metal com uma função trabalho mais negativa irá apresentar a formação de um óxido de maior espessura.

Um mecanismo similar foi também observado na difusão de oxigênio em óxidos de MT (ZrO_2 e MoO_3). A direta exposição destes óxidos a oxigênio atômico resultou em uma inesperada difusão de oxigênio em óxidos estequiométricos em temperatura ambiente. Nesta temperatura, a interação entre oxigênio e óxidos resultou em uma rápida difusão de oxigênio (até oito ordens de grandeza maiores que o estimado para difusão de volume) a uma profundidade limitada, e novamente a estrutura cristalina dos filmes não se mostrou um fator influente na difusão. A análise desenvolvida demonstra que os perfis de isótopos observados são consequentes da formação de um campo elétrico, o qual é formado pela quimissorção de espécies reativas de oxigênio na superfície do óxido, e acumulação de espécies carregadas na região próxima à superfície (flexão positiva das bandas eletrônicas). Estas observações foram fundamentadas pela comparação entre estudos presentes na literatura e os resultados obtidos por modelos matemáticos de difusão aplicados. Este estudo traz a primeira verificação experimental de difusão de oxigênio em óxidos estequiométricos em temperatura ambiente, detectada por meio de análise de

rastreamento de isótopos. As análises desenvolvidas nesta tese permitem a elaboração da hipótese de que estas observações relacionadas à difusão induzida por campos elétricos podem ser estendidas a outros adsorventes aceitadores de elétrons, tais como o nitrogênio: se estas espécies entram em contato direto com o metal ou óxido em uma concentração superficial suficiente, uma difusão assistida por campo elétrico pode ser estabelecida. Estes resultados contribuem para a melhor caracterização e entendimento da interação entre filmes finos e oxigênio, podendo ter um impacto significativo não só no design de materiais e na síntese de filmes finos de metais e óxidos para uma ampla gama de aplicações práticas, mas também no desenvolvimento de processos onde espécies reativas são colocadas em contato direto com filmes finos.

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A handwritten signature in black ink, appearing to read "Luis Z". The signature is stylized with a large, flowing "L" and a distinct "Z" at the bottom.

Curriculum Vitae

Cristiane Regina Stilhano Vilas Boas was born on the 18th of March 1991 in Santo André, São Paulo, Brazil. From 2009 to 2014 she pursued a Bachelor of Science and Technology and a Materials Engineering Degree at the Universidade Federal do ABC (UFABC). During this period, she took part on several internships, notably at the Institute of Polymer Materials and Plastics Engineering of Clausthal University of Technology (Germany), where she worked on the mechanical analysis of carbon fibre composites as a DAAD scholarship holder. She then followed the Master in Nanoscience and Advanced Materials at UFABC, during which she developed her thesis entitled "Synthesis and Characterization of Pristine and Nitrogen-Doped Graphene for Electronic Applications", a project derived from a consortium of Brazilian Universities and Institutes. After successfully completing her Master in 2016, she started her PhD at the Industrial Focus XUV Optics Group in the Mesa+ Institute of Nanotechnology of the University of Twente. Her PhD project was part of an NWO research program, supported by Carl Zeiss SMT GmbH, and she worked under the supervision of Prof. Dr. Fred Bijkerk and Dr. Marko Sturm. During this period, she was involved in the investigation of the interaction between oxygen and thin films of transition metal and transition metal oxides. A selection of the results obtained during her PhD years are compiled in this thesis. She currently works as a Postdoc researcher at the Nanolayers group of the Advanced Research Center for Nanolithography (ARCNL), where she investigates the surface contamination of components applied in extreme ultraviolet lithography.