Initial Oxidation of Zirconium: Chemistry, Atomic Structure, Transport and Growth Kinetics

by

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Wen Ma

Submitted to the Department of Nuclear Science and Engineering
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in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Nuclear Science and Engineering

Abstract:

The objective of this thesis is to uncover the chemical states and atomic structure of the initial oxide on zirconium and the oxygen transport kinetics through this oxide under electric field. This goal is important for enabling more accurate zirconium oxidation models, for example for nuclear reactor materials, as well as for assessing the mechanisms that govern the performance of zirconia based technologies, such as redox based resistive switching memory devices, gate dielectric for metal oxide semiconductor devices, and electrolytes for solid oxide fuel cells.

First, the chemical state of Zr during the initial stage of oxidation on single crystal Zr (0001) surface was probed by synchrotron x-ray photoelectron spectroscopy (XPS). Quantitative analysis of the Zr 3d spectrum by the spectrum reconstruction method demonstrated the formation of Zr$^{1+}$, Zr$^{2+}$ and Zr$^{3+}$ as non-equilibrium oxidation states, in addition to Zr$^{4+}$, in this early-phase ~1 nm thick oxide. By combining in situ synchrotron-based near-ambient pressure XPS simultaneously with chronoamperometry measurements, we quantified the conditions which induce the formation of reduced ZrO$_2$ (ZrO$_x$ with x < 2) as a function of electrical bias (E), temperature (T) and oxygen partial pressure (P$_{O_2}$). The mechanism behind the formation of ZrO$_x$ was explained based on the electrochemical driving force generated by the applied electric field. A $PO_2$-E-T phase diagram for ZrO$_x$ formation was constructed. These findings resolve the long-debated question of whether it is possible to form any valence states between Zr$^0$ and Zr$^{4+}$ at the metal-oxide interface.

Second, the structure of the initial oxide layers grown on single crystalline Zr (0001) surface by thermal oxidation was studied by scanning tunneling microscopy (STM). After exposing the surface to oxygen at 2×10$^{-8}$ mbar at room temperature and
annealing at higher temperature (530 °C), the first oxide layer exhibits atomic order with a triangular moiré pattern, and the lattice is consistent with a monolayer of cubic ZrO2(111). Interestingly, this first monolayer of oxide has a high concentration of oxygen vacancies. The sub-stoichiometric nature of this oxide layer is quantitatively consistent with the ZrOx (x<2) chemistry deduced from XPS. By increasing the oxygen exposure, the surface forms the second layer of oxide with a square lattice and a moiré pattern of rows. The second layer oxide appears fully oxidized, while the underlying first layer is sub-stoichiometric. The growth kinetics was deduced from the increase of the area of the second oxide layer on top of the first layer, and gave consistent results with the kinetics calculated from XPS. These structures were reported for the first time for the initial oxidation on pure Zr metal.

Third, we proposed a new way to quantify the oxygen diffusion under electric field by taking monoclinic zirconia thin film as a model system. We performed chronoamperometry measurements and modelled the data with a drift-diffusion equation modified to include the surface exchange reactions of oxygen. By comparing the intrinsic oxygen vacancy diffusion coefficient from this model to that produced from the Cottrell equation, we were able to assess the magnitude of electric field effect on the transport kinetics. The experimental approach and the modelling implemented in this work can be adapted to assessing the transport characteristics of other oxides under electric field.

Finally, the effect of temperature, oxidant type and oxidant pressure on the initial oxidation kinetics of zirconium were studied by synchrotron XPS and modelling. For oxidation from -130 °C to -10 °C and at 2×10^-8 mbar of oxygen gas or water vapour, the self-limited oxide thickness decreases with increasing temperature. From 30°C to 190°C, the oxide thickness increases with increasing temperature, and the oxide growth kinetics becomes non-self-limiting. There has been no existing single model that could capture this transition in the temperature dependence of oxide thickness. A new oxidation model was proposed by considering the local electric field distribution, based on the classic drift-diffusion and the Debye-Hückel theory for field distribution. Modelling of the initial oxidation kinetics uncovered the important role of electric potential distribution in the oxide layer in addition to the electric field strength. Competition between the Mott potential and the Debye length and oxygen diffusion could explain the initial decrease of oxide thickness followed by an increase at the higher temperature range studied here.
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1 Motivation and thesis contribution

1.1 Motivation

For many decades, zirconium alloys have found their primary use in the nuclear industry for reactor components, especially in the cladding of the fuel rods, due to zirconium's low neutron absorption and scattering cross-sections, desirable mechanical properties, and good oxidation resistance at low operating temperatures (500-600 K) [1, 2]. For example, Zircaloy 2, Zircaloy 4 and ZIRLO are used as cladding and structural components in light water cooled nuclear reactors; Zr2.5Nb and E125 are used in pressure tubes of CANDU reactors. However, the oxidative corrosion of zirconium alloys in chemically harsh conditions poses a safety and operational limit on light water reactors. The physical-chemical nature of the native oxide formed initially on the metal surface strongly affects the long-term corrosion kinetics on zirconium alloys. The initial oxide layer typically acts as a diffusion barrier between the reactants, thereby inhibiting further fast oxidation of the underlying metallic compound. For example, the (Cr,Fe)2O3 formed on stainless steel surface is able to significantly enhance the corrosion resistance, since the initial chromium oxide forms coherently and uniformly on the surface of the metal [3]. It was also found that a protective and stable initial oxide formed on zirconium alloys could improve the overall corrosion resistance [4]. Advancing the development of fundamental and predictive relations of the zirconium alloy surface structure and composition to the protectiveness and stability of the early-phase zirconium oxide is important for designing improved zirconium alloys against corrosion.

Even though zirconium alloys have been studied for decades, the knowledge related to the oxidative corrosion of zirconium still have gaps, especially for the initial stage oxidation. The microstructure of full oxide grown on the Zr or Zr alloys depends on the structure and chemistry of the initially formed oxide near the metal-oxide interface. It was found [4] that the overall stability or protectiveness of the Zr oxide depends on the stability of the initial oxide: the more protective the early-phase oxide is, the less the overall corrosion rate (Figure 1-1). The studies of oxide growth kinetics, the micro structural evolution, as well as the mechanical and transport properties, of oxide layer grown on zirconium by thermal oxidation have been investigated mainly at the microstructure-level for the thick oxide and at elevated temperatures (T>500K) [5,
At such elevated temperatures, it is impossible to capture the structure of the very first layers of the oxide, because oxidation is very fast and the surface oxide becomes relatively thick. Moreover the oxide/metal interface is buried underneath the thick, full oxide, and this makes it difficult to apply surface sensitive techniques to deduce the chemistry and structure of this critical interface, such as Scanning Tunneling Microscopy (STM) and X-Ray Photoelectron Spectroscopy (XPS). To be able to deduce some information about the chemistry and structure of the buried, initial oxide near the metal-oxide interface, one reasonable way that this thesis pursues is to assess the initial oxide at the onset of oxidation on zirconium.

Figure 1-1: Weight gain versus time for the corrosion of various Zr alloys. Note that the initial phase of oxidation is the same for all alloys, the chemical/physical stability of the initial oxide may determine the overall corrosion kinetics. However, the faster the transition from this early phase, the higher the corrosion at later times. This indicates that the stability of the initial oxide is an important factor for the corrosion rate at extended times. Figure is taken from reference [4].
Figure 1-2: Schematic of the passive oxide layer grown on the zirconium metal substrate. The oxidation process is governed by the oxygen inward diffusion. The new (initial) oxide formed at the metal oxide interface is denoted as “sub-oxide” following the zirconium alloy corrosion literature. However, the chemical and structural nature of this initial oxide has not been clear prior to this work (question mark posted on the figure). Upon further oxidation, the initial oxide gets fully oxidized and moves away from the metal/oxide interface and undergoes phase transition from tetragonal to monoclinic zirconia [4, 7, 8].

At the initial stages of Zr oxidation (Figure 1-2), the kinetics is governed by oxygen inward diffusion. While the oxidation of Zr metal progresses inwards, the incipiently oxidized layer is buried beneath the full oxide that is exposed at the top surface. This inner layer is called the initial oxide or the sub-oxide [9]. This newly formed oxide has not been thoroughly identified in terms of its chemistry and structure before. Several studies using different surface analysis techniques suggested the existence of Zr sub-valence states (valence states between Zr$^0$ and Zr$^{4+}$) as part of this sub-oxide [10-12]. Unlike the reducible oxides such as TiO$_2$ [13], SnO$_2$ [14] and CeO$_2$ [15, 16] (where excess electrons localize at the cation sites or delocalize into the conduction band), the Zr cation in ZrO$_2$ is energetically very difficult to reduce [12, 17, 18], rendering this material practically irreducible. The charge states of Zr are expected to be either Zr$^0$ as in the metal or Zr$^{4+}$ as in the stoichiometric oxide ZrO$_2$. There remains no conclusive proof of the number and nature of the sub-valence states, without a consistency among the reported results. The question mark posted in Figure 1-2 refers
to this open question on the chemical state of the sub-oxide on zirconium alloys. Given this open question, in this work, we are motivated to resolve the chemical states of Zr initial oxide by using synchrotron based in situ x-ray photoelectron spectroscopy (Appendix 1.1: X-ray Photoelectron Spectroscopy), and the surface atomic structure of the initial Zr oxide by scanning tunneling microscopy (Appendix 1.2: Principle of Operation of Scanning Tunnelling Microscopy). This work is also motivated to assess the kinetics of Zr initial oxidation, and resolve and understand the key factors that govern the kinetics.

Another interesting aspect that arises from studying the initial oxide layer and its growth kinetics is the effect of electric field on the transport properties of this thin oxide layer. Due to the large electronegativity of the oxygen, the electrons can tunnel through the thin (1-2 nm) zirconium oxide to the surface and form the oxygen anions. The oxygen anions at the surface then induce a strong electric field across the thin oxide. Given that the initial oxide is on the order of only few nanometres, the magnitude of the electric field could be on the order of MV/cm. Driven by this strong electric field, the oxygen anions transport through the oxide and reach the metal/oxide interface to form the new oxide. In this work, we are motivated to quantify the oxygen transport kinetics under strong electric fields, and for that we implement chronoamperometry measurements and model the data by a modified drift-diffusion equation. The quantification of diffusion kinetics of charged species under strong electric fields is also important for understanding the performance of oxides, such as ZrO₂, in other technologies where electric fields play an important role, such as red-ox based resistive switching memories [19-21], which is a promising future technology for data storage and processing. Zirconium dioxide was found to be a promising candidate material for resistive random access memory (ReRAM) [22, 23]. In the resistive switching memory devise, the core element is the metal/insulator(oxide)/metal “sandwich” structure, which is subject to an electroforming process, where a high electric field (on the order of MV/cm) is applied across it to create conductive paths. The creation of conducting paths are thought to be related to oxygen defect transport and formation of reduced phases. After the electroforming, the device could be set to on (conductive) / off (insulating) states by applying the set / reset bias, which also switch by motion of charged oxygen defects and electronic defects under very high electric fields. It has been shown by DFT calculation that under high electric field, the insulating ZrO₂ could be reduced.
to a conductive $\text{Zr}_2\text{O}_3$ phase [24]. However, a direct experimental support for the formation of such a phase has not been reported yet. Furthermore, the transport of charged species, in particular oxygen vacancies under electric field have not been quantified. These thus-far not-well-defined processes appear to fundamentally and similarly take place both the initial thin oxide layer on zirconium metal and in resistive switching memories made of zirconium oxide. These also motivate this thesis to characterize the chemical/structural states of zirconia under electrical bias and its oxygen transport properties under electrical bias.

### 1.2 Thesis contributions

The key scientific contributions of this have: i) identified the formation of reduced $\text{ZrO}_x$ ($x<2$) during the initial oxidation of Zr and the conditions that induce this seemingly non-equilibrium chemistry of $\text{ZrO}_x$ under electric field, ii) identified the surface atomic structure of the initial oxide that form on Zr (0001), iii) developed a new model for Zr initial oxidation which uncovered the important role of electric potential distribution in the oxide layer on the overall oxidation kinetics, in addition to the electric potential strength; and iv) developed methodologies for probing the surface electric potential distribution and oxygen transport properties in oxides under electric field. These contribution are summarized as follows.

**Scientific Contribution-1: Identified the $\text{ZrO}_x$ formation during initial oxidation of Zr and the formation conditions of this reduced oxide under electric field**

In this work, we have resolved a long-debated question [9-12] by showing the formation of $\text{Zr}^{1+}$, $\text{Zr}^{2+}$ and $\text{Zr}^{3+}$ as non-equilibrium oxidation states using synchrotron x-ray photoelectron spectroscopy and physically based spectrum analysis. The formation conditions of $\text{ZrO}_x$ as a function of electrical bias (E), temperature (T) and oxygen partial pressure ($P_{O_2}$) has been quantified by *in situ* synchrotron-based ambient pressure x-ray photoelectron spectroscopy and simultaneous chronoamperometry measurements. The mechanism behind the formation of $\text{ZrO}_x$ phases was explained based on the electrochemical driving force generated by the applied electric field. The $P_{O_2}$-$E$-$T$ phase diagram for $\text{ZrO}_x$ formation was constructed for the first time.

**Scientific Contribution-2: Identified for the first time the surface atomic structure of the Zr initial oxide formed on Zr (0001)**
Although the initial oxides formed on metal surfaces have been studied for several decades on many metal/oxide systems using Scanning Tunneling Microscopy, the initial oxide structure formation of pure Zr metal has been rarely studied [25], and the atomic structure of this initial Zr oxide has been missing from literature. The reason is the fact that Zr metal has high affinity to the oxygen [26], as soon as exposed to the oxygen, the oxide forms rapidly at the surface, which makes it hard to capture the detailed structure of this initial oxide. In this work, we overcame this difficulty by ultrafine-controlled oxidation conditions in the ultra-high-vacuum system. For the first time, we found a highly defective ultra-thin O-Zr-O cubic ZrO$_2$ (111) with triangular moiré pattern formed as the first oxide layer on Zr(0001) single crystal. The high concentration of oxygen vacancies in this first layer of the oxide is consistent with the presence of reduced ZrO$_x$ chemistry found from our in situ XPS study [27]. The second layer of the oxide was found to have a square lattice and a moiré pattern of “row” structure. The oxidation kinetics found in this STM work also shows consistence with our in situ XPS study [27]. These detailed atomic level pictures of the initial Zr oxide offers the possibility of developing a mode accurate model for Zr initial oxidation.

**Scientific Contribution-3: Developed a new model for Zr initial oxidation which uncovered the important role of the electric potential distribution on the overall oxidation kinetics**

The effect of temperature, oxidant type and oxidant pressure on the initial oxidation kinetics of zirconium were studied by synchrotron XPS and modelling. For oxidation from -130 °C to -10 °C and at 2.6×10$^{-8}$ mbar of oxygen gas or water vapour, the self-limited oxide thickness decreases with increasing temperature. From 30°C to 190°C, the oxide thickness increases with increasing temperature, and the oxide growth kinetics becomes non-self-limiting. There has been no existing single model that could capture this transition in the temperature dependence of oxide thickness. We then developed a new oxidation model by considering the local electric field distribution based on solving in a coupled way the drift-diffusion equation [28] and the Debye-Hückel theory for field distribution. The quantitative modelling of the initial oxidation curves uncovered the important role of electric potential distribution in the oxide layer in addition to the electric field strength. Competition between the Mott potential, the Debye length and oxygen diffusion could explain the initial decrease of oxide thickness.
followed by an increase at the higher temperature range studied here. While this model was developed for Zr initial oxidation, the idea of considering the electric field distribution in the oxidation modelling could be extended the study of oxidation of other metals.

**Methodology Contribution-1: Characterization of the surface electric potential distribution on an oxide under electric bias**

This thesis described a method to deduce the local surface potentials and chemical states of zirconium oxide that is under an in-plane electric bias, by modelling the XPS data. The idea of using XPS to measure the local electrical potential on the sample surface was first proposed to probe non-Faradaic electrochemical modification of catalytic activity [29]. Due to its merits, such as high spacial resolution and no local contacts that bury the surface, the method of using XPS to probe the local electrical potential has been applied in the study of solid oxide electrochemical cells [30-32], charging dynamics of dielectric materials [33] and depth-profiling by controlled surface charging [34]. This thesis further developed this method to study the ZrO_x formation under electrical field. The new model provided the possibility to resolve the change of the chemical states in the oxide under electric bias, as well as the temporal and spatial evolution of the local electrical potential across the oxide surface. This method could also be used in other material systems and have the potential to be extended to study electrochemical processes that take place heterogeneously on the sample surface in situ.

**Methodology Contribution-2: Characterization of oxygen transport properties in an oxide under electric field**

Oxygen transport in solids under electric field is an important elementary processes for many applications, such as metal oxidation resistance[13, 14, 35], red-ox based non-volatile memory and semiconductor devices[19-21]. In particular for oxidation and red-ox based memory devices, the operation temperature is relatively low (room temperature to a few hundred °C). On the other hand, diffusion measurements (mainly by secondary ion mass spectrometry) focus on the high temperature regime. To date, experimental and theoretical work on the oxygen transport under electric field at low-to-intermediate temperature regime has been rarely reported. In this work, we used chronoamperometry to characterize the oxygen diffusion under electric field by taking
monoclinic zirconia thin film as a model system. The data was modelled with a drift-diffusion equation modified to include the surface exchange reactions of oxygen. By comparing the intrinsic oxygen vacancy diffusion coefficient from this model to that produced from the Cottrell equation [21], we were able to assess the magnitude of electric field effect on the transport kinetics. The experimental approach and the modelling implemented in this work can be adapted to assessing the transport characteristics of oxides under electric field, for example in metal oxidation and for switching mechanisms and kinetics in red-ox based resistive switching memories.

1.3 Thesis organization

The thesis consist three parts. The first part focuses on the characterization of chemical states and atomic structure of the initial sub-stoichiometric Zr oxide (ZrOₓ, x<2) formed on the metal surface, as well as the formation conditions for ZrOₓ. Chapter 2 presents the chemical states of the initial Zr oxide formed on Zr(0001) single crystalline surface, where the existence of the ZrOₓ during the initial oxidation has been confirmed. The formation conditions for the ZrOₓ are assessed and discussed in details in Chapter 3. In Chapter 4, the atomic structures of the initial oxide formed on Zr(0001) surface are revealed. The defective nature of the first oxide layer found from scanning tunnelling microscopy images are consistent with the reduced Zr chemical states found by XPS in Chapter 2. The second part is related to the characterization of the oxygen transport properties in ZrO₂ under electric field. The newly proposed experimental method and models for quantifying the oxygen diffusion under electric field are found in Chapter 5. The last part is related to modelling and quantifying the initial oxidation kinetics of Zr (0001) under different gas pressures, temperatures and oxidants, as described and discussed in Chapter 6. In particular, a new oxidation model for Zr initial oxidation has been proposed and implemented in Chapter 6. Finally we conclude the thesis in Chapter 7 with a summary and brief discussion of future research directions that this thesis has seeded.
2 Non-equilibrium Oxidation States of Zirconium during Early Stages of Metal Oxidation

Abstract

The chemical state of Zr during the initial stage of oxidation on single crystal zirconium (0001) was probed by synchrotron x-ray photoelectron spectroscopy. Quantitative analysis of the Zr 3d spectrum by the spectrum reconstruction method demonstrated the formation of Zr$^{1+}$, Zr$^{2+}$ and Zr$^{3+}$ as non-equilibrium oxidation states, in addition to Zr$^{4+}$ in the stoichiometric ZrO$ _2$. This finding resolves the long-debated question of whether it is possible to form any valence states between Zr$^0$ and Zr$^{4+}$ at the metal-oxide interface. The presence of local strong electric fields and the minimization of interfacial energy are assessed and demonstrated as mechanisms that can drive the formation of these non-equilibrium valence states of Zr.

2.1 Introduction

Knowing the chemical and structural nature of the initial oxide formed on metal surfaces is important for quantifying the oxidation mechanism and kinetics in corrosion science [4, 36, 37], as well as for fundamental studies in electrochemistry [38-40] and catalysis [41-43]. The oxidation of zirconium is of interest for various technologies, including structural materials for nuclear reactors [2], corrosion-resistant coatings [2, 44], electrolytes for advanced solid oxide fuel cells [45], redox based resistive switching memory devices [46], gate dielectric for metal oxide semiconductor devices [47-49], and even for bio-implants [50].

It is well known that oxygen diffuses inwards across the oxide film while cations are relatively immobile during the oxidation of Zr [51, 52]. Therefore, the new oxide layers form at the metal/oxide interface as the oxidation progresses. Oxygen diffusion assisted by an electric field (Mott potential) governs the early stages of metal oxidation [28, 53-56]. The transport kinetics of oxygen through the oxide layer is controlled by the defect chemistry and mobility, and by the electric field strength that depends on the electronic structure of the oxide. Thus, it is important to know the chemical and electronic state of the zirconium oxide to develop accurate oxidation models. However, the chemical state of the early oxide on zirconium has remained elusive for almost three
decades due to prior challenges in experimental and analytical approaches. In this work, by combining synchrotron x-ray photoelectron spectroscopy (XPS) measurements and physical modelling of the spectrum, we revealed unequivocally the presence of 1+, 2+, and 3+ as non-equilibrium oxidation states of Zr during the initial stages of oxidation, in addition to the expected 4+ state of the stoichiometric oxide. We have proven the mechanisms for the stabilization of these unexpected lower oxidation states of Zr to be the presence of a strong local electric field during the oxidation process, and the reduction of the interfacial energy between the metal and the oxide.

Unlike the reducible oxides such as TiO$_2$ [13], SnO$_2$ [14] and CeO$_2$ [15, 16] (where excess electrons localize at the cation sites or delocalize into the conduction band), the Zr cation in ZrO$_2$ is energetically very difficult to reduce [12, 17, 18], rendering this material practically irreducible. The charge states of Zr are expected to be either Zr$^0$ as in the metal or Zr$^{4+}$ as in the stoichiometric oxide ZrO$_2$. While the oxidation of Zr metal progresses inwards, the incipiently oxidized layer is buried beneath the full oxide that is exposed at the top surface. This inner layer is called the initial oxide or the sub-oxide [9]. Several studies using different surface analysis techniques suggested the existence of Zr sub-valence states (valence states between Zr$^0$ and Zr$^{4+}$) as part of this sub-oxide [10-12], that we define here as ZrO$_x$ ($x<2$). However, there remains no conclusive proof of the number and nature of the sub-valence states, without a consistency among the reported results.

We believe there are three reasons to explain the large discrepancy among results related to Zr sub-valence states characterized by previous XPS studies [57-60]. First, most of the XPS measurements on Zr 3d photoelectron spectrum scanned only the main peak (175eV-190eV), omitting the intrinsic energy loss contribution arising from the coupling of the core hole with collective electron oscillations at higher binding energies (190 eV - 210 eV). Neglecting this intrinsic energy loss contribution leads to inaccuracies [61], because the cross section of intrinsic energy loss is different for Zr metal and for Zr oxide(s). The second possible reason behind the discrepancy is the limitation of instrumental resolution of laboratory XPS equipment used, both in terms of depth and energy, which makes it impossible to resolve any states from the thin sub-oxide buried underneath the full oxide[62]. Third, the analyses of the Zr 3d photoelectron spectra in most of the prior studies were performed by simple peak fitting, using conventional background subtraction and standard peak shapes. This
empirical approach is not sufficient to resolve the complicated photoelectron emission peaks of Zr 3d which has an intrinsic energy loss.

In this work, we employ the “spectrum reconstruction” method of Lyapin and Graat [61, 63] to quantitatively analyze our Zr 3d photoemission peaks that were measured using high-resolution synchrotron XPS. The essence of the spectrum reconstruction method is the inclusion of models and corrections that are all based on the physical process of photoelectron emission, including the intrinsic energy loss peak. In addition, the soft x-ray radiation from synchrotron sources, with enhanced signal intensity, superior energy resolution and lower photon energy (400 eV; IMFP=0.69 nm, as used in this work) enabled high sensitivity to the formation of the initial thin oxide on Zr.

2.2 Experimental Details

The oxidation experiment was performed on a single crystalline Zr (0001) sample (purchased from Princeton Scientific Corp.). The surface was mechanically polished to within 1° of this orientation. The native oxide and other contaminants on the Zr surface were removed by Ar⁺ ion sputtering (1.5 kV for thirty minutes) prior to the experiment. The sample was annealed under UHV at 1000 K for one hour. After 1-2 cycles of sputtering and UHV annealing, an XPS survey spectrum confirmed the absence of oxygen and any contaminants from the surface. Oxide films were grown at 100-500 K by in situ exposure of the Zr (0001) surface to pure oxygen with a total pressure of 2.6 x 10⁻⁸ mbar in an ultra-high vacuum (UHV) system, and was probed by XPS in the same UHV system with a base pressure of 6.5x10⁻¹¹ mbar.

Synchrotron x-ray photoelectron spectroscopy (S-XPS) was performed at Brookhaven National Lab (Upton, NY) at beam line U12A of the National Synchrotron Light Source. The radiation source was tunable, monochromatized soft x-rays in the energy range of 100-600 eV with a resolution ΔE/E of 2x10⁻²-10⁻³. The analyzer of the XPS system is VSW EAC 125. In accessing the chemical states of Zr, the 3d core level photoelectron emission of Zr was measured over the binding energy range from 176 eV to 206 eV with a step size of 0.05 eV at constant pass energy of 20 eV. X-ray photon energy of 400 eV was used during the measurement. The measurement geometry is shown in Figure 2-2a.

32
In order to verify the formation of $\text{ZrO}_x$ under electric field, a separate experiment was conducted. Fully oxidized $\text{ZrO}_2$ thin films were deposited onto STO (001) substrates by pulsed laser deposition (PLD) from a $\text{ZrO}_2$ target. A KrF excimer laser with wavelength of 248 nm under energy constant mode (400 mJ) and pulse frequency of 10 Hz was used during deposition. The deposition conditions for $\text{ZrO}_2$ films were 640 °C of substrate temperature and 0.01 mbar of oxygen partial pressure. Following growth, the films (about 200nm thick) were cooled down to room temperature in 2.6 mbar oxygen pressure to ensure full oxidation of the films. The deposited $\text{ZrO}_2$ thin films were monoclinic, as confirmed by X-ray diffraction (Figure 2-1). Then, dense interdigitated Ti (20nm) / Pt (100nm) microelectrodes prepared by DC sputtering and a photolithographic lift-off process were deposited onto the $\text{ZrO}_2$ films. The finger width and inter-electrode spacings were 20 μm. (Figure 2-5)

![X-ray diffraction pattern](image)

Figure 2-1: X-ray diffraction pattern (2θ-ω scan, with a logarithmic intensity scale) for $\text{ZrO}_2$ thin film grown by PLD on STO (001) single crystal substrate. (Monochromatized Cu Kα1 x-ray emission ($\lambda=0.154$ nm) was used in this measurement)

2.3 Analysis of X-ray Photoelectron Spectrum by the Spectrum Reconstruction Method

The essence of the spectrum reconstruction method is the inclusion of models and corrections that are all based on the physical process of photoelectron emission. In summary, we begin by setting up a zero-loss photoelectron peak for the metallic $\text{Zr}^0$ and fully-oxidized $\text{Zr}^{4+}$ cases (Doniach-Sunjic function for $\text{Zr}^0$ and Lorentz function for $\text{Zr}^{4+}$, respectively). The intrinsic (asymmetric tail at high binding energy) and extrinsic (inelastic scattering background) energy loss contributions are calculated from previous
electron energy loss spectra [64]. The instrument-induced peak broadening is also applied, finally giving very good agreement with the experimentally measured spectra (Figure 1b in the main text). From these reference spectra, subsequent intermediate oxidation spectra are fitted by fixing the asymmetric factor, spin orbit splitting, ratio between Zr 3d_{3/2} and Zr 3d_{5/2} peak intensities, ratio of the loss peak to main peak intensity, FWHM of the intrinsic loss peak and FWHM of the instrumental Gauss function.

Details of the spectrum reconstruction method are as follows:

One of the important features of the Zr 3d photoelectron spectrum is the presence of an additional asymmetric tail at high binding energies. Such asymmetric tail is the intrinsic contribution, originating from the coupling of the core hole with collective electron oscillations (plasmons). Previous work often ignored the analysis of this tail by unsuitable background subtraction. Neglecting this contribution, which is not contained in the main peaks, leads to inaccurate results. For obtaining a precise quantitative analysis, spectrum reconstruction method is used in this work. This method has been developed by A. Lyapin and P.C.J. Graat [61, 63] on metals such as Mg, Al and Zr with a significant intrinsic contribution within the plasmon peaks. The analysis used in this work followed procedure introduced in Ref [61, 63].

The Zr 3d spectra contain contributions originating from the intrinsic core-level excitations, the extrinsic energy losses, X-ray energy distribution and instrumental factors. The spectra reconstruction procedures are described as following:

1) Core level main peak

The Zr 3d core level is split into Zr 3d_{5/2} and Zr 3d_{3/2} due to the spin-orbit splitting. Thus the main peak is calculated as:

\[
I_M(E) = H_M \cdot I_{MP}(E) + a_{3d_{3/2}} \cdot H_M \cdot I_{MP}(E - E_{split})
\]

2.1

where \(E\) is the electron binding energy, \(E_{split}\) is the core level splitting, \(H_M\) is height of the Zr 3d_{5/2} peak. For pure metallic Zr, we use Doniach-Sunjic function as line shape \(I_{MP,m}\); for Zr oxide, we use Lorentz function as \(I_{MP,o}\).
F(1 - aM) \cdot \cos \left( \frac{\pi a_M}{2} + (1 - a_M) \cdot \tan^{-1} \left( \frac{E_M - E}{0.5\gamma_M} \right) \right)

I_{MP,m}(E) = \frac{\Gamma(1 - \alpha_M)}{((E_M - E)^2 + (0.5\gamma_M)^2)^{(1 - \alpha_M)/2}}

I_{MP,0}(E) = \frac{2}{\pi \gamma_M} \frac{1}{4(E_M - E)^2 / \gamma_M^2 + 1}

where \( \Gamma \) is the gamma function, \( E_M \) is the core level binding energy, \( \gamma_M \) is the FWHM of the line shape and \( \alpha_M \) is the singularity index.

2) Intrinsic energy loss

In order to get the intrinsic contribution, we need to convolute Zr 3d main peak with intrinsic excitation cross section \( K_i(E_L) \). But this cross section has not been characterized before. As in ref [61, 63], we assume it will take the same form as extrinsic energy loss cross section. Therefore, we have:

\[ I_{p,i}(E) = bI_M(E) * K_i(E_L) + I_M(E) \]

where \( b \) is the ratio between intrinsic energy loss peak to main peak, symbol * represents convolution.

3) Extrinsic energy loss

The extrinsic excitations of Zr 3d spectra is calculated by using the following Werner formalism[65]:

\[ I_{e+i,s}(E) = \sum_{n=0}^{\infty} P_{n,s} L_{n,s}(E_L) * I_{i,s}(E) \]

where \( I_{e+i,s}(E) \) is the intrinsic and extrinsic contributions of the spectra originating from the surface region; \( P_{n,s} \) is the partial intensity, represents the relative contribution of n times inelastic scattering to the spectra; \( L_{n,s}(E_L) \) is the probability for extrinsic energy loss \( E_L \) after n inelastic scattering.
surface layer with thickness $D_s$, the partial intensity has the following representation:

$$P_{n,s} = \int_0^{D_s} C_s \varphi_{n,s}(z) \, dz = C_s \lambda_s \cos(\theta) \left( 1 - \sum_{j=0}^{n} \varphi_{j,s}(D_s) \right)$$

2.6

where $C_s$ is the concentration of the considered element in the surface region; $\lambda_s$ is the inelastic mean free path of the electrons in the surface region; $\theta$ is the detection angle with respect to surface normal; $\varphi_{n,s}(z)$ is the depth distribution function, which is given by:

$$\varphi_{n,s}(z) = \frac{1}{n!} \left( \frac{z}{\lambda \cos(\theta)} \right)^n \exp \left( - \frac{z}{\lambda \cos(\theta)} \right)$$

2.7

where $z$ is the depth from the surface. The partial loss functions could be represented as:

$$L_{n,s}(E_L) = L_{n-1,s}(E_L) \ast K_{e,s}(E_L)$$

2.8

where $K_{e,s}(E_L)$ is the cross section for one inelastic scattering event in the surface region.

For the spectra originating from the bulk region, the formalism is similar to the surface contribution but with some modifications:

$$L_{e+i,b}(E) = \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} P_{p,n-p,b} L_{p,n-p}(E_L) \ast I_{i,b}(E)$$

2.9

$$P_{p,n-p,b} = C_b \lambda_b \cos(\theta) \varphi_{n-p,s}(D_s)$$

2.10

$$L_{p,n-p}(E_L) = L_{p,b}(E_L) \ast L_{n-p,s}(E_L)$$

2.11
The extrinsic cross-sections for bulk and surface region are calculated by using the data from reflection electron energy loss spectroscopy (REELS) measurements\[64].

4) **X-ray energy distribution and instrumental broadening**

Since it is very hard to distinguish the X-ray energy distribution and instrumental broadening, only single Gaussian function is used to describe it:

\[
I_G(E) = \frac{1}{\sqrt{\pi} \gamma_G/2} \exp \left[ - \left( \frac{E}{\gamma_G/2} \right)^2 \right]
\]

where \(E\) is the energy difference between detected electron energy and true energy; \(\gamma_G\) is the FWHM.

5) **Total spectrum**

The total spectrum \(I(E)\) could be calculated by convolution of bulk and surface spectra with X-ray and instrumental broadening:

\[
I(E) = \left[ I_{e+i,s}(E) + I_{e+i,b}(E) \right] * I_G(E)
\]

These equations were coded in Matlab and used for analysing the total spectrum. In getting the optimum value of the fitting parameters for the experimental data, the Levenberg-Marquardt algorithm implemented in Matlab has been used. Figure 1 shows good agreement of the calculated and experimental spectrum for pure zirconium metal and zirconium dioxide. The fitting parameters are listed in Table 2-1. The asymmetric factor, spin orbit splitting, ratio between \(3d_{3/2}\) and \(3d_{5/2}\), ratio of loss peak to main peak, FWHM of intrinsic loss peak, FWHM of instrumental Gaussian function were set as fixed values when fitting the intermediate oxidation spectrum.

The quantitative analysis of the Zr 3d photoelectron emission is performed by using the spectrum reconstruction method, instead of the routine peak fitting method. Before analysing intermediate oxidation states, the pure metallic and pure oxidic spectra were measured on single crystal Zr sample before and after fully oxidation. These two spectra serve as reference spectra for analysis of the intermediate oxidation states, and were fitted by the formalism introduced above. The reconstructed Zr 3d spectra could fit the experimental data very well. More importantly, we could get
relative intensity and FWHM of intrinsic energy loss peak, which could not be obtained from direct EELS measurements [61, 63]. The fitting parameters (except \(H_M\) and \(\gamma_M\)) in Table 2-1 are used as fixed input values in analysing intermediate oxidation states spectra. The fitting results are shown in Figure 2-3 for all the oxidation spectra taken at different times.

All the spectra analysed in this work were renormalized before the fitting (maximum to 1, and minimum to 0). The sum of squared residuals (\(\delta\)) is calculated by taking the sum of squared difference between the renormalized experimental data \(I_e\) and the reconstructed spectra \(I_r\), shown as following:

\[
\delta = \sum (I_e - I_r)^2
\]
Table 2-1: Fitting parameters for reconstructing the Zr 3d photoelectron spectrum for
Zr$^0$ and Zr$^{4+}$ reference states.

<table>
<thead>
<tr>
<th>Fitting parameter</th>
<th>For metal (Zr$^0$)</th>
<th>For oxide (Zr$^{4+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main peak position (eV)</td>
<td>178.6±0.2</td>
<td>183.1±0.3</td>
</tr>
<tr>
<td>Asymmetric factor for main peak</td>
<td>0.804±0.003</td>
<td>N/A</td>
</tr>
<tr>
<td>FWHM of main peak</td>
<td>0.130±0.008</td>
<td>0.78±0.01</td>
</tr>
<tr>
<td>Main peak height</td>
<td>11.1</td>
<td>35.9</td>
</tr>
<tr>
<td>Spin orbit splitting (eV)</td>
<td>2.39±0.01</td>
<td>2.38±0.01</td>
</tr>
<tr>
<td>Ratio of 3d$^{3/2}$ to 3d$^{5/2}$</td>
<td>0.627±0.002</td>
<td>0.667±0.002</td>
</tr>
<tr>
<td>Ratio of loss peak to main peak</td>
<td>0.32±0.01</td>
<td>0.083±0.008</td>
</tr>
<tr>
<td>FWHM of intrinsic loss peak</td>
<td>5.5±0.5</td>
<td>5.8±0.3</td>
</tr>
<tr>
<td>Inelastic scattering peak shift</td>
<td>1.07</td>
<td>1</td>
</tr>
<tr>
<td>Cross section normalization factor</td>
<td>0.37±0.05</td>
<td>0.794±0.03</td>
</tr>
<tr>
<td>Surface plasmon peak position (eV)</td>
<td>9.68±0.07</td>
<td>12.5±0.1</td>
</tr>
<tr>
<td>Surface thickness (nm)</td>
<td>5.4±0.7</td>
<td>0.5±0.3</td>
</tr>
<tr>
<td>FWHM of Gauss function</td>
<td>0.91±0.05</td>
<td>0.91±0.05</td>
</tr>
</tbody>
</table>

2.4 Results and Discussion

2.4.1 Zr 3d XPS Spectrum Evolution during Initial Oxidation

The evolution of the Zr valence state as a function of increasing oxygen exposure (time) could be captured from the Zr 3d spectra (Figure 2-2). The geometry used in the experiment and in the spectrum reconstruction analysis for the initial oxidation of Zr (0001) is illustrated in Figure 2-2a. The x-ray (with photon energy 400 eV) is incident at 30° with respect to sample normal, while the XPS analyzer collects electrons at 35° to the sample normal. The two-layer oxide model is used in the photoelectron spectrum reconstruction; the Zr sub-oxide (ZrOx) layer is sandwiched
between Zr metal on the bottom and ZrO$_2$ on the top. The Zr 3$d$ x-ray photoelectron spectra of pure Zr metal (Zr$^0$ in Zr metal) and the fully oxidized Zr surface (Zr$^{4+}$ in ZrO$_2$) are shown in Figure 2-2b as reference, including both the measured data and the reconstructed final spectrum for each. A distinctive feature of the spectra is the intrinsic contribution at high binding energy (190 eV-210 eV) originating from the coupling of the core hole with collective electron oscillations [61]. The final reconstructed spectra for Zr$^0$ and Zr$^{4+}$ states here gave a very good agreement with the experimentally measured spectra. By using these reference spectra, subsequent intermediate oxidation spectra were fitted.

Figure 2-2c shows the Zr 3$d$ photoelectron peaks for a series of successive O$_2$ exposures at 300 K and 2.6×10$^{-8}$ mbar of oxygen pressure. Prior to oxidation (at time = 0 minute), only metallic peaks are visible in the spectra. As the oxidation time is increased to 0.5 minutes and 1.5 minutes, the metallic peaks broaden due to the formation of ZrO$_x$. After 3.5 minutes O$_2$ exposure, the Zr$^{4+}$ peaks become prominent, and continue to increase in signal intensity with further O$_2$ exposure, indicating the formation of stoichiometric ZrO$_2$ oxide at the surface. For the oxidation spectra obtained after 3.5 minutes, 7.5 minutes and 13.5 minutes, intermediate peaks appear, not coinciding either with the Zr$^0$ or Zr$^{4+}$ peaks, giving a strong evidence for the formation of ZrO$_x$. 
Figure 2-2: Zr 3d x-ray photoelectron spectra during oxidation of Zr(0001) single crystal in 2.6×10⁻⁸ mbar dry oxygen at 300K, measured with photon energy of 400 eV. (a) Schematic of the geometry used in the XPS experiment and in the spectrum reconstruction analysis for the initial oxidation of Zr(0001). (b) Reference Zr 3d spectra for Zr⁰ (obtained prior to oxidation) and for Zr⁺⁺ (obtained after 2 hours of oxidation in 2.6×10⁻⁶ mbar dry oxygen at 500 K). Solid lines refer to the spectrum reconstruction results for Zr⁰ and Zr⁺⁺. (c) Consecutive Zr 3d spectra from 0 min to 83.5 min of oxygen exposure. (d-g) Spectrum reconstruction results for Zr 3d spectra taken at 13.5 minutes of oxidation in 2.6×10⁻⁸ mbar dry oxygen at 300 K, with (d) no sub-valence state peaks, (e) one sub-valence state peak, (f) two sub-valence state peaks, (g) three sub-valence state peaks. Zr⁺⁺ in (e) and (f) denotes the sub-valence that is either 1+, or 2+, or 3+. The sum of squared residuals of the reconstructed normalized spectra with respect to the experimental normalized spectra is 11.8 in (d), 4.2 in (e), 0.4 in (f) and 0.1 in (g) [62].

We lend further credence to the existence of ZrOₓ through our quantitative analysis of the Zr 3d photoelectron spectra from the oxidized samples. Accurate fitting
could not be achieved with just the metallic and one oxidic component alone (Figure 2-2d). Instead, several additional doublet peaks corresponding to the Zr sub-valence states had to be added to attain the best fit to the spectra. Between one and three additional sub valence states were successively included in the reconstruction of the spectra, as shown in sequence of Figure 2-2e, Figure 2-2f and Figure 2-2g. The quality of each fit was compared, based on square residual errors. The best fit reconstructed spectra was obtained by adding three sub-valence states, Zr\(^{1+}\), Zr\(^{2+}\) and Zr\(^{3+}\), peaks between the metallic (Zr\(^{0}\)) and the fully oxidic (Zr\(^{4+}\)) peaks (Figure 2-2g). The line shape of the individual sub-valence peaks was assumed to be the same as oxidic (Zr\(^{4+}\)) peak. The average binding energy (BE) values of 179.83 ± 0.05 eV, 180.99 ± 0.05 eV and 182.10 ± 0.05 eV, as determined for the positions of the main Zr 3\(d\) peak of sub-valence Zr\(^{1+}\), Zr\(^{2+}\) and Zr\(^{3+}\) components, are in between the corresponding BE values of the metallic and ZrO\(_{2}\) main peaks at 178.66 ± 0.05 and 183.25 ± 0.05 eV, respectively. The almost equal spacing of the sub-valence state peaks is in agreement with the fact that the valence charge transfer (ionization energy) and the crystalline field (Madelung energy) contributions to the chemical shift are expected to be approximately proportional to ionicity or oxidation state [66]. Our result on the formation of the Zr\(^{1+}\), Zr\(^{2+}\) and Zr\(^{3+}\) components in the sub-oxide is applicable to all the spectra taken at times 0.5 min to 83.5 min as shown in Figure 2-3.

2.4.2 Zr Initial Oxide Stoichiometry and Oxidation Kinetics

The fraction and relative intensity of ZrO\(_{x}\) states in the total oxide layer was quantified from the spectrum reconstruction. The ZrO\(_{x}\) states are formed after less than 2 minutes of exposure. As the oxide thickens, the fraction of Zr\(^{4+}\) (full oxide) increases while the aggregate signal from the ZrO\(_{x}\) states drops to a constant level (Figure 2-4a and b). More interestingly, the ZrO\(_{x}\) persists at a constant thickness at the Zr/ZrO\(_{2}\) interface for the oxidation times at or longer than 20 minutes (Figure 2-4a). The average composition within the ZrO\(_{x}\) layer is ZrO\(_{1.05}\), which is calculated by taking the average of the fractional contributions of Zr\(^{1+}\), Zr\(^{2+}\) and Zr\(^{3+}\) from Figure 2-4a, as plotted then in Figure 2-4b. It must be noted that the earlier observation of a “ZrO” stoichiometry found by atom probe tomography in the ZrO\(_{x}\) upon oxidation of Zr [9] does not mean that the only oxidation state is 2+ as in ZrO. An average of all Zr\(^{1+}\), Zr\(^{2+}\) and Zr\(^{3+}\) can give rise to a ZrO-like composition, while the local chemistry and coordination can be different than ZrO, as found in this work.
Some evidence to the formation of ZrO\textsubscript{x} is also seen in the oxidation kinetics of Zr in these experiments. Incipient metal oxidation kinetics are typically modelled using the Cabrera-Mott model [28], which considers electric field-assisted ion migration through a single oxide layer, based on the self-generated electric field (Mott-potential). We modelled the kinetics of Zr oxidation by using the Cabrera-Mott model after quantifying the time evolution of the oxide and the ZrO\textsubscript{x} thicknesses (Figure 2-4c and d). This model did not give a satisfactory fit to our data of total oxide thickness, especially at the fast-rising earlier phase of oxidation (Figure 2-4d). This mismatch of the Cabrera-Mott model to the Zr oxidation data also suggests that the Zr-oxide is more complex than just a single layer of ZrO\textsubscript{2}. With different charge transfer properties, the presence of ZrO\textsubscript{x} layer would impact the overall oxidation kinetics and its formulation. A more accurate representation of the data requires a more comprehensive model to take into account the interface ZrO\textsubscript{x} that has a significant fraction especially at the early stage of oxidation.

The general characteristic of the oxidation curves in Figure 2-4c and d involve a rapid initial growth of both the ZrO\textsubscript{x} and ZrO\textsubscript{2} layers up to 10 minutes of oxygen exposure, followed by a decrease in the growth rate as the layers reach their limiting thickness. The near-limiting thickness is attained at 0.8 nm and 0.3 nm for the ZrO\textsubscript{2} and ZrO\textsubscript{x} layers, respectively.
Figure 2-3: Spectrum reconstruction results for Zr 3d x-ray photoelectron spectra during oxidation of Zr (0001) single crystal in $2.6 \times 10^8$ mbar dry oxygen at 300K, measured with photon energy of 400 eV from 0.5 minutes to 83.5 minutes.
2.4.3 Driving Forces for the Formation of ZrO\textsubscript{x}

At thermodynamic equilibrium\cite{18, 67, 68} with the temperatures and oxygen pressure used in our experiments, the 1+, 2+ and 3+ oxidation states of Zr are not expected to exist in the bulk of zirconium oxide. Here we propose two possible drivers for the stabilization of these sub-valence states of oxidation: i) the strong electric field (Mott potential) present across the oxide layer, and ii) the minimization of the interfacial energy. First, we assess the role of the electric field. Mott potential is treated as a driver to the oxidation kinetics by assisting oxygen migration in the classical Cabrera-Mott model \cite{28}. However, electric field can also couple to the thermodynamics of the oxide as an external energy source, and can drive the formation of intermediate reduced states of Zr during oxidation. By fitting our oxidation kinetics data to the Cabrera-Mott model (Figure 2-4d), the Mott potential was found to be 0.069 V, yielding a very strong electric field (E = 0.6 MV/cm) across the 1.1 nm oxide. The presence of this electric field can change the energy landscape of the metal-oxide
interface and lead to the stabilization of the ZrO\textsubscript{x} compositions that are far from the equilibrium state. While the formation of a non-equilibrium Zr-oxide composition under electric field was suggested by prior ab initio computations [24], no prior experiment was able to directly prove the formation of such a sub-stoichiometric Zr-oxide under an electric field. To verify this argument, we applied 10 V of bias laterally on a thin film of the fully oxidized ZrO\textsubscript{2} between the two sets of finger-like electrodes (Figure 2-5-inset), and measured the evolution of the Zr 3\textit{d} spectrum. The applied bias corresponds to an electric field of 0.005 MV/cm in this geometry; a substantial field magnitude. A clear shoulder was found to evolve at binding energies lower than the Zr\textsuperscript{4+} peaks in the Zr 3\textit{d} spectrum (Figure 2-5). The position of this new contribution to the spectrum does not match that of Zr\textsuperscript{0} peaks, and thus, is not associated with a full reduction of the oxide down to the metallic state. By using the positions of the intermediate oxidation states of Zr that we deduced in Figure 2-2, we identified that the new composition formed in the ZrO\textsubscript{2} film under electric field include Zr\textsuperscript{3+} and/or Zr\textsuperscript{2+} states. From these results, we can conclude that the even stronger electric field present during the initial oxidation of Zr (0.6 MV/cm here) is a plausible driver to the stabilization of the 1+, 2+ and 3+ states of Zr in the early oxide.

![Figure 2-5: Zr 3\textit{d} photoelectron spectrum before and after applying 10V electric bias to the ZrO\textsubscript{2} thin film, corresponding to an average electric field of 0.005 MV/cm between the interdigitated electrodes. The inset shows the schematic drawing of the interdigitated electrode structures used for applying electric field through the PLD-deposited monoclinic ZrO\textsubscript{2} dense film. The sample was kept at 550 K and 1.3\times10^{-10} mbar in both data sets (with 0 V and at/after 10 V).]
Second, we assess the effect of the interfacial energies by modelling the thermodynamic stability of a thin amorphous ZrO\textsubscript{x} layer between the full oxide and the metal. The detailed deductive steps for calculating the Gibbs free energy difference between the systems with and without ZrO\textsubscript{x} layer is shown as the following[69]: two scenarios, shown schematically in Figure 2-6, are considered: model (a) is a layer of full oxide (ZrO\textsubscript{2}) with thickness $h_1$ formed directly on single crystal Zr (0001) (Figure 2-6a), and model (b) is a ZrO\textsubscript{x} layer (thickness $h_s$) sandwiched between the full oxide (ZrO\textsubscript{2} with thickness $h_2$) and single crystal Zr (0001) (Figure 2-6b). To fix the same amount of oxygen that was involved in the oxidation in both models, the thickness of layers is constrained by the following relation:

$$\frac{2h_1}{\Omega_o} = \frac{2h_2}{\Omega_o} + \frac{xh_s}{\Omega_s}$$

2.15

where $\Omega_o$ and $\Omega_s$ are the molar volumes of ZrO\textsubscript{2} and ZrO\textsubscript{x}, respectively. According to our low energy electron diffraction (LEED) measurements (Figure 2-7) and reports in the literature [59, 70], at relatively low oxidation temperatures (up to ~573 K), the initial surface oxide film grown on the Zr metal is amorphous. We therefore assume the ZrO\textsubscript{2} layer in both models to be an amorphous phase under our experiment conditions. Thus, the total Gibbs free energy per unit area for model (a), $G_a$, and for model (b), $G_b$, can be expressed as [69]:

$$G_a = \frac{h_1}{\Omega_o} G_{ZrO_2} + \gamma_{m/o} + \gamma_{o/v}$$
\[ G_b = \frac{h_z}{\Omega_o} G_{ZrO_2} + \frac{h_s}{\Omega_s} G_{ZrO_x} + \gamma_{m/s} + \gamma_{s/o} + \gamma_{o/o} \]

where \( G_{ZrO_2} \) and \( G_{ZrO_x} \) are the bulk Gibbs free energy of 1 mol of amorphous \( ZrO_2 \) and \( ZrO_x \), respectively; \( \gamma_{m/o} \), \( \gamma_{o/o} \), \( \gamma_{m/s} \), and \( \gamma_{s/o} \) represent the interface energy between \( Zr/ZrO_2 \), \( ZrO_2/vacuum \), \( Zr/ZrO_x \) and \( ZrO_x/ZrO_2 \), respectively. The formation of \( ZrO_x \) layer is stable as long as the Gibbs free energy difference \( \Delta G = G_a - G_b > 0 \). Since the experimental values of interfacial energies between metal substrate and amorphous-oxide film are not available, the “macroscopic atom” approach was used here to derive the interfacial energies \[69, 71-73\]. In this approach, to assess the interfacial energies \( \gamma_{m/o} \) and \( \gamma_{m/s} \), the interface between a crystalline solid and a configurationally frozen liquid is considered \[71, 73\]. The interfacial energy can then be expressed as \[69\]:

\[ \gamma = \gamma_{interaction} + \gamma_{entropy} + \gamma_{enthalpy} \]

\[ \gamma_{interaction} = \frac{p \Delta H_{O in m}^0}{A_o} \]

\[ \Delta H_{O in m}^0 \approx 1.2 \Delta H_o^f + 1 \times 10^5 \; (J \; mol^{-1} \; O) \]

\[ \gamma_{entropy} = -\frac{T \Delta S_{ZrO_x}^{deficient}}{x A_x} - \frac{0.904RT}{x A_x} \]

\[ \gamma_{enthalpy} = \frac{p H_m^{fuse}}{A_m} \]

where \( \Delta H_{O in m}^0 \) is the enthalpy of mixing at infinite dilution of 1 mol O atoms in Zr crystalline metal; \( p \) is the fraction of total interface area of O atomic cell in contact with Zr metal atom in crystalline metal; \( A_o A_x A_m \) are the interfacial area of the cell that containing 1 mol of oxygen atoms / zirconium atoms; \( \Delta H_o^f \) is the formation enthalpy per mole O in oxide; \( \Delta S_{ZrO_x}^{deficient} \) is the decrease of configurational entropy per mole \( ZrO_x \); \( H_m^{fuse} \) is the enthalpy of fusion of Zr metal. For the interfacial energy between the amorphous ZrO2 and amorphous ZrOx, \( \gamma_{entropy} \) and \( \gamma_{enthalpy} \) are approximately
zero, assuming the amorphous phase oxide acts as a configurationally frozen liquid. By plugging those equations into $\Delta G = G_a - G_b$, and assuming the configurational constraint at ZrO$_2$/ZrO$_x$ interface of $2A_o = xA_x$, we obtain:

$$\Delta G = \frac{h_s}{\Omega_s} \left( \frac{x}{2} G_{\text{ZrO}_2} - G_{\text{ZrO}_x} \right) + p \left[ \frac{\Delta H_{\text{ZrO}_2}^{\infty} + \Delta H_{\text{ZrO}_2}^{\infty} - \Delta H_{\text{ZrO}_2}^{\infty}}{2A_o} \right]$$

2.23

For the ZrO$_x$ layer with average $x=1$, $\Delta G$ could be expressed as:

$$\Delta G = \frac{h_s}{\Omega_s} \left( \frac{1}{2} G_{\text{ZrO}_2} - G_{\text{ZrO}_x} \right) + \frac{p}{2A_o} \left( \Delta H_{\text{ZrO}_2}^{\infty} - \Delta H_{\text{ZrO}_2}^{\infty} \right)$$

2.24

Values for oxide thicknesses ($h_1, h_2, h_3$) grown on Zr (0001) were obtained by calculating the attenuation of the metal zero loss peak intensity. Figure 2-4 c and d show the calculated ZrO$_x$ and ZrO$_2$ thicknesses. The free energy of amorphous ZrO$_2$ is obtained by assuming it to be the same as ZrO$_2$ liquid: $G_{\text{ZrO}_2} = -972.661$ kJ/mol [74]. Since there are no previously reported values of $\Omega_s, G_{\text{ZrO}}$ and $\Delta H_{\text{ZrO}}^{\infty}$ for amorphous ZrO$_x$, we use the value for crystalline ZrO reported in the literature [75], as $\Omega_s = 0.0875$ nm$^3$, $G_{\text{ZrO}} = -539$ kJ/mol and $\Delta H_{\text{ZrO}}^{\infty} \approx 1.2G_{\text{ZrO}} + 100 = -547$ kJ/mol. We take $\Delta H_{\text{ZrO}}^{\infty} = -449$ kJ/mol [76], $p = \frac{1}{3}$ [69] and $A_o = 0.127$ nm$^2$. The resulting Gibbs free energy difference between model (a) and model (b) is $\Delta G = G_a - G_b = 3.3$ eV/nm$^2$. This analytical estimation based on interface formation energies indicates that a tri-layered structure of ZrO$_2$/ZrO$_x$/Zr (as in model (b)) is energetically more stable compared to an abrupt interface between stoichiometric ZrO$_2$ and crystalline metal Zr.

![Figure 2-7: LEED pattern of Zr (0001) (a) before and (b) after 2 hours oxidation in 2.6x10$^{-8}$ mbar oxygen at 300K. No pattern observed in (b) means that the oxide formed at the surface is not crystalline.](image)
We believe that the formation of the Zr valence states between 0 and 4+ is a signature of oxide precursor formation on metals that have high solubility of oxygen. For example, the Ti$^{2+}$ and Ti$^{3+}$ were found to form preferentially at the metal/oxide interface during the Ti metal oxidation, where the full oxide is TiO$_2$ [77]. Tantalum also is known to form Ta$_2$O, TaO and Ta$_2$O$_3$ states prior to the fully oxidized state in Ta$_2$O$_5$ [53]. Similarly one can expect ZrO$_x$ formation during oxidation of Hf, though not yet demonstrated. Interestingly, even metals like Pt [41] and Pd [78], which are “less active” to oxygen, also form precursor states at the surface prior to full oxidation. The difference of Zr compared to Ti or Ta is that electron localization on the zirconium cation in ZrO$_2$ is energetically very, very expensive compared to that in TiO$_2$ or Ta$_2$O$_5$ (for example, as a local metric, a neutral oxygen vacancy formation energy in ZrO$_2$ is 7.2 eV compared to 4 eV in TiO$_2$ [12]). This literally irreducible nature of ZrO$_2$ under any practical condition has made it more difficult to observe the intermediate oxidic components clearly and systematically prior to our work.

The ZrO$_x$ states identified in this work could also reveal the mechanism for the red-ox based resistive switching in memory devices made of ZrO$_2$. Indeed, there is evidence from experiments [22, 79] and computational simulations [24] that lower-resistance states (with higher electronic conductivity) in such devices are due to the formation of sub-stoichiometric oxides. However, no direct in situ observation of such ZrO$_x$ states under electric field has been achieved before for ZrO$_2$. The finding of Zr$^{2+}$ and Zr$^{3+}$ after applying an electric field on fully oxidized ZrO$_2$ films could provide the chemical states responsible for the resistive switching observed in this material. This is a realization of the electric field modulation of oxygen defects in oxides, whose importance is being realized more recently for oxide-based electronic and electrochemical devices [80, 81].

2.5 Conclusions

In summary, we uncover the non-equilibrium valence states of Zr during the early stage oxidation of the metal in oxygen gas, probed by high resolution synchrotron x-ray photoelectron spectroscopy and analyzed by physical modelling of the spectrum. Although the average composition yields a stoichiometry of ZrO, as also observed by previous atom probe tomography measurements [9], the local chemical environments
in such ZrO_x deviate from only the 2+ oxidation state of Zr and include all three Zr^{1+}, Zr^{2+} and Zr^{3+} states. The mechanisms that drive the formation of ZrO_x at the metal/oxide interface under these experimental conditions have been verified to be: 1) the presence of a strong electric field that changes the energy landscape and modulates the red-ox processes in the oxide, and 2) the minimization of the interfacial energy by forming ZrO_x at the metal-oxide interface. Revealing the presence of such ZrO_x is critical for enabling more accurate oxidation models, as well as for assessing the switching mechanisms and kinetics in red-ox based resistive switching memories.
3 Reduction of ZrO$_2$ Induced by Electrical Bias

Abstract

The chemical state of Zr in ZrO$_2$ oxide under electric filed was probed simultaneously by \textit{in situ} synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS) in controlled temperature and oxygen pressure condition, and by chronoamperometry measurements. APXPS allows for the quantification of the Zr chemical state and the potential distribution. The chronoamperometry (CA) measurements show electrical signature for the transition from ZrO$_2$ to ZrO$_x$, with an increase in the electrical conductivity at the onset of this transition. The results from both methods consistently uncovered the conditions which induce the formation of ZrO$_x$ ($x < 2$) as a function of electrical bias ($E$), temperature ($T$) and oxygen partial pressure ($P_{O_2}$). The mechanism behind the formation of ZrO$_x$ phases was explained based on the electrochemical driving force generated by the applied electric field. We present the results finally in the form of a $P_{O_2}$-$E$-$T$ phase diagram.

3.1 Introduction

The response of materials under electric field is a fundamental and scientifically interesting problem in many fields, such as piezoelectric [82], ferroelectric phase transition [83], metal oxidation, electrochemical reaction and redox based resistive switching memory [46]. Knowing the chemical and structural nature of the material under electric field is a key for understanding and quantifying electric field-induced phenomena. Bulk properties of materials under electric field can be characterized but the detection of small chemical state changes in the material under electric field is challenging. The role of electrochemical potential of oxygen [84] (in oxide systems) and the thermodynamic stability of secondary phases under electric field have been rarely explored before. In this work, we choose ZrO$_2$ as a model system, and characterized the formation conditions for ZrO$_x$ ($x < 2$) under electric field. Zr dioxide is normally considered as an oxide that is extremely difficult to thermally reduce, in other words, it has a very high energy of oxygen vacancy formation (for example, as a local metric, a neutral oxygen vacancy formation energy in ZrO$_2$ is 7.2 eV [12]). Here our results show that the high of defect formation could be overcome by externally
applied electric field or electrochemical potential. The important role of oxygen electrochemical potential and the dielectric property of ZrOx is also discussed.

Zirconia (ZrO2) is found in a number of important technological applications. In particular, ZrO2 plays important role as the corrosion passivating film on structural materials in nuclear reactors [2, 44]. It is also a promising candidate material for redox based resistive switching memory, which is considered as a promising next-generation non-volatile memory that is ultra-fast and scalable to very small dimensions. The chemical state and electronic structure under the influence of strong electric field is important to understand for quantifying the performance of ZrO2 in these applications. Therefore, it is important to characterize the chemical and electronic state of the zirconium oxide under electric field to develop a precise mechanism of the corrosion and memory switching process. From our previous study [27] (and see Chapter 2), we have identified the formation of ZrOx during the initial oxidation, which resolved a long-standing question about the chemical state of the Zr during initial oxidation. Further, we have verified that the strong electric field may induce this reduction from ZrO2 to ZrOx and stabilization of the ZrOx by applying electric field on the ZrO2 thin films. However, the detailed conditions for the ZrOx formation is still not clear. The goals of this chapter is to systematically reveal the boundary conditions for the formation of ZrOx as a function of electric bias, temperature and oxygen pressure, and to uncover the mechanism by which electric field induces ZrOx. We probe these questions by in situ techniques combining synchrotron x-ray photoelectron spectroscopy (XPS) and chronoamperometry.

Assessing the local chemical states and electric potential of an oxide under electric bias by in situ x-ray photoelectron spectroscopy is challenging because of the difficult measurement conditions, involving high temperature and gas environment, and the difficulty of attaching probes across the area of interest while exposing enough material surface to be accessed by x-rays. Ambient pressure X-ray photoelectron spectroscopy (APXPS) that is available in a few synchrotrons in the world provides a feasible solution to identifying the local chemical states and their correlation to local electric potential on a sample surface laterally. When measuring the X-ray photoelectron spectrum on a biased sample, the sample has a relative potential difference with respect to the ground of the XPS analyser, therefore the electron kinetic energies will show a shift. The shifts come from the change of local Fermi level
corresponding to the local potential. For example, if the sample is held at +10 V potential, then the kinetic energy of the photoelectron will decrease by 10 eV. Therefore, the spectrum will shift 10 eV towards the higher binding energies. So this direct correlation between the kinetic energy shift and the local potential provide a contactless way to measure the local electrical potential on the sample surface. This approach was first proposed to probe non-Faradaic electrochemical modification of catalytic activity [29]. Due to its merits, such as high spacial resolution and no local contacts that bury the surface, the method of using XPS to probe the local electrical potential has been applied in the study of solid oxide electrochemical cells [30-32], charging dynamics of dielectric materials [33] and depth-profiling by controlled surface charging [34].

In this work, we describe a method to deduce the local surface potentials and chemical states of zirconium oxide that is under an in-plane electric bias, by using in situ synchrotron based APXPS. APXPS allows for the quantification of the Zr chemical state and the potential distribution. We also characterize and confirm the formation of ZrOₓ by chronoamperometry under different electrical bias, temperature and oxygen partial pressure conditions. The chronoamperometry (CA) measurements show electrical signature for the transition from ZrO₂ to ZrOₓ, with an increase in the electrical conductivity. The results obtained from APXPS and CA for the onset of ZrO₂ reduction to ZrOₓ are consistent. Finally, we map a range of ZrOₓ formation conditions by using the electrical signature of the chronoamperometry measurement, and reveal the correlations between temperature, oxygen partial pressure and electric field in inducing the formation of ZrOₓ. We present the results finally in the form of a PO₂-E-T phase diagram.

3.2 Experimental Details

Fully oxidized ZrO₂ thin films were deposited onto Al₂O₃ (0001) single crystal substrates by pulsed laser deposition (PLD) from a ZrO₂ target. The use of insulating Al₂O₃ (0001) as a substrate prevents the electric and ionic current leakage through the substrate during the electrical characterization. A KrF excimer laser with wavelength of 248 nm under energy constant mode (400 mJ) and pulse frequency of 10 Hz was used during deposition. The deposition conditions for ZrO₂ films were 640°C of substrate temperature and 1.3×10⁻² mbar of oxygen partial pressure. Following the
growth, the films (about 20 nm thick) (measured by a profilometer) were cooled down to room temperature in 2.6 mbar oxygen pressure to ensure full oxidation of the films. Then, dense interdigitated Pt(100nm) microelectrodes (Figure 3-1a) prepared by DC sputtering and a photolithographic lift-off process were deposited onto the ZrO$_2$ films. The finger width and inter-electrode spacings were 20 µm. The deposited ZrO$_2$ thin films were monoclinic, as confirmed by X-ray diffraction (Figure 3-1c).

Synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS) was performed at the beam line 9.3.2 of the Advanced Light Source at Lawrence Berkeley National Lab. The radiation source was tunable, monochromatized soft x-rays in the energy range of 100-800 eV. The photoelectron detector employs a differentially pumped electrostatic lens system, which allows the XPS measurement at near-ambient pressures (up to 2.6 mbar). In accessing the chemical states of Zr, the 3d core level photoelectron emission of Zr was measured over the binding energy range from 176 eV to 206 eV with a step size of 0.05 eV at constant pass energy of 20 eV. X-ray photon energy of 490 eV was used during the measurement. The IMFP for Zr 3d photoelectrons measured here is 1.167 nm.[74]

The chronoamperometry measurements were performed simultaneously with the in situ APXPS measurement. Each set of the interdigitated Pt electrode was connected to EC-LAB SP-300 Potentiostat by spring press. During the chronoamperometry measurements, the applied potential was kept at a constant level, the current flow between the two set of Pt electrodes was recorded.

In order to find more detailed bias on-set points for ZrO$_x$ formation in mapping out the conditions that induce ZrO$_x$, the chronoamperometry measurements with finer voltage steps were performed in a different chamber. The oxygen partial pressure of the chamber could be controlled form $1.3 \times 10^{-7}$ mbar to $1.3 \times 10^{-1}$ mbar. Temperature of the sample could be changed for room temperature up to 400 °C. A thermocouple was placed on top of the sample in order to measure the temperature of the sample precisely. A SourceMeter (Keithley 2400) was used to apply electrical bias and record current with time, and was controlled by a LabVIEW program.
Figure 3-1: (a) Schematic drawing of the sample geometry. ZrO$_2$ thin film was deposited by PLD on single crystal Al$_2$O$_3$ (0001) substrates. Dense interdigitated Pt (100 nm thick) electrodes were deposited onto the ZrO$_2$ thin film by DC sputtering and photolithographic lift-off process. (b) Zoomed in sketch from the top, for the sample surface with more details of the sample geometry. The finger width and inter-electrode dimension is 20 μm. The electric field is applied across the Pt electrodes on the surface laterally. (c) X-ray diffraction pattern (2θ-ω scan, with a logarithmic intensity scale) for ZrO$_2$ thin film, indicating the monoclinic ZrO$_2$ (m-ZrO$_2$). Monochromatized Cu Kα1 x-ray emission (λ=0.154 nm) was used in this measurement.

3.3 Results and Discussion

3.3.1 Chronoamperometry for detecting the formation of reduced ZrO$_x$ under in-plane electric field

The electrical characteristics of ZrO$_2$ under different magnitude of bias was studied by chronoamperometry as described above. Similar measurements have been used to study the memory resistive switching kinetics in SrTiO$_3$ system [21]. Figure 3-2 displays an example of the chronoamperometry characteristics for a constant bias applied between the two sets of interdigitated electrode for one hour. Between every bias step, the sample was annealed in 0.13 mbar oxygen at 300°C for 2 hours to reset to system back to its equilibrated zero-bias state, in order to avoid any hysteresis interference on the results. The equilibrium state is confirmed by the conductivity measurement, where no further change could be found in the conductivity of the sample. The time scale of the measurement is chosen so that the current flows through the system reach a steady state.
Figure 3-2: An example of the chronoamperometry measurements under varying electrical biases to find the on-set for the current increase at 125°C, 1.3×10^-7 mbar. The onset of current increase (shown by an arrow on each plot) is associated with the bias that triggers the transition from ZrO₂ to ZrOₓ (x<2). These onset biases found for each temperature and pressure are then used for constructing the thermodynamic equilibria diagrams of ZrO₂ and ZrOₓ.

At 6.3V in Figure 3-2 the current drops during the first tens of seconds, which could be the result of capacitive charging and/or ionic migration to equilibrium distribution. After about 500 seconds, the current stays at a stable limiting current. The system reaches a final state by a drift-diffusion equilibrium. Upon increasing the magnitude of bias until 6.5V, a small increase of current before reaching steady state could be observed at around 1000 seconds. This onset of the increase of conductivity is attributed to the formation of a reduced ZrO₂ or another structure that we denote as ZrOₓ (x<2).[22, 24] This typical electronic signature under electric bias (where current initially increases with time, and then saturates at a limiting current) could also be found in other material systems [21, 85]. This characteristic “current hump” was believed to be the sign of new phase nucleation and growth [85, 86]. The increase of current with time can be interpreted as the initiation and progression/growth of the reduced ZrOₓ phase. The magnitude of the current increase is determined by the amount of the ZrOₓ that has been formed. By further increasing the applied bias, the increase of the conductivity becomes more prominent (at 6.6V and 6.8V in Figure 3-2).
Therefore, the on-set bias for the ZrO$_x$ formation at 125°C, 1.3x10$^{-7}$ mbar could be found by this measurement as 6.5V. By using this method, we could map the on-set bias for ZrO$_x$ formation across a range of temperatures and oxygen partial pressures, and construct a quantitative relation between the on-set bias, temperature and oxygen partial pressure.

Following the same procedure as in Figure 3-2, The ZrO$_x$ formation conditions have been measured under different temperature (ranging from 100°C to 225°C) and oxygen partial pressure (ranging from 1.3x10$^{-1}$ mbar to 1.3x10$^{-7}$ mbar) (Figure 3-3). By converting the electric potential into the average electric field strength, we could plot this boundary condition into a $PO_2$-$E$-$T$ phase diagram. The electric field strength required to trigger the ZrO$_x$ formation is on the order of kV/cm, which is much smaller than the electric field strength applied for ferroelectric phase transition [87, 88] and memory resistive switching applications [22]. The low bias requirement could be attributed to the fact that this measurement is performed under elevated temperatures, while the measurement for ferroelectric phase transition and memory resistive switching are performed at room temperature or even lower temperatures. From our data, there is a clear trend that by decreasing the temperature, the electric field strength required for forming the ZrO$_x$ increases. Another reason could be the sample geometry. Our sample has its surface exposed to the environment, and the open surface could provide available sites for oxygen exchange. In the ferroelectric and memory resistive switching applications, the sample is “sandwiched” between electrodes without an exposure to the environment. So the exchange of oxygen between the electrode and the oxide will impose another energy penalty for the formation of ZrO$_x$, which in turn require higher electric fields.
Figure 3-3: On-set biases (and equivalently, the average electric field strengths) under different temperatures and oxygen partial pressures for the formation of ZrO$_x$ (x<2) from ZrO$_2$, determined by electrical chronoamperometry measurements.

3.3.2 Ambient pressure x-ray photoelectron spectroscopy for detecting the formation of reduced ZrO$_x$ under in-plane electric field

One of the most important implications from the chronoamperometry measurements (Figure 3-2 and Figure 3-3) is that, the conductivity increases while forming the ZrO$_x$ state. In order to explore and confirm the formation of ZrO$_x$ with Zr valence states lower than 4+, we employed in situ synchrotron APXPS, which could provide more detailed chemical information, along with simultaneous chronoamperometry measurements.

3.3.2.1 Effect of in-plane electrical bias on the XPS spectrum

Since we have applied in-plane electric field across the thin-film sample (see Figure 3-1a), the x-ray photoelectron spectrum collected in this configuration is altered from the ideal spectrum shape of the core level emissions. The analysis of this spectrum under varying electric potential across the sample requires careful analysis. The
magnitude of the kinetic energy shift for the core level emissions equals the local surface potential according to the relation $\Delta E_k = e \times V$. By measuring the $\Delta E_k$ of the photoelectrons of the selected core levels at various lateral positions between the electrodes on the ZrO$_2$/ZrO$_x$ film, we can directly assess the local surface potential. An example is shown in Figure 3-4. When 6 V bias is applied between the two sets of interdigitated Pt electrodes, the Pt 4f XPS peak splits into two sets of doublets. This is because one set of (half of) the Pt electrodes at the ZrO$_2$ surface (shown in Figure 3-1a) is at 6 V higher than the remaining half of the Pt electrodes (that are at 0 V) at the oxide film surface. The shift of the binding energy is 6 eV, which is consistent with the potential we applied across the Pt electrodes. This result confirmed the validity of the way we use XPS to measure the potential distribution on the sample surface. Similar methods have been used in the literature to measurement the local potential of the sample.[29-34]

Figure 3-4: XPS spectrum of Pt 4f on two sets of Pt electrodes (shown in Figure 4-1a and 4-1b) measured simultaneously. One set of Pt electrodes is grounded and the other set is at 6 V electrical bias. The Pt 4f doublet was split into two doublet sets. The energy difference between these two sets is 6 eV, consistent with the potential applied across the two sets of Pt electrodes at the surface of the ZrO$_2$ film.
3.3.2.2 Potential distribution across ZrO₂ obtained by analysis of the Zr 3d photoelectron spectrum measured under bias

The X-ray spot size of 200 μm is much larger than the surface pattern feature size or 20 μm, and the potential has a distribution across the ZrO₂ surface when we apply electric bias. Thus, the Zr 3d photoelectron spectrum that is convoluted over a varying range of electric fields across the surface is much complicated than the Pt 4f peak split exemplified in Figure 3-4. In order to extract useful information about the surface potential distribution and local chemical states, the photoelectron spectrum has to be analysed carefully. Here we proposed a new way, which has not been reported before, to reconstruct the spectrum under electric field by using the convolution of the un-biased spectrum with the reciprocal of the surface potential gradient. The essence of this method is based on the fact that the XPS peak position shift depends on the local potential on the surface and that the XPS peak intensity is proportional to the local concentration of the selected element. More specifically, the following equation is used to reconstruct the Zr 3d x-ray photoelectron spectrum under electric field:

\[
I_{bias}(E_{binding}) = \int C \cdot I_{no-bias}(E_{binding} - V(x)) \, dx
\]

\[
= \int C \cdot I_{no-bias}(E_{binding} - V(x)) \frac{dx}{dV} \, dV
\]

\[
= C \cdot I_{no-bias}(E_{binding}) \ast \frac{dx}{dV(x)}
\]

where \( I_{bias}(E_{binding}) \) is the intensity under electric bias, \( I_{no-bias}(E_{binding}) \) is the intensity without bias, \( x \) is the space coordinate on the sample surface (we only need to consider one dimension in our configuration shown in Figure 3-1), \( V(x) \) is the potential distribution across the sample surface from one Pt electrode to the next, \( C \) is a proportionality constant, symbol * represents the convolution operation. A brief explanation of Equation 3.1 will be provided as follows. In order to take the potential difference for all the material on the surface into account, the intensity of the spectrum need to be integrated over spatial coordinates, \( x \). But the function \( I_{no-bias}(E_{binding} - V(x)) \) is not a direct function of \( x \), and we do not know \( V(x) \) in advance. Thus, the function was then converted to be integrated with respect to \( dV \). By integrating \( I_{no-bias}(E_{binding} - V(x)) \) over the whole surface (the whole potential difference range in the integral over \( dV \)), the final form of the function becomes the convolution...
function shown in equation 3.1. Then equation 3.1 were coded in Matlab and used for analysing the Zr 3d spectrum under electric field. In getting the chemical states of the Zr, in addition to the Zr\(^{4+}\) state, other possible Zr sub-valence states were also fitted into the spectrum. Given the fact that it is not reasonable to fit all the three possible Zr sub-valence states into the spectrum due to the complexity imposed by the applied electric potential, only Zr\(^{2+}\) state were fitted into the spectrum with a wider FWHM (1.5×normal value). This approximates the contribution from all the possible sub-valence states (1+, 2+, 3+) with one that is averaged (the 2+). The potential distribution, V(x), is another fitting parameter, and is calculated from ten spatially evenly distributed points. In order to find a unique fitting result for the spectrum, the constraint on the total sub-valence states is imposed during the peak fitting. A reasonable and important assumption used is that the total concentration of sub-valence states in ZrO\(_2\) is proportional to the change of conductivity of the film (measured from the simultaneous electrical chronoamperometry).[26, 75, 89, 90] Since the electronic conductivity of the ZrO\(_x\) is predicted to be higher than ZrO\(_2\) [24], the increase of the sub-valence states will lead to higher current density in the film, which is consistent with the total current increase during bias. One important overall assumption used in obtaining the solution is that the change in total electrical conductivity is linearly dependent on the total concentration of the oxygen vacancies. This assumption would be accurate if the total conductivity was only based on the oxygen anion conductivity. However, the total electrical conductivity measured here has both an ion conduction and an electronic conduction contribution. And the electronic conductivity is also affected by the oxygen vacancy concentration in an oxide upon its reduction. The form of the dependence of the electronic conductivity on oxygen vacancy concentration upon the reduction of zirconium oxide is not clear. It may simply increase the concentration of electrons in the conduction band [18] and also linearly increase the electronic conductivity. However, if the motilities of electrons or concentrations of other charged defects are also affected, then the relation would deviate from linearity. Therefore, the assumption of the linear dependence of electrical conductivity on vacancy concentration could be treated as only as a first order approximation in this model, and future advancements of the model could introduce more accurate relations while keeping the general framework of the solution. In getting the optimum value of the fitting parameters for the experimental data, the Levenberg-Marquardt algorithm implemented in Matlab was
used. Figure 3-5 shows a simple example of how the magnitude of the total potential (with a linear distribution across the electrodes) could affect the shape the Zr 3d XPS spectrum (Figure 3-5a for Zr$^{4+}$ without Zr sub-valence state, Figure 3-5b with Zr$^{4+}$ and one Zr sub-valence state of Zr$^{2+}$). Under no electric bias (0.0 V), there is no change induced to the peaks. As the magnitude of the bias increases, the peak merely broadens under smaller biases (1 to 2 V). Under larger biases (3 to 5 V), the peak changes to a different shape, and loses the doublet feature.

Figure 3-5: Simulated Zr 3d photoelectron spectrum under in-plane (0V to 5V) electric bias, with a linear potential distribution from one Pt electrode to another across the ZrO$_2$ sample. (a) There is only Zr$^{4+}$ state in the spectrum. (b) Zr$^{2+}$ state was added to the spectrum with 20% intensity (1.5×FWHM) of total spectrum. Blue: Zr$^{4+}$ state; Red: Zr$^{2+}$ state; Black: overall spectrum. As the magnitude of this applied in-plane electric bias is increased from 0V to 5V, the Zr 3d 4+ and 2+ peaks get broader and the shape of each of the doublets changes as well.

Figure 3-6a shows the Zr 3d XPS spectrum evolution under 7V bias between the Pt interdigitated electrodes. Both the peak shift and the shape change could be observed by increasing time under bias. The peak shift and shape change are a strong indication of the chemical state change of the sample, as well as the potential distribution change on the sample surface. Figure 3-6b is the current measured between
the interdigitated electrodes simultaneously with the XPS measurement. The current increases with increasing the bias time. After certain time, the increasing rate decreases, and then the system eventually reaches a steady states with a limiting current.

The trend of current change is also consistent with the trend of XPS peak shift and shape change by time under bias. By using the peak reconstruction method, more quantitative results of the Zr chemical states and their concentration as well as the surface potential distribution could be obtained (Figure 3-6 c and d). The total concentration of the Zr sub-valence states increases with time.

Figure 3-6d illustrates the time dependence of the potential distribution by traversing from one set of interdigitated electrode to the other. At the beginning, the potential has a quasilinear distribution. With increasing time under bias, the Zr sub-valence states are populated into the film by the large electric driving force, the populated sub-valence states increase the local conductivity (as well as the global conductivity Figure 3-6b). The change of the local conductivity will change the local potential distribution due to ohm's law. When reaching the steady states, the potential loss on the surface is mainly near the Pt/ZrO$_2$/gas triple phase boundary. The reason for this shape of potential distribution is that, the ZrO$_x$ has been populated in the film and formed a more conducting Zr-oxide layer between the Pt electrodes. Therefore the potential drop is no longer across the Zr-oxide film but remains to be dominant rather near the triple phase boundary instead at the new electrochemical equilibrium.
Figure 3-6: ZrO$_2$ thin film bias experiment with 7V electric bias between the Pt electrodes at the surface, in 1.3×10$^{-5}$ mbar oxygen at 125°C. (a) Zr 3d photoelectron spectrum evolution under 7V bias as a function of time. The lower binding energy contribution to the total intensity increases with time at 7V. (b) Total current as a function of time at 7V difference between the interdigitated Pt electrodes on the ZrO$_2$ thin film. The increase of the current with time means that the total conductivity of the ZrO$_2$ thin film increases under electric bias. (c) Concentration of the ZrO state (or the average/overall Zr sub-valence state) during electric bias deduced from the current measured in (b). (d) Electrical potential distribution across in the 20 μm open space on the ZrO$_2$ thin film between the interdigitated Pt electrodes. The change of the potential distribution is consistent with the time-dependent change of the current and the Zr sub-valence state concentration.

The change of electrical potential distribution and Zr sub-valence states are consistent with the change of current. This is consistent with our assumption that the conductivity is proportional to the amount of ZrO$_x$ formation. Even though the conductivity of the ZrO$_x$ has not been studied experimentally before, there are several
computational works showing that the Zr$_2$O$_3$ [24], ZrO$_x$($x = \frac{1}{6} \sim \frac{1}{2}$) [75] and ZrO [75] have higher conductivity than ZrO$_2$. So it is reasonable that increasing the concentration of ZrO$_x$ increases the conductivity and the total current from the oxide film.

3.3.3 Stability diagram for the reduced ZrO$_x$ based on the relation between conductivity and chemical state

The relation between the conductivity and the reduced ZrO$_x$ could be clearly seen from the simultaneously conducted XPS and chronoamperometry measurements. Figure 3-7 shows the chemical state change and conductivity change under different biasing conditions and oxygen partial pressures at 125°C. The ZrO$_x$ formation clearly depends on the magnitude of the applied bias. For example, Figure 3-7a show the chemical states change (inserted image) and the conductivity increase at 125°C, 1.3×10$^{-7}$ mbar oxygen under 7V bias. While at the same temperature and oxygen partial pressure (125°C, 1.3×10$^{-7}$ mbar), but lower electrical bias (6V), Figure 3-7b shows no change on the chemical states and conductivity of the sample. This means that the onset of ZrO$_x$ formation is between 6V and 7V at 125°C, 1.3×10$^{-7}$ mbar, which is consistent with the condition shown in Figure 3-3.

The oxygen partial pressure dependence of the required voltage for forming ZrO$_x$ is shown in Figure 3-7. While increasing the oxygen partial pressure from 1.3×10$^{-7}$ mbar to 1.3×10$^{-1}$ mbar, the voltage required to form ZrO$_x$ stays between 6V and 7V. The temperature dependence of the voltage requirement for ZrO$_x$ formation is shown in Figure 3-8. By increasing the temperature from 100°C to 150°C, the voltage required to form ZrO$_x$ decreases (Figure 3-8 a,c,e). All the onset conditions found in the XPS measurements are consistent with the onset condition found by the chronoamperometry measurements (Figure 3-3).
Figure 3-7: Time-evolution of the current at 125°C under different oxygen partial pressures and electric biases. Zr 3d spectrum evolution at the same condition is in the inset for each panel. The time-evolution of the spectrum stacking is from bottom to top. (a) $1.3 \times 10^{-7}$ mbar, 7 V; (b) $1.3 \times 10^{-7}$ mbar, 6 V; (c) $1.3 \times 10^{-5}$ mbar, 7 V; (d) $1.3 \times 10^{-5}$ mbar, 6 V; (e) $1.3 \times 10^{-1}$ mbar, 7 V; (f) $1.3 \times 10^{-1}$ mbar, 6 V.

Figure 3-9 is a summary of the conditions for the formation of ZrOx found from both the APXPS and the chronoamperometry measurements. These figures could be seen as part of the T-PO2-E phase diagrams for the ZrO2-ZrOx system. The red squares represent the conditions from APXPS measurements, where ZrOx formation has been observed. The black triangles are the conditions from APXPS measurement, where no ZrOx has been found. So the on-set biases for ZrOx formation should then lie between the red squares and black triangles. The blue circles are the on-set biases measured by fine-step electrical measurements. As expected, the blue circles indicating the on-set of ZrOx formation lie between the red squares and black triangles. The PO2 vs. Bias (or T vs. Bias) plot could be divided into two regions. The region above the blue circles are the conditions that could form ZrOx in addition to ZrO2 (shaded as the pink region in Figure 3-9). The region below the blue circles are the conditions that are not strong enough to drive the formation of ZrOx, so only ZrO2 is stable in that regime (shaded as the blue region in Figure 3-9).
Figure 3-8: Time-evolution of the current at 1.3x10^-5 mbar oxygen partial pressure at different temperatures and electric biases. Zr 3d spectrum evolution at the same condition is is in the inset for each panel. The time-evolution of the spectrum stacking is from bottom to top. (a) 100 °C, 9 V; (b) 100 °C, 8 V; (c) 125 °C, 7 V; (d) 125 °C, 6 V; (e) 150 °C, 6 V; (f) 150 °C, 5 V.

The trend of oxygen partial pressure dependence of the on-set bias could be observed in Figure 3-9a. By increasing the oxygen partial pressure, the bias required to form ZrOₓ also increases. Since the chemical potential of oxygen in the film increases with increasing oxygen partial pressure, the chemical driving force needed to form the oxygen deficient ZrOₓ should also increase, which in turn could be reflected to the on-set bias increase.

The temperature dependence of the on-set bias is shown in Figure 3-9b. The required on-set bias for ZrOₓ formation decreases with increasing temperature. It can be qualitatively interpreted in the following way: since the ZrOₓ is oxygen deficient phase, it requires reducing conditions for its formation. By increasing the temperature and providing thermal energy, it is easier to reduce the oxide, so the bias needed to trigger the decrease would decrease.
Figure 3-9: Temperature, PO₂ and bias conditions found for the formation of ZrOₓ from the XPS measurements shown in Figure 3-7 and Figure 3-8 and from the electrical chronoamperometry measurements shown in Figure 3-3. These plots could be interpreted as T-PO₂-V phase diagrams for the ZrO₂-ZrOₓ system. (a) The experiments are performed at the same temperature (125°C). Red squares correspond to the data taken at the experimental conditions in Figure 3-7 (a), (c) and (e); Black triangles correspond to data taken at the experimental conditions in Figure 3-7 (b), (d) and (f); Blue circles correspond to the data from Figure 3-3 (b). (b) The experiments are performed at the same oxygen partial pressure (1.3x10⁻⁵ mbar). Red squares correspond to the data taken at experimental conditions in Figure 3-8 (a) (c) and (e); Black triangles correspond to the data taken at experimental conditions in Figure 3-8 (b) (d) and (f); Blue circles correspond to the data from Figure 3-3(b).

By applying electrical bias on the sample surface, it is known that the surface effective oxygen partial pressure is also altered [84, 91]. We justify the results described above based on the change of the surface oxygen chemical potential that is altered by the applied bias. The surface potential dependence of the oxygen chemical potential is expressed as [84, 91, 92]:

\[
\mu = \mu_0 + kT \ln(pO_2) + ze\Delta E
\]

where \(\mu_0\) is the standard chemical potential, \(z\) is the number of charge of oxygen ion, \(e\) is the charge of electron, \(\Delta E\) is the electric potential, \(k\) is the Boltzmann constant and \(T\) is the temperature. Figure 3-10 shows how the applied electric potential changes the surface oxygen chemical potential. This plot of \(\mu\) is found for the initial surface electric potential distribution shown in Figure 3-6d at 125 °C 1.3x10⁻⁵ mbar oxygen gas pressure, and the electric potential applied between the two electrodes is 7V. As seen in Figure 3-10, a very large oxygen chemical potential gradient was calculated on the
sample surface. This large oxygen chemical potential gradient could be the main driving force for the ZrO$_x$ formation in ZrO$_2$.

The relation used in Equation 4.2 also explains certain trends we have seen in the electrical bias that was needed for the formation of ZrO$_x$ as a function of temperature and oxygen gas pressure, as summarized in Figures 4-9. By lowering the temperature, the required electrical bias for inducing the formation of ZrO$_x$ should increase for obtaining the same magnitude of oxygen chemical potential (in the reducing condition $kT \ln(pO_2) < 0$), as the driving force. By increasing the oxygen gas pressure, $pO_2$, the required electrical bias should increase as well. This also explains the fact that the change of the required bias for the formation of ZrO$_x$ is more sensitive to the change in temperature compared to the change in oxygen gas pressure (as shown in Figure 4-9) because the contribution of the temperature is in the pre-logarithmic term of equation 3.2, while the contribution of the oxygen gas pressure is in the logarithmic term. Even though this is only a qualitative estimation of how the onset bias should depend on temperature and oxygen pressure in inducing ZrO$_x$ from ZrO$_2$, it serves as a good guide in understanding the experimental observations in Figures 4-9. Thermodynamic parameters for the ZrO$_x$, which aren’t present literature, are required to deduce more quantitative analysis of the formation of ZrO$_x$.

![Graph](image)

**Figure 3-10:** The oxygen chemical potential found from Equation 4.2 for the initial surface electric potential distribution found in Figure 3-6d at 125°C 1.3x10$^{-5}$ mbar oxygen gas pressure, and the electric potential applied between the two electrodes (separated by 20 $\mu$m) is 7V. The zero chemical potential is renormalized to the chemical potential without the applied electric field.
3.4 Conclusions

In summary, we uncovered the formation conditions of ZrO\textsubscript{x} under electrical bias at different temperature and oxygen partial pressures, probed by ambient pressure synchrotron x-ray photoelectron spectroscopy and simultaneous chronoamperometry measurements. The x-ray photoelectron spectra of Zr on ZrO\textsubscript{2} were found to change with time under strong electric fields, which indicates the change of chemical states in the Zr-oxide films. This result is consistent with, and further verified, our previous results of formation of ZrO\textsubscript{x} (x<2) during the initial oxidation of Zr metal [27], that was explained in detail in Chapter 2. Consistent with the variation in the XPS signature, the chronoamperometry measurements exhibit by a momentary current increase, followed by a new steady state under bias. This typical electronic signature has also been found in other oxide systems [21, 85], which indicate the nucleation and growth of secondary phases. Then, this chronoamperometry characteristic was used to determine the ZrO\textsubscript{x} formation conditions. The temperature, oxygen partial pressure and electric bias dependence of the ZrO\textsubscript{x} formation have been resolved: by increasing the strength of applied electric bias, the temperature (oxygen partial pressure) required for ZrO\textsubscript{x} formation decreases (increases). The mechanism of the temperature, pressure and electric bias coupling for ZrO\textsubscript{x} formation could be explained by the coupling of the large surface electrochemical potential gradient induced by the applied electrical bias to the oxygen chemical potential. Revealing the presence and formation conditions for such ZrO\textsubscript{x} is critical for understanding the Zr metal oxidation kinetics, as well as for assessing the switching mechanisms and kinetics in red-ox based resistive switching memories.
4 Structure of the Initial Oxide on Single-Crystalline Zirconium (0001) Surface Probed by Scanning Tunneling Microscopy

Abstract

The structure of the initial oxide layers grown on single crystalline Zr (0001) by thermal oxidation of Zr was studied by scanning tunneling microscopy (STM). Upon exposure to oxygen at 2.6×10⁻⁸ mbar at room temperature for one minute, small oxide clusters form at the surface, without a well-defined crystalline order. After annealing at higher temperature (530°C) in ultra-high vacuum conditions, the oxide layer surface exhibits atomic order and forms a triangular moiré pattern, consistent with a monolayer of cubic ZrO₂ (111). This first layer of the oxide has a high concentration of oxygen vacancies, ~45% on the oxygen sub-lattice counted in the STM images, consistent with the presence of reduced ZrOₓ chemistry found from our in situ XPS study reported in Chapter 2. Elastic energy minimization achieved by lattice contraction and strong electric field across the oxide during the initial oxidation are likely mechanisms for the formation of such a high sub-stoichiometry in the first oxide layer on Zr (0001). By increasing the oxygen exposure, the surface forms the second layer of oxide, which appears fully oxidized. The growth kinetics was deduced from the increase of the area of the second oxide layer. This was found to be consistent with the oxidation kinetics calculated from our in situ XPS analysis during the initial oxidation of Zr (0001) reported in Chapter 2. The second layer of the oxide has a square lattice and a moiré pattern of "row" structure. The corresponding atomic structure for this surface is likely cubic ZrO₂ (001), however the confirmation of this structure requires atomic level modelling.

4.1 Introduction

4.1.1 Overview

The structure of the oxide grown on metals is an important factor that determines the transport and heterogeneous gas-solid reaction kinetics on them [93-95]. The thin oxide films formed on the metallic substrate surface under oxidizing conditions have a critical influence also on corrosion resistance [2, 44], electrical and
catalytic activity [45], redox based resistive switching memory devices [46], and even for bio-implants [50].

Zirconia, ZrO$_2$, has a number of important technological applications. It serves as the corrosion passivating native oxide film on fuel cladding and structural materials in nuclear reactors [2, 44]. It is also a promising binary oxide for red-ox based resistive switching devices, which are considered as the next-generation, low-energy, ultra-fast and highly scalable non-volatile memory elements. The atomic structure of the surface and interface is crucial in determining the electronic and chemical properties of the material. From our previous study [27] explained in Chapter 2, we have identified formation of reduced Zr-oxide, ZrO$_x$ with $x<2$, during the initial oxidation of Zr. Furthermore, we have verified in Chapter 3 that the strong electric field and the electrochemical potential during the initial oxidation process can be the governing factor that induces the formation of ZrO$_x$. The goal of the work reported in this Chapter is to resolve the atomic structure of the initial Zr oxide, ZrO$_x$, under continuous oxygen exposure, by in situ scanning tunneling microscopy (STM).

STM is a powerful tool to study the surface atomic structure and surface structure evolution. Since its advent in 1981, numerous studies on the initial stage of thermal oxidation on metallic surfaces have been resolved by STM, for example, for Sn [14], Al [35], Ti [13], Ni [96, 97], Cu [98, 99], Au [100], Ag [101] and Pd [102, 103]. The growth of ZrO$_2$ thin oxide films on dissimilar metal surfaces, such as Ag(100) [104] and Pt(111) [105, 106] by reactive deposition of Zr in an oxygen environment have also been reported by STM studies. Ultra-thin zirconia trilayer (O-Zr-O) films were observed when grown by oxidation of Pt$_3$Zr (0001) [107] and Pd$_3$Zr (0001) [108] alloys. The growth of ZrO$_2$ was found to be self-limiting: O$_2$ does not dissociate on the oxygen terminated surface and thus cannot adsorb. The surface morphology change of Zr (0001) in the temperature range of 300-450 K and at oxygen partial pressure of pO$_2$=1×10$^{-6}$ mbar has been reported as well [25], but without atomic resolution. The detailed atomic structure of the initial oxide formed by thermal oxidation on the Zr (0001) surface remained missing till this thesis work.
4.1.2 Review of STM studies of ZrO$_2$ surface

4.1.2.1 ZrO$_2$ thin films grown on dissimilar metal substrates

Due to its importance in determining the chemical as well as the tribological properties, the surface structure of zirconium oxide have been extensive studied by STM. The ZrO$_2$ thin films were reported to be successfully deposited on various metal (or semiconductor) substrates. The ZrO$_2$ deposited on Pt (111) surface is one of the most well defined systems [105, 106]. Thin ZrO$_2$ films were prepared by deposition of Zr in an O$_2$ atmosphere on Pt (111) followed by post-annealing also in O$_2$ environment. ZrO$_2$ (111) was found on the surface. Depending on the film thickness and preparation conditions, several surface reconstruction structures have been observed. For example, Figure 4-1 shows the surface structure change from (2 x 2) to (2$\sqrt{3}$ x 2$\sqrt{3}$) after UHV annealing the sample to higher temperatures. The surface structure also evolved with the increase of the film thickness. Figure 4-2 is the summary of the sequence of structures during ZrO$_2$ film formation on Pt (111) as a function of film thickness and temperature. Starting with (1 x 1) structure after deposition, (2 x 2) structure is formed after annealing in oxygen environment and finally (2$\sqrt{3}$ x 2$\sqrt{3}$) evolves upon annealing at high temperature. However, given that the lattice misfit between the Pt (111) substrate and ZrO$_2$ (111) is relatively large (about 23%), the detailed mechanism in forming such superstructures is still not clear.
Figure 4-1: LEED pattern and STM images of a 2.7 ML thick ZrO$_2$ film on Pt (111). (a) Annealed at 980 K in $1 \times 10^{-6}$ mbar oxygen, (b) annealed at 1250 K for 1 min in UHV, (c) annealed at 1300 K for 1 min in UHV. Figures are taken from ref. [106].
4.1.2.2 \(ZrO_2\) thin films grown on Zr-containing alloys

The ultra-thin cubic zirconia (111) tri-layer, O-Zr-O, films were reported to form by oxidation of Pt\(_3\)Zr (0001) and Pd\(_3\)Zr (0001) alloys [107, 108]. The thin films were grown by first oxidizing the alloys at 400 °C in \(7\times10^{-9}\) mbar oxygen, and then post-annealing at 870 °C or higher temperature in UHV for 10 min. Atomic resolution STM images could reveal a \((\sqrt{19} \times \sqrt{19}) R23.4^\circ\) superstructure (Figure 4-3). The DFT calculations show that the oxide binds to the substrate via some of its Zr atoms, causing a large rumpling of the Zr layer in the oxide (Figure 4-4). This finding was new because previously it was commonly believed that the surface oxide bind to the substrate via oxygen [107].

The oxide formed on Pd\(_3\)Zr (0001) is quite similar to the one formed on Pt\(_3\)Zr (0001). The film is also cubic zirconia (111) with an O-Zr-O trilayer. However, a different supercell \((\sqrt{217} \times \sqrt{217}) R10.16^\circ\) is observed, due to the different lattice misfit to Pd\(_3\)Zr (0001) compared to that to Pt\(_3\)Zr (0001).
Figure 4-3: (a) STM image of the Pt3Zr (0001) surface oxidized at 400 °C. (b) Atomically resolved image of the oxide annealed at 1000 °C in UHV. (c) Fourier transform of (b). Figures are taken from ref. [107]

Figure 4-4: Calculated models for a ZrO2 (111) trilayer adsorbed on Pt/Pt3Zr (0001): (a) top view, the rhombus shows the unit cell. (b) Side view, vertical dotted lines indicate atoms on top of each other. Figures are taken from ref. [107]
The reason of using the Zr alloy single crystals instead of pure Zr single crystals in these previous works to form the surface oxide is two-fold. The first reason has to do with the temperature needed to induce crystalline order the oxide at the surface. In general, adsorption of oxygen at room temperature leads to the formation of amorphous oxide layer. Subsequent annealing to elevated temperatures orders the oxide films and growth of thin, well-ordered films.[109] On the other hand, the phase transition temperature of Zr single crystal substrate is quite low (about 1000 K), while the temperature used in these works (~1300 K) to form the ordered oxide film is much higher than the Zr phase transition temperature. Given that there is no phase transition for Pt₃Zr and Pd₃Zr alloys before melting (melting point: Pt₃Zr (2523 K) [110] and Pd₃Zr (2163 K)[111]), the substrates could be annealed under high temperature while crystallizing the oxide. The second reason has to do with the high reactivity of Zr to oxidation and to residual gasses in the UHV chamber. By reducing the Zr content in the material (from 100 at.% to 25 at.% in the alloys), the oxidation speed can be slowed down, and the reactions (or contamination tendency) with the residual gasses can be suppressed, ultimately rendering the high-resolution STM imaging of the surface oxide easier than on pure Zr.

4.1.2.3 ZrO₂ thin films grown on Zr single crystal

There is only one work that reported the surface structure of the oxide forming on pure Zr single crystal during oxidation [25]. The oxidation experiment was performed in the temperature range of 300-450 K, at pO₂=1×10⁻⁶ mbar, on the basal and prism planes of Zr. Since the oxidation temperature is relatively low, the oxide was not observed to be crystalline (Figure 4-5). During the initial oxygen exposure, the surfaces are covered with small oxide clusters/protrusions. The consecutive processes of oxide nucleation, growth and coalescence lead to a “laterally-closed” oxide layer. With increasing the oxidation temperature, the grain size of the oxide also increased.
Figure 4-5: STM images of the oxide surface after oxidation of Zr at 450 K for 300 s, 600 s, 1200 s, 2400 s and 7200 s on the (a-e) basal and (f-j) prism plane surfaces. Figures are taken from ref. [25]
The lack of atomically resolved images limits the information that we can extract from this oxidation experiment. It is still not clear how the interface between the Zr metal substrate and the surface oxide would be arranged, as well as the atomic structures of the initial surface oxide. In their work, they also mentioned that the bare Zr metal surface is highly reactive to the residual gas in the UHV chamber. Even after a very short period in the UHV chamber, the adsorbed contaminate atoms could be observed on the surface. This probably made it difficult to obtain atomically resolved oxide at the surface.

4.1.3 Focus of this work

In this work, we report on the growth of the zirconium oxide initial layer by oxidation of Zr (0001) surface. The surface structure and its evolution were characterized with STM. The oxidation of the surface undergoes a layer by layer process. For the first two layers of oxide, the oxidation kinetics observed from STM measurements is consistent with our previous XPS studies on the same single crystal Zr (0001) surface as reported in Chapter 2. Two kinds of moiré patterns, triangles and rows, have been observed after the oxygen exposure and UHV annealing of Zr (0001). The atomic models for these structures have also be proposed and discussed.

4.2 Experimental Details

The experiments were performed on a single crystalline Zr (0001) (10mm×5mm×2mm, purchased from Princeton Scientific Corp.). The surface was mechanically polished to within 1° of this orientation. All the measurements were performed in an ultra-high vacuum (UHV) system, which has an STM chamber connected with the preparation chamber. The native oxide and other contaminants on the Zr surface were removed by Ar+ ion sputtering (3 kV for thirty minutes) prior to the oxidation experiment in the preparation chamber. Then the sample was annealed under UHV (2.6×10⁻¹⁰ mbar) at 580°C for three hours. After five cycles of sputtering and UHV annealing, an XPS survey spectrum confirmed the absence of oxygen and any contaminants from the surface. In order to eliminate the effect of surface re-contamination even in UHV, the sample was transferred immediately into the STM characterization chamber for the oxidation measurements.

Scanning tunneling microscopy images were collected in order to visualize the evolution of surface initial oxide formed during oxygen exposure on Zr(0001) at room
temperature. An STM system (Omicron VT-STM; Omicron Nanotechnology, GmbH, Germany) was used under UHV conditions with a base pressure of $2.6 \times 10^{-10}$ mbar. The STM imaging was performed under constant current mode with a bias voltage in the range of -2 V to 2 V and constant tunneling current in the range of 0.2 nA to 2 nA. The \textit{in situ} oxygen dozer was placed about 5 cm away from the sample surface on the STM stage. During the oxygen exposure, pure dry oxygen gas (purity>99.999 vol.%) was introduced into the STM chamber by a ultra-fine leak valve. The oxygen partial pressure was controlled to stabilize at $2.6 \times 10^{-8}$ mbar during all the oxygen exposure experiments. STM images were subjected to a global flattening procedure and horizontal noise removal using SPIP 4.8.4 software from Image Metrology (Denmark).

4.3 Results and Discussion

4.3.1 The Zr (0001) Surface

After cycles of sputtering and annealing, the Zr (0001) surface showed very large terraces (Figure 4-6 a). The surface is atomically flat, the step height for a single layer is about 0.51 nm. The high resolution STM image (Figure 4-6 b) shows a hexagonal atomic structure with a lattice constant of 0.319 nm at the surface, which is close to the bulk value reported in the literature (0.323 nm) [112]. The bare Zr surface is highly reactive, and it is prone to the oxidation by the residual gas in the UHV chamber (mainly H$_2$O and CO$_2$). The dark spots in Figure 4-6a are the surface contaminations (even in a UHV chamber with base pressure of $2.6 \times 10^{-10}$ mbar). In order to eliminate the effect of surface contamination to the oxidation experiment, the oxidation was performed as soon as the sample was cleaned by cycles of sputtering and annealing.
4.3.2 Surface Structure Evolution during Oxygen Exposure of Zr (0001)

In order to prepare the oxidized Zr (0001) surface, $2.6 \times 10^{-8}$ mbar oxygen was exposed to the sample surface for 1 min, 3 min, 6 min, 10 min, 15 min, 25 min, 40 min, 60 min and 95 min at room temperature. After each oxygen exposure, the sample was annealed in UHV at 530°C for 4 hours to crystallize the oxide. The STM images were recorded right after the oxygen exposure (Figure 4-7) and right after UHV annealing (Figure 4-8).

Figure 4-7a shows the Zr (0001) surface right after the first 1 min of oxygen exposure at room temperature. The surface was covered with disordered, small oxide clusters. Such small clusters has been previously reported in the Zr oxidation experiments [25]. From our previous LEED characterization (Figure 2-7) and literature report [25], the oxides grown on Zr (0001) surface at room temperature are amorphous. After annealing in UHV at 530 °C, the surface showed very interesting triangular structures. The triangle structure covered almost the entire surface. This structure will be discussed in detail in the next section. We will focus on the surface structure evolution under oxygen exposure in this section first.

Then, the sample undergoes an additional oxygen exposure for 2 min $2.6 \times 10^{-8}$ mbar at room temperature. Figure 4-7b shows some disordered dots and clusters on top of the triangular structures, which indicates the newly formed oxide or oxygen

Figure 4-6: STM image of Zr (0001) surface after preparation by cycles or sputtering and annealing in UHV. Large terraces in (a) and atomic resolution of the hcp lattice in (b) could be observed. (a) $V_{\text{sample}} = 0.5$ V, $I_{\text{tunnel}} = 1.2$ nA. (b) $V_{\text{sample}} = 0.3$ V, $I_{\text{tunnel}} = 1.0$ nA.
adsorbates. The sample was then annealed in the same UHV condition as in the previous step again. A new structure was found forming on top of the triangular structure (highlighted by red boarders in Figure 4-8b). It has a “row” like structure (shown at higher resolution in Figure 4-9), and it will be discussed in the following sections. More interestingly, upon increasing the oxygen exposure (following the same exposure and UHV annealing steps), the fractional coverage “row” area in the image also increases (Figure 4-8 b-i). After 95 min (in total) oxygen exposure, the surface was almost fully covered with the “row” structure (Figure 4-8i). Only a few small patches of the triangular structure remained after 95 minutes. The increase of the coverage of the “row” structure is negligible with subsequent oxygen exposure, which means that the surface oxide reaches a limiting thickness (Figure 4-9).
Figure 4-7: STM images of Zr (0001) surfaces after oxidation at 2.6×10⁻⁸ mbar in oxygen at room temperature (V_{sample} = 0.5 V, I_{tunnel} = 1.2 nA). The oxygen exposure time (cumulative): (a) 1 min; (b) 3 min; (c) 6 min; (d) 10 min; (e) 15 min; (f) 25 min; (g) 40 min; (h) 60 min; (i) 95 min.
Figure 4-8: STM images of Zr (0001) surfaces after oxidation at 2.6×10^{-8} mbar in oxygen at room temperature (V_{sample} = 0.5 V, I_{tunnel} = 1.2 nA). Before taking these images, the sample was annealed in the UHV chamber for 4 hours at 530 °C. The oxygen exposure time (cumulative): (a) 1 min; (b) 3 min; (c) 6 min; (d) 10 min; (e) 15 min; (f) 25 min; (g) 40 min; (h) 60 min; (i) 95 min.

We compared the oxide growth kinetics observed by STM images to that deduced from our previous X-ray Photoelectron Spectroscopy (XPS) characterization of the Zr(0001) initial oxidation kinetics (Chapter 2 Figure 2-4) [27]. The resulting oxide growth kinetics from STM and XPS are shown in (Figure 4-10), and the kinetics appear to be well consistent among these two different methods. The “number of layers” in the STM images was counted by calculating the coverage of the row structure on top of the triangular structure at the surface. The triangular patterns form the initial
(first) layer oxide, and the row structure is the second layer. From Figure 4-10, during the initial oxidation stage (before 10 min), the oxide grows rapidly. As the surface covered with more and more "row" structures, the oxidation kinetics decreases and finally reaches the limiting thickness.

Figure 4-9: (a) STM image of the second layer of the oxide grown on Zr (0001) after 95 min oxygen exposure (2.6x10^-8 mbar) with subsequent UHV annealing (2.6x10^-10 mbar, 530°C) (V_sample = 0.3 V, I_tunnel = 1.2 nA). The darker patches show the first layer of the oxide with the triangular structure, underneath the second layer with the row structures. (b) Height profile of the white line in (a). The measured 0.52±0.05 nm of height is very close to the lattice constant of cubic zirconia (5.14 nm [106]) and of tetragonal zirconia (5.18 nm [126]).

Figure 4-10: Oxide growth kinetics on the Zr (0001) surface as a function of oxygen gas exposure time (1 min, 3 min, 6 min, 10 min, 15 min, 25 min, 40 min, 60 min, and 95 min) at room temperature in 2.6x10^-8 mbar. Black squares are the data from XPS measurements also shown in Figure 2-4 of Chapter 2. Blue circles are the data retrieved from the STM images by calculating the fractional coverage of the area with the row structures that makes the second layer of oxide, on top of the first layer with a triangular moiré pattern.
4.3.3 The triangular moiré structure of the first oxide layer

As described above, after the first cycle of oxygen exposure and UHV annealing, most of the sample surface was covered by a large triangular moiré pattern (Figure 4-8 and Figure 4-11). There are brighter and darker triangles, with black dots on the vertex. The periodicity of the large triangle moiré structure is about 8.8 nm. The in-plane inter-atomic distance measured from Figure 4-11b is 0.331 nm. From the previous oxidation measurements on the Pt$_3$Zr (0001)[107] and Pd$_3$Zr (0001)[108], it was proposed that the initially formed surface oxide has a cubic zirconia structure with (111) orientation normal to the surface. From our STM images (Figure 4-11 and Figure 4-12) of the surface structure, here too the surface is likely to be cubic zirconia (111). More interestingly, the surface is highly defective (the black dots). In order to determine whether the black dots are surface oxygen vacancies or surface oxygen adsorbents, the tunneling voltage was reversed from 0.2 V to -0.2 V (Figure 4-12). The contrast of the images do not change with the bias polarization, which eliminates the possibility that the black dots are surface adsorbents. Therefore, we propose that the surface is an oxide, with the O-Zr-O (111) orientation, and with a high concentration of oxygen vacancies on the top layer of oxygens.

The O-O inter-atomic distance at the surface from our STM images is 0.331 nm, smaller than the bulk cubic zirconia (0.361 nm [106]) (about 8% less). The formation of oxygen vacancies can reduce the lattice constant [113], so the smaller lattice constant on the surface with respect to bulk value is consistent with observation of the defective surface. The oxygen vacancy concentration (Figure 4-13) is about 45% ($y=1.8$ for $y$ in ZrO$_{2-y/2}$). We can use the relation between the chemical expansion and defect concentration to calculate how much of lattice contraction is expected for the vacancy concentration found on our surface oxide: $\varepsilon = \alpha_{v} \cdot y$, where $\alpha_{v}$ is the chemical expansion coefficient, $\alpha_{v} = -0.044$ for zirconia [113]. By substituting the value of $y$ and $\alpha_{v}$ into the equation, we can get $\varepsilon = -0.0792$, which means that the vacancy concentration at $y=1.8$ could give rise to a lattice contraction of about 7.9%. This estimated contraction is very close to our experimental observation that the lattice for the initial surface Zr oxide is about 8% less than the bulk value. In other words, the lattice spacing measured by STM on this first oxide layer is consistent with that of Zr-oxide, ZrO$_{2-y/2}$, with a high concentration of oxygen vacancies at $y=1.8$. This high concentration of oxygen vacancies is seemingly unexpected, and we explore further...
whether the vacancy formation is an outcome of elastic energy minimisation at the interface that is achieved by lattice contraction. The inter-atomic distance of the surface oxide we measured from STM images is 0.331 nm, that is 8% smaller than that of the bulk fully oxidized cubic zirconia 0.361 nm. However, the 8% reduced lattice parameter of 0.331 nm is closer to the interatomic spacing of the Zr (0001) substrate (0.319 nm) than that of the fully oxidized cubic zirconia. This would correspond to a strain energy release in the oxide film, by going from 0.361 nm to 0.331 nm on the Zr (0001) substrate with 0.319 nm atomic spacing. The biaxial stain energy, \( E(\alpha) \), induced by the metal-oxide interface could by calculated by [114]:

\[
E(\alpha) = \frac{(c_{11} + 2c_{12})[(c_{11} - c_{12})(h^4 + k^4 + l^4) - (c_{11} - c_{12} - 6c_{44})(h^2k^2 + h^2l^2 + k^2l^2)]}{c_{11}(h^4 + k^4 + l^4) + 2(c_{12} + 2c_{44})(h^2k^2 + h^2l^2 + k^2l^2)} \alpha^2V
\]

4.1

where \( \alpha \) is the biaxial strain, \( c_{ij} \) are the elastic constants, the biaxial strain is applied in the (hkl) and \( V \) is the volume of the strained material. In our case, we have 8% (\( \alpha = -0.08 \)) compressive strain on the (111) plane of c-zirconia. The elastic constants were taken from ref [115] for undoped cubic ZrO\(_2\): \( c_{11} = 630 \) GPa; \( c_{12} = 152 \) GPa; \( c_{44} = 100 \) GPa. In order to calculate the volume of the unit cell, the lattice constant for c-zirconia was taken as 0.509 nm. By putting these parameters into equation 4.1, the strain energy released by the oxygen vacancy could be calculated by taking the difference between the strain energy of bulk cubic ZrO\(_2\)(0.361 nm)/Zr(0001)(0.319 nm) (11.6\% compressive) and surface defective ZrO\(_2\)(0.331 nm)/Zr(0001)(0.319 nm) (3.6\% compressive). Then the resulting stain energy release for one unit cell is 4.20 eV. This is a large compressive strain energy release. The oxygen vacancy formation energy in this phase was found to be 6.15 eV in literature [116]. Given that the oxygen vacancy concentration in the first layer oxide is about 45\%, the energy required to form this highly defective structure per unit cell is \( 6.15 \times 0.9 = 5.54 \) eV. This value is close to but still larger than the strain energy released by the 8\% lattice contraction. Therefore, strain energy release alone could not form this highly defective surface oxide layer. There is another driving force for the ZrO\(_x\) formation that we have identified in previous chapter (Chapter 3), which is the strong electric field (electrochemical potential gradient).
The surface oxide layer with a high concentration of oxygen vacancies as seen in this work induces a large under-coordination of the Zr in this oxide layer. This atomic structure could also explain the observation of Zr sub-valence states (3+, 2+, and even possibly 1+) from our XPS measurement [27] (Chapter 2 Figure 2-2). The valence states of Zr is proportional to the number of surrounding oxygen atoms in the lattice site. When a doubly positively charged oxygen vacancy (dominant oxygen defect in zirconium oxide) [18] is generated, two excess electrons are released into the lattice. Importantly, the average composition of first layer oxide is ZrO_{1.1} (Figure 4-13), which is consistent with average composition we found from our XPS study of the Zr initial oxide in Chapter 2. It is also interesting to note that the oxygen vacancies at the surface are clustered along preferred direction [110]. The detailed electronic structure and mechanism for the formation of extended oxygen vacancy clusters on ZrO_2 surface need further theoretical and computational justification.

Figure 4-11: Structure of the Zr (0001) surface after 1 min in 2.6\times 10^{-8} mbar oxygen exposure at room temperature with subsequent annealing at 530°C in UHV. (a) The large scale overview STM image shows large triangular moiré structures. (V_{sample} = 0.2 V, I_{tunnel} = 1.2 nA) The structure featured bright triangles (highlighted as an example in red solid triangle) and dark triangles (highlighted as an example in blue dashed triangle) (b) Atomic resolution image of the surface (V_{sample} = 0.2 V, I_{tunnel} = 1.5 nA). The surface is highly defective with oxygen vacancies (black dots).
Figure 4-12: Atomic resolution STM image of the surface oxide layer with a triangular moiré pattern, measured in the same region but with different sign of tunneling biases. (a) $V_{\text{sample}} = 0.2$ V, $I_{\text{tunnel}} = 1.5$ nA. (b) $V_{\text{sample}} = -0.2$ V, $I_{\text{tunnel}} = 1.2$ nA.

Surprisingly, the oxygen vacancy concentration in the triangular moiré structures does not change while the second oxide layer grows on top of the first one with increasing the oxygen exposure. Figure 4-13 shows the oxygen vacancy concentration under different oxygen exposures. The fraction of oxygen vacancy concentration on the surface is calculated by counting the number of black dots on the atomic resolution images on the triangular structures remaining at the surface. There is almost no change in the oxygen vacancy concentration of this first oxide layer with increasing the oxygen exposure, although the second oxide layer grows on top. The reason for the high stability of this oxygen-deficient surface oxide layer could be explained based on the reduction of the interface strain energy between the oxide and the metal. Oxygen deficiency in the oxide layer reduces the lattice parameter of the oxide, making it get closer to that of the underlying metal. In this way, the strain energy, which is 2.36 eV/unit cell for 8% compressive strain, induced by the interfacial lattice mismatch between the thin oxide and underlying metal substrate is reduced. If the concentration of the oxygen vacancies were to decrease during longer exposure to oxygen, the lattice mismatch and the interfacial strain energy would increase.
Figure 4-13: Oxide growth kinetics on Zr (0001) surface based on the surface oxide layers counted in the STM images, and the surface oxygen vacancy concentration in the first oxide layer that has a triangular moiré pattern. Black squares are the data retrieved from the STM images by calculating the fractional coverage of the area with the row structures that makes the second layer of oxide, on top of the first layer with a triangular moiré pattern. Blue triangles are the fraction of oxygen vacancies on the first oxide layer (triangular moiré structure) that remains uncovered as the second oxide layer grows on top. There is no observable change of the oxygen vacancy concentration on the first oxide layer while the second oxide layer grows upon increasing the oxygen exposure.

Another important question about the highly defective surface oxide layer is that whether the formation of such triangular moiré structure is due to the difference of the oxygen vacancy distribution. The uniformity of the oxygen vacancy concentration could be verified by the filtering the triangle pattern from the STM images (Figure 4-14). Figure 4-14a shows the original STM image of the triangle structure, the blue cycle is the dark vertex region, and the red cycle is the bright triangle region. After subjecting the image in Figure 4-14a to FFT filtering to remove the background contrast, we find no observable difference of the oxygen vacancy concentration in these two regions (Figure 4-14b). Therefore, the formation of the large triangle structures could not be attributed to the difference of the oxygen vacancy concentration in different zones.
Figure 4-14: Atomic resolution STM image of triangle structure. ($V_{\text{sample}} = 0.2$ V, $I_{\text{tunnel}} = 1.5$ nA) (a) Original image; (b) image after FFT filter process.

Figure 4-15: Visualization of Moiré pattern. There are two sets of hexagonal lattices with a misorientation angle of 10° between them; when they are overlapped together, another hexagonal lattice with larger periodicity appears, which is the resulting moiré pattern by rotation. Figure is taken from ref [117].

In fact, the moiré structure in Figure 4-11 is commonly observed in other thin films grown on single crystal substrate, such as graphene grown on Ru (0001)[118], FeO grown on Pt (111)[119, 120], CoO on Pt (111)[121] and Al₂O₃ on TiAl (111)[122]. This moiré pattern originates either from the lattice mismatch between the substrate and the film or rotation of the surface film with respect to the substrate [117, 123-125]. We
have tested both possibilities. The moiré structure originating from rotation (Figure 4-15) for the hcp system is quite different from the structure in Figure 4-11. The lattice constant for the Zr (0001) substrate is 0.319 nm, and this is smaller than the surface oxide interatomic distance of 0.331 nm measured in our STM. Therefore, we think that the triangular moiré structure in Figure 4-11 may originate from the lattice mismatch mechanism. Moreover, the period of the moiré structure could be obtained from the period of the thin film and the substrate by:

\[
\frac{1}{P_m} = \frac{1}{P_s} - \frac{1}{P_o}
\]

where \(P_m\) is the period of the moiré structure, \(P_s\) is the period of the substrate and \(P_o\) is the period of surface oxide. By taking \(P_s = 0.319 \text{ nm}\) and \(P_o = 0.331 \text{ nm}\) into the equation, we get \(P_m = 8.799 \text{ nm}\), which is very close to the value we measured from the STM images (8.8 nm).

The contrast in the triangular moiré pattern comes from the different stacking sequence of the thin oxide layer with respect to the substrate. Based on the previous STM and DFT work on the surface oxide formed on the Pt\_Zr (0001)[107] and Pd\_Zr (0001)[108], we choose cubic ZrO\_2(111) trilayer as the initial surface oxide. Figure 4-16 shows typical stacking sequences. The triangular pattern can be seen in these stackings. The validity of this model needs further examination by atomistic simulations, especially in the case for the surface with extensive oxygen vacancies.
Figure 4-16: Models for different stacking sequences that induce trilayer cubic ZrO$_2$ (111) with respect to the Zr (0001) substrate. (a) ABCA stacking sequence (corresponding to the dark vertex in the STM image); (b) ABCB stacking sequence (corresponding to the middle of the bright triangles in the STM image); (c) ABCC stacking sequence (corresponding to the middle of the dark triangles in the STM image); (d) STM image of the large triangular moiré pattern. ($V_{\text{sample}} = 0.2$ V, $I_{\text{tunnel}} = 1.2$ nA); (e) 17 nm x 17 nm top view of the atomic model of the cubic ZrO$_2$ (111) on top of Zr (0001). The corresponding stacking sequences in (a), (b) and (c) are marked my squared on this figure.

4.3.4 The “row” structure of the second oxide layer

After the first cycle of the oxygen exposure and UHV annealing, further oxygen exposure forms a second layer of oxide on the surface with a different structure (Figure
4-8 and Figure 4-9). It has a “row” like structure, which is also a moiré pattern originating from the difference of the lattice symmetry and lattice constant. The period of the “row” is about 2.2 nm. With atomic resolution STM on the “row” structure (Figure 4-17), a cubic lattice constant 0.359 nm could be observed, which is very close to the literature value for the interatomic distance (O-O) for cubic zirconia (0.361 nm [106]) and for tetragonal zirconia (0.360 nm [126]). In Figure 4-9b, the height of the second oxide layer was measured to be 0.52±0.05 nm. Again, this value is quite close with the lattice constant of cubic zirconia (0.514 nm [106]) and tetragonal zirconia (0.518 nm [126]). Only based on the in-plane and out-of-plane lattice constants measured from the STM image, it was not enough to confirm the phase the oxide. In the following, we will choose the cubic zirconia (001) as a possible model for the structure of the second layer oxide, while a similar argument and atomic structure could also be constructed for tetragonal zirconia (001). It is important to note that it does not mean that the formation of cubic zirconia is more favourable than tetragonal zirconia. Further theoretical calculations are required to confirm which phase of the oxide is more stable under these experimental conditions, thus could be formed on the surface as the second layer oxide.

From Figure 4-9, it is clear that the “row” structure, as the second layer of oxide, is grown on top of the triangular structure which was the first layer oxide. Therefore, a corresponding model could be proposed (Figure 4-18). An O-Zr two-atom-layer is formed on top of O-Zr-O trilayer. The interatomic distances for these layers are the values measured from the STM images (Figure 4-12 and Figure 4-17). In Figure 4-18, the Zr atoms are lined up with a period of 2.29 nm in a “row” like manner (red dashed line in Figure 4-18).
This kind of surface orientation change upon increasing the oxygen exposure have never been reported on Zr surface before. The initially formed triangular moiré pattern, which has a cubic ZrO$_2$ (111) structure on Zr (0001), has a similar lattice symmetry as the substrate Zr (0001). It could serve as a buffer layer for the further growth of the ZrO$_2$ (001). It was also reported in the study of ZIRLO oxidation in pure water environment at 360 °C, that the tetragonal zirconia (001) is formed within 0.3–0.5 μm of the metal-oxide interface [127]. However, the detailed analysis of the formation energy and stability of such oxide at metal-oxide interface has not been discussed before. Further theoretical calculations are needed to verify this hypothesis.
2.29 nm

Figure 4-18: Model for the “row” moiré pattern on the second oxide layer on Zr (0001). This structure is constructed from a 2-atom-layer Zr-O (001) on top of tri-atomic layer O-Zr-O cubic ZrO2 (111). The periodicity of the “row” is 2.29 nm, which is consistent with the STM observation.

4.4 Conclusions

We have studied the surface structure of the initial oxide formed on Zr (0001) single crystal surface by using scanning tunneling microscopy (STM). By exposing the sample to oxygen at 2.6×10⁻⁸ mbar at room temperature for 1 min and annealing, the first layer of the surface oxide form a large triangle moiré pattern. Atomic resolution STM images show the surface of the triangle moiré pattern has a c-ZrO₂ (111) orientation, with an O-Zr-O trilayer structure is proposed for this triangle moiré pattern. This first oxide layer has a large concentration of oxygen vacancies. The presence of such a highly sub-stoichiometric surface oxide is quantitatively consistent with the formation of ZrOₓ (x<2) states we found in our XPS studies in Chapter 2 [27]. The formation of the surface oxygen vacancies at 45% is consistent with an 8% shrinkage of the lattice constant. The strain energy released by the shrinkage of the lattice constant was estimated to be 4.20 eV/unit cell, and we think that this energy release combined with strong electric field formed across the oxide during the initial oxidation could provide the driving force to stabilize the high sub-stoichiometry in the first oxide layer on Zr (0001). By further oxygen exposure and annealing, a second layer of oxide grows
on top of the first layer, with intermediate steps up to 95 minutes. The structure of this second oxide layer has a “row” moiré pattern. The growth of the oxide on the surface is self-limiting, which is consistent with our previous oxidation kinetic studies by XPS on the same sample. The surface of the “row” pattern has a squared lattice, which could be cubic or tetragonal ZrO₂ (001) surface. A possible model for the “row” moiré pattern is proposed. The detailed atomic level structure of the initial Zr oxide presented in this work should pave the way for modelling and interpreting the oxidation properties of Zr and Zr alloys as well as the surface properties of the oxide formed on them.
Oxygen Transport Properties of Monoclinic ZrO$_2$ under Electric Field

Abstract

Oxygen transport in solids under electric field is an important elementary processes for metal oxidation resistance, red-ox based non-volatile memory and semiconductor devices, separation membranes, and fuel cells. In particular for oxidation and red-ox based memory devices, the operation temperature is relatively low (room temperature to a few hundred °C). On the other hand, diffusion measurements (mainly by secondary ion mass spectrometry) focus on the high temperature regime. To date, experimental and theoretical work on the oxygen transport under electric field at low-to-intermediate temperature regime has been rarely reported. In this work, we used chronoamperometry to characterize the oxygen diffusion under electric field by taking monoclinic zirconia thin film as a model system. By modelling the data with drift-diffusion equation, and by Cottrell equation [21], we were able to separate the self-diffusion coefficient from the effect of the electric field. The activation energy of the intrinsic oxygen vacancy diffusion coefficient was found to be $0.82 \pm 0.07$ eV, which is close to the oxygen vacancy migration barrier in cubic ZrO$_2$ without the electric field acceleration. The experimental approach and the modelling implemented in this work can be adapted to assessing the transport characteristics of oxides under electric field, for example in metal oxidation and for switching mechanisms and kinetics in red-ox based resistive switching memories.

5.1 Introduction

The migration of charged species under an external electric field is the basic question when considering various electrical effects occurring in the bulk or on the surface of solid state devices [19, 128, 129]. Electronic and ionic transport acts in numerous electrochemical devices including fuel cells, batteries, separators, and gas sensors. [128, 130-135] Among applications using metal oxides, the electric field forces oxygen ions/vacancies or other mobile charged species to redistribute. The oxygen vacancies exist in a dynamic equilibrium with the electronic holes. Probing the electronic and ionic transport properties is needed to understand the fundamental
mechanisms and performance of such devices. Such information could also facilitate
the understanding of some detrimental effects, such as corrosion [56, 136], dielectric
breakdown [137, 138] and current leakage for semiconductor devices [139, 140].

In Chapter 3, we have discussed the formation of oxygen deficient ZrO_x phase
by applying electric field or electrochemical potential to the ZrO_2 thin films. And the
surface electric potential distribution could be mapped by *in situ* X-ray Photoelectron
Spectroscopy (XPS). But the detailed mechanism behind this phenomenon has not been
discussed in detail. In this chapter, we will focus on the oxygen ion/vacancy transport
under electric bias, and characterize the diffusion kinetics by *in situ* XPS and
chronoamperometry measurements.

In order to access the kinetic parameters for the charged species diffusion,
corresponding models are needed to describe the experimental observations. There are
several different models used in the literature to capture the characteristics of the
charged species diffusion. Depending on the experimental setup, the form of the
equations may be varied to some extent, but the essential element of the equations is
the diffusion process:

\[
\frac{\partial C(x, t)}{\partial t} = \nabla \cdot [D(x, t) \nabla C(x, t)]
\]

where x is the coordinate, t is the time, C(x, t) is the concentration of the species,
D(x, t) is the diffusion coefficient. Eq. 5.1 only considers the self-diffusion with a
concentration gradient, where no external source or driving force is applied to the
system. Applying electric bias requires the electric drift term to be added to this
equation. Furthermore, subjecting the material to the environment where the material
can exchange species, such as oxygen, requires that the surface exchange reaction is
added to this equation. In the next section, we will briefly review the development of
the diffusion model in different fields of studies. Then, the model that describes our
experimental setup will be proposed, and the kinetic parameters found by fitting the
date with our model will be discussed.
5.2 Review of Diffusion Models in Describing the Systems under Electric Field

5.2.1 Classic Cottrell Model

The classic Cottrell equation describes the change in the electric current with respect to time under a controlled potential. It is a very classic and well-established equation in electrochemistry. The basic idea is to solve Fick’s second law of diffusion (Eq.5.1) for a planar electrode:

\[ i = \frac{nFAc_j^0 \sqrt{D_j}}{\sqrt{\pi t}} \]

where \( i \) is the current, \( n \) is the number of electrons, \( F \) is the Faraday constant, \( A \) is the area of the electrode, \( c_j^0 \) is the initial concentration of the charged species, \( D_j \) is the diffusion coefficient, \( t \) is the time.

The classic model works very well with a simple red-ox event, the kinetics depends on the rate at which the analyte diffuses to the electrode. The Cottrell approach has also been applied to study the kinetic of memristive switch behaviour in oxides that transport charged species [21]. Figure 5-1 shows the diffusion constants modelled in ref. [21] by Cottrell equation for SrTiO$_3$-6 under electric field. The diffusion coefficient is shown to depend on the magnitude of the electric field applied on the sample - the larger the field applied, the larger the diffusion constant. On the other hand, according to the definition of the diffusion constant, it should not be a function of external electric field, it is rather an intrinsic property of the material. The controversy stems from the fact that the classic Cottrell equation is derived from the diffusion equation, Eqn. 5.1, which does not take the electric field induced drift term into account. Therefore, the resulting diffusion constant in ref. [21] is actually a combination of self-diffusion coefficient and the electric field induced drift. The magnitude of electric drift is proportional to the strength of the electric field. So in total, the diffusion constant in Figure 5-1 has dependency on the electric field applied.
Figure 5-1: Analysis of specific time and diffusion constants for a memristive PtSrTiO$_3$-δ/Pt bit via the memristor-based Cottrell equation. (a) Analyzed time constant, determined via the memristor-based Cottrell equation for the memristive oxide SrTiO$_3$-δ with respect to electric field strength and bias at room temperature for increasing bias voltage (solid symbols) and decreasing bias voltage (open symbols). (b) Calculated oxygen vacancy diffusion constant, for the memristive oxide SrTiO$_3$-δ with respect to electric field strength and bias at room temperature. Extrapolation of vacancy diffusion constants in literature from high to room temperature without electric field. Figures a and b are taken from ref. [21]

5.2.2 Coupled Diffusion-Drift Model

A more sophisticated model to describe the electric field induced dynamics of charged species is proposed and studied in several works [128, 141]. In reference [128], the diffusion of charged species in metal oxide/electrode system has been considered. The species migration followed the electric field application is described by one-dimensional initial-boundary-value diffusion problem:

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \mu E \frac{\partial n}{\partial x} + A - B 
\]

\[5.3\]

\[
D \frac{\partial n}{\partial x} = \mu E n \big|_{x=0, x=L} 
\]

\[5.4\]

\[A = B \big|_{t=0} \]

\[5.5\]

where \( n \) is the concentration of the migrating species, \( D \) and \( \mu \) are the diffusivity and mobility of the migrating species, \( E \) is the strength of the electric field, \( x \) is the spatial
coordinate along the electric field, and \( t \) is the time. \( A \) is the source and \( B \) is the sink for the migrating species.

There is one implicit assumption in this model - it assumes that the electric field applied to the sample is small, so that the drift term in Eq.5.3 has linear dependence on electric field strength. Thus, when considering the systems under strong electric field, this model is not valid. In addition, when the system is open to the gas environment, and free to exchange species with the gas environment, another term considering the surface exchange reaction is also needed in the model.

In our work, our system is under strong electric bias and is open to the gas phase oxygen. An accurate drift term and the surface exchange term needs to be considered in the model. The details about our model will be discussed in section 5.4.4.

5.3 Experimental Details

\( \text{ZrO}_2 \) thin films were deposited onto \( \text{Al}_2\text{O}_3 \) (0001) substrates by pulsed laser deposition (PLD) from a \( \text{ZrO}_2 \) target. A \( \text{KrF} \) excimer laser with wavelength of 248 nm under energy constant mode (400 mJ) and pulse frequency of 10 Hz was used during deposition. The deposition conditions for \( \text{ZrO}_2 \) films were 640 °C of substrate temperature and 0.013 mbar of oxygen partial pressure. Following growth, the films (about 20 nm thick) were cooled down to room temperature in 2.6 mbar oxygen pressure to ensure full oxidation of the films. The deposited \( \text{ZrO}_2 \) thin films were monoclinic, as confirmed by X-ray diffraction (Figure 5-2a). Then, dense interdigitated \( \text{Ti}(20\text{nm})/\text{Pt}(100\text{nm}) \) microelectrodes prepared by DC sputtering and a photolithographic lift-off process were deposited onto the \( \text{ZrO}_2 \) films. The finger width and inter-electrode spacing were 20 \( \mu \text{m} \) (Figure 5-2b).

Electrical measurements were done using a home-made sample holder made from alumina tube and vacuum fittings. A four-bore ceramic tube was used for electrical lead and thermocouple feedthroughs. A thermocouple was placed adjacent to the sample in order to measure the temperature of the sample precisely. The whole sample holder was placed into a quartz tube which was put in a tube furnace (Lindberg/Blue M). A SourceMeter (Keithley 2400) was used to apply electrical bias and record current with time, which is controlled using LabVIEW program.
In order to confirm the chemical states of the sample and formation of Zr sub-valence states during the electrical biasing, Synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS) was performed at Lawrence Berkeley National Lab at beam line 9.3.2 of the Advanced Light Source. The radiation source was tunable, monochromatized soft x-rays in the energy range of 100-800 eV. The photoelectron detector employs a differentially pumped electrostatic lens system, which allows the XPS measurement at ambient pressure (up to 2.6 mbar). In accessing the chemical states of Zr, the 3d core level photoelectron emission of Zr was measured over the binding energy range from 176 eV to 206 eV with a step size of 0.05 eV at constant pass energy of 20 eV. X-ray photon energy of 490 eV was used during the measurement.

Figure 5-2: (a) X-ray diffraction pattern (2θ-ω scan, with a logarithmic intensity scale) for ZrO₂ thin film. (Monochromatized Cu Kα1 x-ray emission (λ=0.154 nm) was used in this measurement.). (b) Schematic drawing of the sample geometry. ZrO₂ thin film is deposited on single crystal Al₂O₃ (0001) substrate. Then the dense interdigitated Pt (100nm) electrodes were deposited onto the ZrO₂ thin film by DC sputtering and photolithographic lift-off process. The finger width and inter-electrode dimension is 20 μm. (c) Resistance of the pristine ZrO₂ thin film measured across the two sets of Pt electrodes shown in (b) at 200 °C in 1.3×10⁻¹ mbar oxygen under 0.2V DC bias.

5.4 Results and Discussion

5.4.1 Polarization of Zirconium Dioxide Thin films

In the previous chapters, we have demonstrated the formation of Zr sub-valence states by oxidizing metallic single crystal Zr (Chapter 2) and by applying electric field on ZrO₂ thin films (Chapter 3). The in situ suboxide formation during the electrical bias
of the sample could be observed in Figure 5-3. The broad peak, which is deviating from
the doublet feature of Zr 3d photoelectron emission, is due to the convolution between
the lateral electric potential distribution and the Zr 3d photoelectron spectrum. The
lower binding energy shoulder increases with biasing time, strongly indicating the
formation of Zr sub-valence states in ZrO\textsubscript{2}. By quantitative analysis of the spectrum
(Chapter 3), the sub-oxide contribution in the whole spectrum increases up to 20\%.
However, due to the broad nature of the spectrum, we could not precisely resolve the
valence states of the formed suboxide (Chapter 3).

Since the formation sub-valence states of Zr should be associated with oxygen
vacancies, formation of either the localized defect states or of delocalized electrons can
change the conductivity of the film (for the case of Zr\textsubscript{2}O\textsubscript{3}, the DFT calculation [24]
found that it has a semi-metallic character). Figure 5-3b is the current recording during
the electric biasing. The increase of the current (decrease of the resistance) is
accompanied with the peak shift in the XPS spectrum and increasing of the Zr sub-
valence states (Figure 5-3a, c). Here Figure 5-3 is shown as a repeat of Figure 3-6 to
recall the correlation between the electrical conductivity increase and the reduced Zr-
oxide formation deduced from the analysis of the Zr 3d photoelectron spectrum. This
result (also analysed and presented in detail in Chapter 3) confirmed that the formation
of Zr sub-valence also changes (increases) the electrical conductivity. By doing a
thorough spectrum analysis as described in Chapter 3, the electric potential distribution
on the 20 μm open space could be computed (Figure 5-3d). Initially, the electric
potential is almost linearly distributed across the film surface. The small deviation from
the perfect linear distribution is due to the local defect concentration difference. After
transformation into the low resistance state, the potential on the film is also
redistributed, and the magnitude of the electric field strength is smaller than before. The
nonlinear distribution of potential indicated either the accumulation of negative charges
in the vicinity of the positively biased electrode or large contact resistance near the
electrode region. Similar phenomenon is also observed in Ca-substituted BiFeO\textsubscript{3}[135]
and LiNbO\textsubscript{3}[142]. This result demonstrated that the electric field, or the electrochemical
potential in the film changes with time during the bias measurement, and the field
distribution impacts the local defect concentration and conductivity. In treating this
problem, not only the nonlinear drift relation, but also a nonlinear electric field
distribution must be considered.
Figure 5-3: ZrO₂ thin film bias experiment under 7V electric bias in 1.3×10⁻⁵ mbar oxygen at 125°C. (a) Zr 3d XPS spectrum evolution under 7V bias. The lower binding energy contribution increases with biasing time. (b) Total current between the interdigitated electrodes during the biasing experiment. The increase of the current with time means that the total conductivity of the ZrO₂ thin film increases under electric bias. (c) Concentration of the ZrO state (or the average/overall Zr sub-valence state) during electric bias deduced from the current measured in (b). (d) Electrical potential distribution in the 20 μm open space between the interdigitated electrodes. The change of the potential distribution is consistent with the change of the current and the Zr sub-valence states concentration.

5.4.2 Electric Potential and Defect Distribution under Electric Bias

In order to test the electrical response under different biases, the cell was tested by biasing with a step function, starting from the pristine and uniformly equilibrated distribution of charged defects. +8 V step is applied to one of the electrodes while the other one is grounded. The electrode at +8 V is the anode, and the grounded electrode
relatively is the cathode. Oxygen vacancies will be generated near the triple phase boundary of the anode, since the high electric potential provides enough driving force to evolve oxygen gas from ZrO$_2$. Moreover, the electric field in the film drives the oxygen vacancies formed at the anode to drift toward the cathode. This defect formation and drift mechanism decreases the total electrical resistance of the cell (Figure 5-4). After 1000 seconds, the polarization is reversed, and the reverse process takes place. Oxygen vacancies are annihilated at cathode (at 0V), which initially increases the film resistance. On the other hand, the vacancies drift from the anode side toward the cathode side. After the system reaches the low resistance state around 7000 seconds, the polarization was reversed again. Similar electrical response was observed, but the kinetics is much faster, which may indicate that some reactive path way has been formed during the previous polarization step.

![Figure 5-4](image)

Figure 5-4: Square wave polarization (top and middle panel) of the monoclinic ZrO$_2$ thin film at 1.3×10$^{-1}$ mbar oxygen gas pressure at 200 °C, and the corresponding resistance of the film (bottom panel). The formation and drift of the oxygen vacancies under electrical bias lead to the change of conductivity. The change of the resistance of the sample is reversible upon switching the polarization of the bias.
5.4.3 Oxygen Transport Kinetics under Electric Field Characterized by Chronoamperometry Measurements

In order to quantify the diffusion kinetics of oxygen vacancies in ZrO₂, chronoamperometry measurement was performed. The method of chronoamperometry has been proposed to probe anionic diffusion in the study of re-dox based resistive switching [21, 143]. In this method, the current evolution is recorded over time with respect to a constant applied bias. Figure 5-5 shows the chronoamperometry characteristics of ZrO₂ thin film for constant bias in the range of 4 to 8 V. Before each set of measurement, the sample was annealed in pure dry oxygen for more than 2 hours to reset to the high resistance state. For all the bias we applied, the current over time characteristics are very similar, and can be categorized into three regimes. At the very initial stage (regime I in Figure 5-5), the current drops over time (dI/dt<0), which is due to the capacitive charging process. In the second regime (regime II in Figure 5-5), the current increases over time (dI/dt>0) until a limiting current is reached. As discussed in the earlier part, the defect formation (oxygen vacancies and Zr sub-valence states) and migration under electric field is responsible for the decrease of the resistance and increase of the current. In the final regime (regime III in Figure 5-5), the current reaches a constant limiting current, which means that the drift-diffusion equilibrium of oxygen vacancies has been established.

![Figure 5-5: Chronoamperometry Characteristics of ZrO₂ Thin Film](image-url)
Figure 5-5: Current vs. time measured in chronoamperometry experiments under different bias voltages at 240 °C in 1.3×10⁻¹ mbar of oxygen. The transition points between three regimes in the I-t curves were indicated by the dashed lines and defined in the text.

The transition point from the increasing current regime to constant limiting current regime is indicated by the dashed line in Figure 5-5. By increasing the magnitude of the bias, the time that is required to reach the steady state becomes shorter at the same temperature. The migration flux of oxygen vacancies/ions is related to the strength of electric field. The increase of the bias provides stronger driving force for oxygen vacancies/ions move in the oxide, which in turn facilitated the system reaching the steady state faster. The curvature of each I-t curve in Figure 5-5 will be used to model the oxygen vacancy diffusion kinetics and extract kinetic parameters of the ZrO₂ thin film in the next section.

### 5.4.4 Modelling of Oxygen Vacancy Transport under Electric Field

In order to extract useful kinetic quantities, a drift-diffusion model has been used to simulate the experimental data. Assuming the kinetic reaction for oxygen reduction and oxygen evolution at sample surface, the oxygen surface exchange rate should also be considered. As long as we apply electrical bias, the oxygen vacancies could be generated at cathode, while the anode will be a sink for oxygen vacancies. We also assume that the initial oxygen vacancy distribution in the ZrO₂ thin film is homogeneous, and assume that the ZrO₂/electrode interfaces are impenetrable for the oxygen ions. Then the dependence of oxygen vacancy migration on the electric field strength as well as the chemical gradient in one dimension could be expressed as:

\[
\frac{\partial C_V(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_V \frac{\partial C_V(x, t)}{\partial x} - \frac{2D_V}{a} \sinh \left( \frac{qV(x, t)}{2kT} \right) C_V(x, t) \right]
\]

\[+ k \left( C_{V0} \exp \left( \frac{qV(x, t)}{kT} \right) - C_V(x, t) \right) \]

\[C_V(x, 0) = C_{V0} \]

5.6

5.7
where $C_v(x, t)$ is the oxygen vacancy concentration, $D_v$ is the oxygen vacancy diffusion coefficient, $a$ is the ionic elementary jump distance, $q$ is the ion charge, $V(x, t)$ is the electric potential, $k$ is Boltzmann constant, $T$ is the temperature, $k$ is the surface exchange rate, $x$ is the spatial coordinate along the electric field within the limits $x=0$ at the cathode and $x=L$ at anode, $C_{v0}$ is the oxygen vacancy concentration at equilibrium without applied electrical bias, and $t$ is the time. Below at the end of this subsection, we will provide a quantification for $C_{v0}$.

From our XPS results, the electric field strength is not homogenous within the film during the bias, and it changes with time (Figure 5-3d). The nonlinear field distribution also needs to be considered in the model. Here we assume that the local field strength is proportional to the local electrical resistance, which means no charge accumulation in the film, the current is uniform along the film. The electric potential could be calculated by the Poisson’s equation:

$$\nabla^2 \varphi(x, t) = -\frac{1}{\varepsilon_0 \varepsilon_r} \rho(x, t)$$

5.9

$$\rho(x, t) = 2eC_v(x, t)$$

5.10

where $\varphi(x, t)$ is the electric potential, $\rho(x, t)$ is the charge density, $e$ is the charge of an electron, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity.

Unfortunately, it is not possible to obtain an analytical solution for these nonlinear coupled partial differential equations. Therefore, numerical calculations are employed while solving these equations (5.6 to 5.10). These equations were coded in Matlab by using finite difference method. In getting the optimum value of the fitting parameters for the experimental data, the Levenberg-Marquardt algorithm implemented in Matlab has been used. One important assumption used in obtaining the solution is that the change in total electrical conductivity is linearly dependent on the total concentration of the oxygen vacancies [67, 144-146]. This assumption would be accurate if the total conductivity was only based on the oxygen anion conductivity.
However, the total electrical conductivity measured here has both an ion conduction and an electronic conduction contribution. And the electronic conductivity is also affected by the oxygen vacancy concentration in an oxide upon its reduction. The form of the dependence of the electronic conductivity on oxygen vacancy concentration upon the reduction of zirconium oxide is not clear. It may simply increase the concentration of electrons in the conduction band [18] and also linearly increase the electronic conductivity. However, if the motilities of electrons or concentrations of other charged defects are also affected, then the relation would deviate from linearity. Therefore, the assumption of the linear dependence of electrical conductivity on vacancy concentration could be treated as only as a first order approximation in this model, and future advancements of the model could introduce more accurate relations while keeping the general framework of the solution. Figure 5-6 shows the relation between the ionic and electronic conductivity of monoclinic ZrO\textsubscript{2} from the conductivity measurement (the data is taken from ref. [144]). A linear relation could be observed. Since the ionic conductivity is linearly depending on the oxygen vacancy concentration, and the electronic conductivity has a linear dependent on ionic conductivity, the assumption that the total conductivity is linear with the oxygen vacancy concentration may be reasonable.

Figure 5-7 shows the simulation results of current v.s. time characteristics during biasing. Surface exchange coefficient $k$ is the parameter that characterizes how fast the oxygen vacancies could be generated on the surface. So the higher $k$ value will lead to faster increase of the total conductivity of the thin film. On the other hand, the oxygen vacancy self-diffusion coefficient $D_V$ is the measure of how fast the oxygen vacancies could be dissipated into the system. By increasing the ratio of $k$ to $D_V$, the initial increase of the chronoamperometry characteristics will become faster (Figure 5-7).
Figure 5-6: Ionic conductivity vs. electronic conductivity of monoclinic ZrO$_2$ at 990 °C. The data points show a linear relation between the ionic and electronic conductivity. The data is from ref. [144] Fig.6.

Figure 5-7: The simulated influence of the surface exchange coefficient $k$ and oxygen vacancy diffusion coefficient $D_V$ on the shape of the chronoamperometry characteristics. The higher the ratio between the $k$ and $D_V$ is, the steeper the curvature of the kinetic will be.
Figure 5-8a shows the fitting of the I-t data by using the model we discussed above. The fitting parameters are the surface exchange coefficient \( k \), oxygen vacancy self-diffusion coefficient \( D_v \) and a scaling parameter \( \alpha \). The scaling parameter \( \alpha \) was used to scale the experimentally measured current with the calculated oxygen vacancy concentration:

\[
I = \frac{U}{R} = \frac{\sigma AU}{l} \frac{AU}{l} z e \mu C = \frac{AU}{l} z e \mu C_v = \alpha C'
\]

5.11

\[
\alpha = \frac{AU}{l} z e \mu C_v \]

5.12

where \( I \) is the current, \( U \) is the electrical bias, \( R \) is the resistance of the whole film, \( \sigma \) is the conductivity, \( A \) is the area of the cross-section of the film, \( l \) is the length between the electrodes, \( z \) is the number of charge, \( e \) is the charge of electron, \( \mu \) is the mobility of the charge carriers, \( C \) is the oxygen vacancy concentration, \( C' \) is the scaled oxygen vacancy concentration with \( C_{\text{VO}} \) (oxygen vacancy concentration at equilibrium without applied electrical bias). Estimation of \( C_{\text{VO}} \) from the found value of \( \alpha \) is provided below.

![Figure 5-8: (a) Chronoamperometry experimental data on the ZrO\textsubscript{2} thin film, and the modelling result used for fitting the data at 220 °C under 6 V bias in 1.3×10\textsuperscript{-4} mbar oxygen. (b) The evolution of defect (oxygen vacancy) concentration distribution across the thin ZrO\textsubscript{2} film from one electrode to another under the same conditions as in (a).](image-url)
The features of the chronoamperometry characteristics are well reproduced by using our model. From the model, we could also get the oxygen vacancy concentration evolution in the ZrO₂ thin film (Figure 5-8b). From the vacancy concentration, the diffusion front corresponds very well with the increase of the current. The oxygen vacancies are generated from the anode, and then migrate to the cathode. Depending on the magnitude of the electric field applied to the surface and experimental conditions, the vacancy concentration profile eventually reaches a steady state and does not change over time, which gives rise to the limiting current in the I-t plot. By equation 5.12, from the scaling parameter α, we could estimate the oxygen vacancy concentration at equilibrium without applied electrical bias \( C_{V0} \) with the following parameters:

\[
A = 1.6 \times 20 \text{ nm (sample geometry)}; \quad l = 20 \mu \text{m (sample geometry)}; \quad z = 2; \quad U = 6 \text{ V}.
\]

Since we don’t know the mobility of electron in this oxide, in the purpose of estimation, we just take the mobility of oxygen vacancies into the equation, which may give us an overestimate of the equilibrium oxygen vacancy concentration \( C_{V0} \). The mobility term could be expressed as \( \mu = zeD_v/kT \), where \( D_v = 1.1 \times 10^{-18} \text{ cm}^2/\text{s} \), \( k = 8.6 \times 10^{-5} \text{ eV/K} \), \( T = 493 \text{ K} \). By fitting the experimental curve in Figure 5-8a, we get \( \alpha = 1.6 \times 10^{-18} \text{ A} \). Finally we get \( C_{V0} = 1 \times 10^{19}/\text{m}^3 \). Given that the volume of the unit cell for monoclinic zirconia is 0.14 \( \text{nm}^3 \), which will give \( C_{V0} = 1.4 \times 10^{-9} \text{ per unit cell} \). Given the fact that the intrinsic defect concentration in undoped, pure zirconia is usually very low [18], the oxygen vacancy concentration mainly depends on the concentration of impurities with valence states lower than 4+. The purity of the target that we used to deposit the thin film is 99.9999%. The estimation for \( C_{V0} \) is very low, low enough to be reasonable in this case.

### 5.4.5 Oxygen Vacancy Self-diffusion Coefficient \( D_v \) and Surface Exchange Coefficient \( k \) Extracted by Modelling the Chronoamperometry Data

Figure 5-9 shows the oxygen vacancy diffusion coefficient under 4 V to 8 V bias in the temperature range from 200°C to 240°C. The diffusion coefficient \( D_v \) increases with increasing temperature and increasing applied bias.

By using the temperature dependence of the diffusion coefficient \( D_v \):

\[
D_v = D_0 \exp \left( \frac{-E_a}{k_BT} \right)
\]

5.13
where $D_0$ is the pre-exponential factor, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant, and $T$ is the temperature, the activation energy of oxygen vacancy diffusion in ZrO$_2$ thin films could be found for different applied bias (Figure 5-10).

Figure 5-9: Oxygen vacancy diffusion coefficient for ZrO$_2$ thin films as a function of applied bias at different temperatures. The results are found by modeling the chronoamperometry data (Figure 5-5) using the model constructed based on Equations 5.6 to 5.10.
Figure 5-10: Activation energy of oxygen vacancy diffusion coefficient under bias range from 4 V to 8 V. The values are obtained by an Arrhenius fit of the data at each bias in Figure 5-9.

The surface exchange coefficient could also be extracted from our model. Figure 5-11 shows the surface exchange coefficient under 4 V to 8 V bias in temperature range from 200°C to 240°C. The effective exchange rate depends on the bias applied between the electrodes. The higher electric bias will result in faster surface oxygen exchange rate. The reason behind this phenomenon stems from two facts: 1) Higher surface potential provides stronger diving force for charge transfer and lowers the surface oxygen incorporation/dissociation barriers. This electric field contribution to the surface exchange rate could in theory be modelled as a “drift-like” term as in dealing with the diffusion term. However, there is no existing model to describe it yet. The surface exchange coefficient deduced from our model is actually an effective k, which includes both the intrinsic k and electric field acceleration of the reaction. 2) Electrochemical potential changes the equilibria of oxygen vacancies that serve as preferential sites to incorporate oxygen from gas to solid. In addition, an increased concentration of oxygen vacancies also changes the electronic structure and facilitates the electron transfer reactions involved in oxygen incorporation or evolution, i.e. the oxygen exchange reactions. The surface exchange coefficient also increases with increasing temperature. The temperature dependence of the surface exchange rate reveals a simple Arrhenius behaviour with the activation energy shown in Figure 5-12. By increasing the external bias, the activation energy of k decreases, indicating that the external electric potential reduces the effective energy barrier for surface exchange, as justified by the argument in reason 1) above.
Figure 5-11: Oxygen surface exchange coefficient on ZrO₂ thin films as a function of applied bias at different temperatures. The results are found by modeling the chronoamperometry data (Figure 5-5) using the model constructed based on Equations 5.6 to 5.10.

Figure 5-12: Activation energy of oxygen surface exchange coefficient on ZrO₂ thin films under bias range from 4 V to 8 V. The values are obtained by an Arrhenius fit of the data at each bias in Figure 5-11.
Our experimental data (Figure 5-5) were also modelled by the classic Cottrell equations (equation 5.2) in order to compare with the results deduced from our drift-diffusion model. The vacancy diffusion coefficient obtained from the Cottrell model is about two orders of magnitude larger than that deduced from solving the drift-diffusion equations. The vacancy diffusion coefficient, $D_v$, deduced from the Cottrell model is an “effective” $D_v$, which includes several contributors to the kinetics: i) the intrinsic self-diffusion, ii) the electric field driven drift velocity of oxygen vacancies, and iii) oxygen surface exchange kinetics. This two orders of magnitude difference then comes from the contribution of ion drift under electric field and the surface exchange reactions, that are convoluted together with the intrinsic diffusion term in the Cottrell solution. The characteristic diffusion length of oxygen vacancy $l_c = 2\sqrt{D_v t}$ was found to be on the order of $0.01 \sim 0.1 \mu m$. Given that the distance between the two electrodes is $20 \mu m$, a lot larger than the characteristic diffusion length, the kinetics of the resistance switching should be diffusion limited. Therefore, the two orders of magnitude difference is mainly from the diffusion process.

![Figure 5-13: Oxygen vacancy diffusion coefficient for ZrO$_2$ thin films as a function of applied bias at different temperatures. The results are found by modeling the chronoamperometry data (Figure 5-5) using the model constructed based on classic Cottrell Equation 5.2.](image)

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5.4.6 Oxygen Diffusion Coefficient and Surface Exchange Coefficient in ZrO$_2$

In this section, we will discuss the oxygen diffusion in ZrO$_2$ in a wider perspective by comparing them with the values reported in the literature. Most of the values reported in the literature were obtained by using $^{18}$O as a tracer and Secondary Ion Mass Spectrometry (SIMS) profiling. Since in the SIMS measurement, the $^{18}$O tracer need higher temperature to diffuse to a considerable distance to enable depth profiling, temperatures higher than 700 K are usually required. On the other hand, in our measurement, due to the electric field applied on the sample, the oxygen ion/vacancies get extra diving force for the diffusion. Therefore the temperature range to observe non-trivial diffusion profiles could be largely reduced. Table 5-1 shows the comparison of data from our work and from literature for the oxygen diffusion activation energy. For the doped systems (CaO- or Y$_2$O$_3$-stabilized zirconia), the activation energies $E_a = 0.8 - 1.3$ eV are much lower than the values found in pure ZrO$_2$ (Table 5-1). The rapid oxygen diffusivity in doped ZrO$_2$ is due to the high concentration of the oxygen vacancies introduced by aliovalent doping. The oxygen diffusion coefficient is determined by the vacancy migration alone in the highly doped zirconia systems, therefore the activation energy should reflect the migration energy barrier alone. On the other hand, for the undoped ZrO$_2$ studied in the literature, the reduced oxygen diffusion coefficient is due to a smaller concentration of oxygen defects (at equilibrium) and the higher activation energy is due to the fact that both the formation and the migration of oxygen vacancies are involved in deducing the oxygen diffusion coefficient.

For our oxygen vacancy diffusion coefficients acquired by modelling the chronoamperometry data, the activation energy should represent the vacancy migration barrier alone. The found activation energy is much smaller than the activation energy of oxygen diffusion coefficient in undoped m-ZrO$_2$ in literature but is quite close to that of the oxygen diffusion coefficient in the highly doped ZrO$_2$ systems. This is consistent with the expectation that the vacancy diffusion barrier is being probed by our experiments and model and not the vacancy formation process.

There appears to be a small bias dependence of the oxygen vacancy diffusion activation energy found by our model. By increasing the bias, the activation energy decreases from 0.97±0.07 eV at 4 V to 0.82±0.06 eV at 8 V. The dependence of the
oxygen vacancy migration barrier on the oxygen vacancy concentration has not been reported experimentally on monoclinic zirconia before. While the similar trend was found in yttria stabilized zirconia: by increase the concentration of yttria (oxygen vacancy), the activation energy for oxygen vacancy diffusion decreases [147]. Further theoretical calculation is needed to verify our experimental results.

Table 5-1: Activation energy $E_a$ for oxygen diffusion or for oxygen vacancy migration (marked as “oxygen” or “oxygen vacancy”, respectively, after the value of the activation energy) in Zr oxides reported in literature. The activation energy found in this work is the energy for oxygen vacancy migration.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_a$ [eV]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-ZrO$_2$ (thin film)</td>
<td>0.82~0.97 (oxygen vacancy)</td>
<td>This work</td>
</tr>
<tr>
<td>m-ZrO$_2$ (bulk)</td>
<td>2.29 (oxygen)</td>
<td>[148]</td>
</tr>
<tr>
<td>m-ZrO$_2$ (grain boundary)</td>
<td>1.95 (oxygen)</td>
<td>[148]</td>
</tr>
<tr>
<td>m-ZrO$_2$</td>
<td>2.41 (oxygen)</td>
<td>[149]</td>
</tr>
<tr>
<td>m-ZrO$_2$</td>
<td>1.96 (oxygen)</td>
<td>[150]</td>
</tr>
<tr>
<td>2.8 mol% Y$_2$O$_3$ stabilized</td>
<td>1.24 (oxygen vacancy)</td>
<td>[151]</td>
</tr>
<tr>
<td>c-ZrO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.2 mol% CaO stabilized</td>
<td>1.35 (oxygen vacancy)</td>
<td>[152]</td>
</tr>
<tr>
<td>c-ZrO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-ZrO$_{2-x}$</td>
<td>0.7<del>1.5 ($x=10^{-6}$</del>$10^{-1}$)</td>
<td>[153]</td>
</tr>
<tr>
<td></td>
<td>(oxygen)</td>
<td></td>
</tr>
<tr>
<td>t-ZrO$_{2-x}$</td>
<td>0.4<del>0.6 ($x=10^{-6}$</del>$10^{-1}$)</td>
<td>[153]</td>
</tr>
<tr>
<td></td>
<td>(oxygen vacancy)</td>
<td></td>
</tr>
</tbody>
</table>
The surface oxygen exchange reaction rate has been rarely reported in the literature for the undoped ZrO$_2$. Figure 5-14 shows the comparison the $k$ values measured in this work and the values reported in the literature. The values reported in the literature are also quite scattered. The reason may be attributed to the fact that the $k$ value from these studies should depend on the surface chemistry. The $k$ values found from our measurements are close to the range extrapolated from some of the high temperature measurements (Figure 5-14).

![Figure 5-14: Comparison of oxygen surface exchange coefficient obtained in this work with the data from the literature. (a) this work for undoped m-ZrO$_2$, (b) 2.8 mol% Y$_2$O$_3$ stabilized c-ZrO$_2$ [151], (c) 14.2 mol% CaO stabilized c-ZrO$_2$[152], (d) 3.0 mol% Y$_2$O$_3$ stabilized porous t-ZrO$_2$ [154], (e) 9.5 mol% Y$_2$O$_3$ stabilized c-ZrO$_2$ [155]](image)

5.5 Conclusions

In conclusion, the oxygen diffusion in the ZrO$_2$ thin films under electric bias was investigated by means of in situ XPS and chronoamperometry measurements. A detailed XPS spectrum analysis revealed that the electric field distribution changes with the increase of the concentration of reduced zirconium species (or equivalently by the increase of oxygen vacancies). By applying electric field to the sample surface, the
oxygen vacancies are generated at the anode and are driven to the cathode side. Chronoamperometry measurements captured the increase of the film’s conductivity by increasing the bias magnitude and time. The time needed to reach a steady state limiting current depends on the temperature and bias: the higher the temperature and bias, the shorter the threshold time. The resulting I-t (current-time) curve was fitted by using the diffusion-drift model, which considered the drift induced by the electric field and the surface oxygen exchange reaction in addition to self-diffusion. From this model, the oxygen vacancy diffusion and oxygen surface exchange coefficients could be extracted. We compared the vacancy diffusion coefficient found from our diffusion-drift model to the effective diffusion coefficient found by the Cottrell equation as described in [21]. We found that the Cottrell equation yields about two orders of magnitude greater vacancy diffusion coefficient. The difference comes from separating the self-diffusion coefficient from the effect of the electric field on ion drift and oxygen surface exchange that are all convoluted in the Cottrell approach. The experimental method and the modelling approach applied in this work could also be applied for assessing the oxygen vacancy diffusion kinetics in other oxides that function under electric field, such as thin oxide films during metal oxidation or red-ox based resistive switching oxides.
6 Effect of Temperature and Partial Pressure of Oxygen and Water Vapor on the Initial Oxidation Kinetics of Single-Crystalline Zirconium (0001)

Abstract

The goal of this work is to characterize and model the effect of temperature, oxidant type and oxidant pressure on the initial oxidation kinetics of zirconium. The initial oxidation kinetics of single crystalline Zr (0001) in dry oxygen and in water vapour as a function of temperature and gas pressure was probed by synchrotron x-ray photoelectron spectroscopy. For oxidation in the temperature range of -130 °C to -10 °C at 2.6×10⁻⁸ mbar, the oxide thickness decreases with increasing temperature. In temperature range of 300 °C to 1900 °C, the oxide thickness increases with increasing temperature, and the kinetics change from self-limiting to non-self-limiting. There is no existing single model that could capture this transition in the temperature dependence of oxide thickness. A new oxidation model was proposed by considering the local electric field distribution, based on the classic Cabrera-Mott model and the Debye-Hückel theory for field distribution. Quantitative modelling of the initial oxidation curves uncovered for the first time the important role of the electric potential strength as well as electric potential distribution in the oxide layer on the overall oxidation kinetics.

6.1 Introduction

Oxidation or corrosion is often a performance-limiting concern for many materials used in harsh environments. For example, the corrosion of the zirconium alloys (as cladding material) by nuclear reactor coolant water is one of most important concern for the safety and life time of the nuclear reactor, since the corrosion often causes undesirable loss of mass. A layer of oxide film is often formed under certain conditions and provides the underlying metal protection against further corrosion. So it is important to study the oxidation of the material under different conditions and the underling oxidation kinetics.

The oxidation kinetics of metals have been extensively studied both theoretically and experimentally in the last decades.[2, 28, 94, 156-158] In the classical vision of oxide film growth, metal oxidation involves both electronic and ionic transport
across the oxide film in order to ionize the metal at the metal-oxide interface and oxidant at gas-oxide interface. The transport of these charge species is determined by the gradients of both the chemical and electrostatic potentials in the oxide film. The electrostatic potential developed during the initial oxidation stage is often assumed as a constant in the oxidation models developed before (a detailed review of the kinetic modelling of the metal initial oxidation will be discussed in the next section). However, the electric field distribution in the oxide does is not necessarily homogeneous. It also depends on the local distribution of the charged species in the oxide film. Therefore, a new model is proposed in this work to model the initial oxidation kinetics (for Zr (0001) single crystal), by taking the local field distribution into account.

In this work, the initial oxidation kinetics Zr (0001) in dry oxygen and in water vapour within the temperature range of -130°C to 190°C and pressure range of 2.6x10^-8 mbar to 2.6x10^-6 mbar was characterized by in situ synchrotron based X-ray Photoelectron Spectroscopy (XPS). The resulting oxidation kinetics are quantitatively described with a new numerical model. The kinetics parameters from the model fitting could provide detailed understanding of the mechanisms governing the oxide-film growth on Zr (0001) surface. It was found that the key parameter that governs the initial oxidation kinetics is the electric field formed across the initial oxide by surface adsorbed oxygen ions, consistent with the Cabrera-Mott model. The interesting and new revelation has been that both the magnitude of the electric potential and the distribution of the electric field within the initial oxide influences the final oxide thickness and the shape of the oxidation kinetics.

6.2 Review of initial metal oxidation models

6.2.1 Cabrera-Mott model for metal initial oxidation (inverse logarithmic law)

The classic Cabrera-Mott [28] model is developed for the modelling of metal initial oxidation under low temperatures. In this model, it is assumed that the oxide growth takes place by cation migration. An ion in the metal at the metal-oxide interface must first pass over a potential barrier, W, to move into an interstitial site in the oxide, and after this it must cross a potential barrier, U, to move to the next interstitial site. In the absence of a field, the probability that an interstitial ion at the potential minima can overcome the barrier, U, and jump to the next potential minima is given by

$$P = \gamma \exp(-\frac{U}{kT})$$
where $\gamma$ is the vibration frequency, $k$ is the Boltzmann constant and $T$ is the temperature. It is assumed that oxygen molecules are dissociatively adsorbed on the surface, producing traps for electrons. The electrons can fill up these traps by quantum mechanical tunnelling if the oxide is very thin (~nm) or by thermionic emission and diffusion if the temperature is sufficiently high. By forming oxygen ions, a field could be set up in the oxide layer. The field will increase until the surface Fermi level reaches the Fermi level in the metal. This built-in potential is the so called Mott potential for the initial oxidation of the metal, and it is usually about 1-2 V for very thin oxide (few nanometres) films.

In the presence of such high electric field, the energy barrier for ion hopping will be lowered in the direction of the field by $\frac{1}{2} qaE$ (where $q$ is the charge of the charged ion, $a$ is the hopping distance, and $E$ is the electric field strength), and increased by the same amount for the hopping in the opposite direction. The drift velocity of the charge carrier is [159, 160]

$$V = \gamma a \exp \left( -\frac{U}{kT} \right) \left[ \exp \left( \frac{qaE}{2kT} \right) - \exp \left( -\frac{qaE}{2kT} \right) \right] = \gamma a \exp \left( -\frac{U}{kT} \right) \sinh \left( \frac{qaE}{2kT} \right)$$

6.2

For a strong field, this expression could be approximated as:

$$V = \gamma a \exp \left( -\frac{U}{kT} \right) \exp \left( \frac{qaE}{2kT} \right)$$

6.3

Then the oxide growth rate could be given by:

$$\frac{dx}{dt} = N\Omega \gamma \exp \left( -\frac{U}{kT} \right) \exp \left( \frac{qaV}{2xkT} \right)$$

6.4

where $N$ is the number of metal atoms located on sites suitable for migration from metal into the oxide (in this model, only the cation migration is considered), $\Omega$ is the volume of the oxide per metal ion, $\gamma$ is the vibrational frequency of the metal lattice, $x$ is the oxide thickness. This definition of the terms assumes that the oxide growth is governed by metal cation out-diffusion. The same formalism would also be applicable to initial oxidation that is governed by oxide ion inward diffusion.
This equation does not have an exact analytical solution. Mott and Cabrera deduced the approximate solution for very thin oxides. The solution gives rise to the inverse logarithmic equation for oxide thickness as a function of time.

\[ \frac{1}{x(t)} = A - Blnt \]

\[ A = -\frac{kT}{qaV} \left[ \ln \left( \frac{N\Omega yqaV}{kTL^2} \right) - \frac{U}{kT} \right] \]

\[ B = -\frac{kT}{qaV} \]

where \( x(t) \) is the oxide thickness depending on time \( t \), \( L \) is the limiting oxide thickness.

There are several inherent assumptions in this theory:

1) Electronic equilibrium between the metal and adsorbed oxygen can be established in a time which is short compared to the time required for an ion to diffuse through the oxide.

2) The total activation energy for dissolution of metal into the oxide is a constant.

3) The equilibrium contact potential between metal and adsorbed oxygen is independent of temperature, oxygen pressure and oxide thickness.

The first assumption is considered to be true only in the range of oxide thicknesses that is sufficiently thin to allow for quantum tunneling of electrons [95]. The second assumption is also reasonable for very thin oxide films.

The third assumption, on the other hand, was shown not to be true. Cai et al. [54, 55, 161] recently showed that the oxide limiting thickness for Al(111) initial oxidation is a function of temperature and oxygen pressure (Figure 6-1). The Mott potential in these measurements increases with increase the oxygen gas pressure and decreases with increasing oxidation temperature. This behaviour stems from the fact that the self-generated electric field (Mott potential) depends on the oxygen surface coverage that exhibits a Langmuir isotherm behaviour with changes in temperature and oxygen pressure. The third assumption in Cabrera-Mott model is only true when the surface coverage reaches the saturation level.
Experimentally, inverse logarithmic type rate laws predicted by Cabrera-Mott model have been reported for a number of metals, such as Al [54, 55, 161, 162], Ti [163] and Ta [164].

![Oxide film thickness as a function of oxidation time and oxygen gas pressure. The oxidation starts with a clean Al(111) surface which is oxidized at 1.3x10^-8 mbar. A stepwise increase in oxygen pressure is applied after a limiting oxide thickness is reached at each oxygen pressure. The plot is taken from reference [55].](image)

6.2.2 Fromhold coupled-currents model

Fromhold has suggested that the single current approach such as that of Cabrera-Mott model is only on limiting case of a more comprehensive theory. He has developed a coupled currents approach to the metal oxidation theory[165]. The ionic current \( J_i \) based on a discrete lattice hopping and assuming no space-charge effects was given by

\[
J_i = 4a\gamma \exp\left(\frac{-W}{kT}\right) \sinh\left(\frac{ZieE_0a}{kT}\right)
\]

\[
\times \left[ C_i(L) - C_i(O) \exp\left(\frac{ZieE_0L(t)}{kT}\right)\right] \left[ 1 - \exp\left(\frac{ZieE_0L(t)}{kT}\right)\right]^{-1}
\]

6.8

where \( W \) is the barrier height in zero field, \( Z_i e \) is the effective charge per particle of the diffusing species, \( a \) is one half the distance between adjacent potential minima, \( E_0 \) is
the homogeneous surface charge field in the oxide, \( C_i(L) \) is the bulk defect concentration of diffusing ion species at oxide-oxygen interface, \( C_i(0) \) is the bulk defect concentration of diffusing ion species at metal-oxide interface, \( L(t) \) is the oxide thickness at time \( t \), \( \gamma \) is the vibrational frequency.

For different oxidation systems, the ionic current will be in balance with another current, e.g. electric current due to quantum tunnelling and electric current due to thermal excitation. For the case of electron tunnelling and ion diffusion, numerical calculations were made and it was shown that in the initial stages of oxidation, the electron tunnelling current prevails, and proved a sufficient number of \( O^- \) states to establish the contact potential. The rate limiting step is the ionic diffusion, and the oxidation rate is of the same form as that obtained by classic Cabrera-Mott model, resulting an inverse logarithmic growth law. The kinetic transition to a second growth stage occurs at oxide thickness exceed 2-3 nm. In the latter growth stage, the electron tunnelling becomes the rate limiting step and a direct logarithmic growth law is observed.

The major concern about this theory when describing the metal initial oxidation is that, the assumption of homogeneous electric field across the oxide. The local electric field should also depend on the local charged ion distribution, so this homogeneous electric field assumption is not always true. Another concern about this theory is that, in order to fit this model with the experimental data, there are quite a lot of fitting parameters that need to be used. This will increase the problem of overfitting the model with the data, and the basis physical characteristics of the parameters extracted from this model becomes more prone to data quality and variance for the fitting procedure.

### 6.2.3 The Fehlner-Mott model

The Fehlner-Mott model [94] was built upon comprehensive evaluation of Cabrera-Mott model with extensive experimental results. More specifically, the low temperature oxidation is considered to go through a period of fast, linear oxidation followed by a slow logarithmic reaction, which may under certain conditions be followed by a rate increase and a second logarithmic stage. The initial linear oxidation is considered as a continuation of chemisorption process by a place-exchange mechanism. Once a stable oxide film has been formed, it is assumed that oxygen ions formed on the surface by dissociation of oxygen molecules and capture of tunnelling
electrons are partially incorporated in the oxide surface and set up a potential across the film which provides a driving force for continued oxidation. The field created across the oxide lowers the potential barriers to ion migration with exist for anions at the oxide-gas interface and for cations at the metal-oxide interface. The Fehlner-Mott model consider the anion migration as well, which is different from Cabrera-Mott model (cation diffusion only).

For the case of anion migration, it is assumed that a partially incorporated oxygen ion at the oxide-oxygen surface must first cross an activation energy barrier, which is reduced by electric field generated by surface adsorbed oxygen. As soon as the oxygen crosses the barrier it is assumed to travel easily to the metal-oxide interface to form new oxide. The electrical field across the oxide is assumed to be constant. This theory also assume that the energy barrier is a function of oxide thickness, and has the form of $W+\mu x$. The ion entry into the oxide is considered to become more difficult as increasing oxide thickness. Then the growth rate is of the form:

$$\frac{dx}{dt} = \text{Cexp} \left( -\frac{W + \mu x - \frac{1}{2} qaE}{kT} \right)$$

The integration of this equation will result a direct logarithmic oxidation law. This model could give a pretty good fitting for the oxidation kinetics with a direct logarithmic law. However, there are some concerns regarding the assumption of this model. The assumption that very thin oxide films, formed by exposure of a metal surface to oxygen gas, are amorphous is too general, even for low temperature oxidation. The experimental determination of the structure of very thin oxide films is rather difficult and reliable data are rarely reported in the literature. Another concern is the structural energy barrier parameter $\mu$, which does not have a well-defined physical meaning. The detailed energy relation with the oxide thickness has to be resolved.

### 6.3 Modelling of Zirconium Initial Oxidation Kinetics

The model we developed for the initial oxidation of Zr metal is based on the basic transport equation but with some key modifications. Since the Nernst-Einstein relationship is no longer valid for oxide film less than 20 nm, we will construct the
diffusion model from the basic atomic hopping process. For diffusion in one dimension, the oxygen diffusion coefficient $D_o$ without an electric field can be expressed as

$$D_o = \frac{a^2 \nu}{2} \exp\left(-\frac{W}{kT}\right)$$

6.10

where $a$ is the ionic elementary jump distance, $W$ is the energy barrier for ion jump, $\nu$ is the vibrational frequency, $T$ is the temperature, $k$ is the Boltzmann constant. Considering the one dimensional ion jump under electric bias, the jump will happen both forward and backward but with a different rate, the net ion drift could be expressed as

$$V = \frac{\partial}{\partial x} \left[ \frac{2D_o}{a} \sinh\left(\frac{qa}{2kT} \frac{\partial \varphi(x,t)}{\partial x}\right) C_o(x,t) \right]$$

6.11

where $x$ is the spacial coordinate, $t$ is the time, $\varphi(x,t)$ is the electric potential, $C_o(x,t)$ is the oxygen ion concentration. Therefore, by adding this drift term into the diffusion equation, we can obtain the diffusion model:

$$\frac{\partial C_o(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_o \frac{\partial C_o(x,t)}{\partial x} - \frac{2D_o}{a} \sinh\left(\frac{qa}{2kT} \frac{\partial \varphi(x,t)}{\partial x}\right) C_o(x,t) \right]$$

6.12

At the interfaces, the boundary conditions:

$$C_o(0,t) = C'$$

6.13

$$C_o(\infty,t) = C_{\infty}$$

6.14

and the initial condition:

$$C_o(x > 0,0) = C_{\infty}$$

6.15

where we assume that the metal is a semi-infinite slab, $x = 0$ is the metal-gas interface, and $x = \infty$ is the metal reference point.
Since the electric field will be generated by the surface adsorbed oxygen, and the distribution of the electric field is not homogenous due to the non-homogenous ion distribution in the initially formed oxide. Even at equilibrium, the electric field will not be uniform in general. If we assume that the system can reach equilibrium quickly, then the Debye-Hückel equation could be used to estimate the electric potential $\varphi(x, t)$

$$\frac{\partial^2 \varphi(x, t)}{\partial x^2} = \frac{\varphi(x, t)}{L_D^2}$$

6.16

$$L_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{\sum_i n_i q_i^2}}$$

6.17

$$\varphi(0, t) = V_M$$

6.18

where $\varphi(x, t)$ is the electric potential, $L_D$ is the normalized Debye-Hückel screening length, $q_i$ is the charge of the ion, $n_i$ is the concentration of the charged species, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity, $V_M$ is the Mott potential.

Due to the non-linear term in equation 6.12, these coupled nonlinear partial differential equations (equation 6.12 - 6.18) are solved by iteration of the finite difference method. In getting the optimum value of the fitting parameters for the experimental oxidation data, the Levenberg-Marquardt algorithm implemented in Matlab has been used. The oxygen diffusivity $D_O$ and Mott potential $V_M$ were used during the optimization between our model and experimental results.

6.4 Experimental Details

The oxidation experiment was performed on a single crystalline Zr (0001) sample (purchased from Princeton Scientific Corp.). The surface was mechanically polished to within 1° of this orientation. The native oxide and other contaminants on the Zr surface were removed by Ar* ion sputtering (1.5 kV for thirty minutes) prior to the experiment. The sample was annealed under UHV at 1000 K for one hour. After 1-2 cycles of sputtering and UHV annealing, an XPS survey spectrum confirmed the absence of oxygen and any contaminants from the surface. The base pressure of the UHV chamber is $6.5 \times 10^{-11}$ mbar.
Synchrotron x-ray photoelectron spectroscopy (S-XPS) was performed at Brookhaven National Lab (Upton, NY) at beam line U12A of the National Synchrotron Light Source. The radiation source was tunable, monochromatized soft x-rays in the energy range of 100-600 eV with a resolution $\Delta E/E$ of $2 \times 10^{-2}$-$10^{-3}$. The analyzer of the XPS system is VSW EAC 125. In accessing the chemical states of Zr, the $3d$ core level photoelectron emission of Zr was measured over the binding energy range from 176 eV to 206 eV with a step size of 0.05 eV at constant pass energy of 20 eV. X-ray photon energy of 400 eV was used during the measurement.

Oxide films were grown at -130°C to 190°C by *in situ* exposure of the Zr (0001) surface to pure oxygen or to water vapour with a total pressure of $2.6 \times 10^{-8}$ mbar, $2.6 \times 10^{-7}$ mbar and $2.6 \times 10^{-6}$ mbar, and was probed by XPS in the same UHV system with a base pressure of $6.5 \times 10^{-11}$ mbar.

### 6.5 Experimental Results and Discussion

#### 6.5.1 Effect of Temperature on Zirconium Initial Oxidation

The Zr (0001) single crystal sample was exposed to dry oxygen molecules under $2.6 \times 10^{-8}$ mbar at different temperatures ranging from -130°C to 190°C (Figure 6-2). All the oxidation kinetic curves show a similar very fast initial oxidation kinetics, but the final self-limiting states is quite different for different temperatures. Figure 6-2a shows the oxidation kinetics at -130°C, -60°C and -10°C. By increasing the temperature under this temperature range, the oxide thickness decreases with increasing temperature. This result is consistent with the finding in the literature that, by increasing the temperature the surface adsorbed oxygen will decrease, which in turn reduce the Mott potential and decrease the oxidation rate[55]. Figure 6-2b shows a very different trend. In the temperature range from 30°C to 190°C, by increasing the temperature, the oxide thickness increases, while it also evolves to a non-self-limiting kinetics. This kinetic transition indicates that some fundamental dynamic parameters have been changed during the increase of the temperature. For example, many metal oxidation experiments have shown that by increasing the oxidation temperature, the resulting oxide could be changed from amorphous to crystal. Therefore, the diffusivity in these different oxide structure will be different, and will have a huge impact on the oxidation kinetics. The underlying mechanism for this kinetic transition will be revealed by fitting
the experimental data with our oxidation model, which will be discussed in detail in later sections.

Figure 6-2: Kinetic growth curves measured by XPS under $2.6 \times 10^{-8}$ mbar oxygen, from $-130^\circ\text{C}$ to $190^\circ\text{C}$. (a) At $-130^\circ\text{C}$, $-60^\circ\text{C}$ and $-10^\circ\text{C}$, the oxide thickness decreases with increasing temperature. (b) At $-10^\circ\text{C}$, $30^\circ\text{C}$, $70^\circ\text{C}$, $110^\circ\text{C}$, $150^\circ\text{C}$, and $190^\circ\text{C}$, the oxide thickness increases with increasing temperature. And the kinetics start to show a transition from self-limiting to non-self-limiting.

6.5.2 Effect of Oxygen Partial Pressure on Zirconium Initial Oxidation

The oxygen partial pressure dependent of the Zr initial oxidation has been examined under constant temperature ($30^\circ\text{C}$). Figure 6-3 reveals that the limiting thickness of the Zr oxide film increases with increasing oxygen pressure. In order to examine the effect of the pre-existing oxide on the subsequent oxidation, the “add-on” oxidation experiment is also performed, in which the experiment will keep on with one higher order of oxygen pressure when the oxide reaches the limiting thickness under the present pressure. It is interesting that the final limiting thickness does not depend on the experimental procedure. This result suggests that the limiting thickness of the oxidation is determined by the oxidation pressure and temperature.
Figure 6-3: Kinetic growth curves measured by XPS at 30°C in $2.6 \times 10^{-8}$ mbar, $2.6 \times 10^{-7}$ mbar and $2.6 \times 10^{-7}$ mbar oxygen. The oxide thickness increases with increasing oxygen pressure.

6.5.3 Comparison of Oxidation in Dry Oxygen and in Water Vapour

The oxidation measurements were performed under different gas environment as well. Figure 6-4 shows the comparison of the oxidation kinetics of Zr (0001) under oxygen gas and water vapour. The observed initially fast oxidation rate followed by a reduction of the oxide film growth is consistent with the classic Cabrera-Mott theory of low-temperature oxidation of metals for both oxygen and water oxidation. By increasing the oxidation temperature, the kinetics start to deviate from the classic self-limiting oxide growth model to a non-self-limiting oxidation kinetics. It is obvious that the oxide films formed by oxygen exposure has a faster growth rate than by water vapour, and the limiting thickness is thicker for the films oxidized in oxygen than in water vapour. For the oxidation by the water vapour, the temperature and pressure dependent of the oxidation kinetics is quite similar to the case of oxidation by oxygen. By increasing the oxidation temperature, the oxidation rate and limiting thickness also increases. Moreover, around 70°C to 110°C, the oxidation kinetics start to transfer to a non-self-limiting process. Since the water vapour will form ice on the surface when
expose the Zr (0001) in water vapour under lower temperatures (<0°C), there is no available data for the water oxidation under lower temperatures. On the other hand, by increasing the water vapour pressure, the oxide thickness increases as well (Figure 6-4d).

![Graphs showing oxidation kinetics](image)

Figure 6-4: Zr (0001) initial oxidation kinetic curves measured by XPS in Oxygen or Water gas environment. (a) Oxidized in $2.6 \times 10^{-8}$ mbar oxygen gas under temperature range between 30°C and 190°C. (b) Oxidized in $2.6 \times 10^{-8}$ mbar water vapor under temperature range between 30°C and 190°C. (c) Oxidized at 30°C in oxygen gas at pressure range between $2.6 \times 10^{-8}$ mbar and $2.6 \times 10^{-6}$ mbar. (d) Oxidized at 30°C in water vapor at pressure range between $2.6 \times 10^{-8}$ mbar and $2.6 \times 10^{-6}$ mbar.

6.5.4 Modelling of Zirconium Initial Oxidation Kinetics

The diffusivity $D$ and Mott potential $V_M$ could be obtained by solving equations 6.12 - 6.18 numerically and fitting the result with the experimental data. The Debye length could also be calculated. Table 6-1 and Table 6-2 show the summary of the fitting parameters for the oxidation kinetic curves. The reason for the difference of the
oxidation kinetics for different oxidants (oxygen and water) and different conditions could be deduced from these kinetics parameters.

For increasing the oxidation temperature from -130°C to 190°C in oxygen gas, the Mott potential decreases from 0.67 V to 0.26 V. For water oxidation, the Mott potential also decreases with increasing the temperature. This trend of temperature dependence of the Mott potential is consistent in the sense that by increasing the temperature with the same gas pressure, the surface adsorbed molecule concentration reduces, so the surface coverage decreases. Given that the Mott potential is generated by the surface adsorbed charged oxygen ions, the reduction of the surface coverage of oxygen in turn reduces the Mott potential[55, 161].

The magnitude of the Mott potential for oxygen oxidation and water oxidation is quite different. The Mott potential for oxygen oxidation is almost twice for the water oxidation (Figure 6-5). At the same gas pressure and oxidation temperature, one oxygen molecule could decompose into two oxygen anions, while one water molecule could only decompose into a hydroxyl radical and hydrogen gas desorbed from the surface. It is clear that one adsorbed water molecule on the surface results in only OH⁻, while one adsorbed oxygen molecule results in two chemisorbed O⁻ available for accepting tunneling electrons. Therefore, there are less surface adsorbed anions for water oxidation under the same pressure as oxygen oxidation. Thus, a smaller Mott potential takes effect for the water vapour oxidation, which then leads to a thinner limiting thickness of the initial oxide film.

The gas pressure dependence of the Mott potential is rather straightforward. With increasing the gas pressure (oxygen and water), the Mott potential increases as well (Table 6-2). With increasing the gas pressure, the surface coverage increases, thus the Mott potential increases. This result indicates that under these experimental conditions, the surface coverage of the adsorbed oxidant does not reach the saturation level.
Table 6-1: Mott potential, Debye length and diffusion coefficient obtained from the fitting of oxidation model at different temperatures for oxygen/water oxidation at 2.6×10⁻⁸ mbar oxidant gas pressure.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mott potential (V)</th>
<th>Debye Length (nm)</th>
<th>Diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen Gas</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-130</td>
<td>0.67</td>
<td>0.42</td>
<td>1.20×10⁻²⁰</td>
</tr>
<tr>
<td>-60</td>
<td>0.53</td>
<td>0.45</td>
<td>3.10×10⁻¹⁹</td>
</tr>
<tr>
<td>-10</td>
<td>0.45</td>
<td>0.50</td>
<td>3.24×10⁻¹⁸</td>
</tr>
<tr>
<td>30</td>
<td>0.43</td>
<td>0.54</td>
<td>5.08×10⁻¹⁷</td>
</tr>
<tr>
<td>70</td>
<td>0.41</td>
<td>0.58</td>
<td>1.06×10⁻¹⁵</td>
</tr>
<tr>
<td>110</td>
<td>0.32</td>
<td>0.61</td>
<td>8.54×10⁻¹⁵</td>
</tr>
<tr>
<td>150</td>
<td>0.29</td>
<td>0.64</td>
<td>7.01×10⁻¹⁴</td>
</tr>
<tr>
<td>190</td>
<td>0.26</td>
<td>0.67</td>
<td>3.00×10⁻¹³</td>
</tr>
<tr>
<td><strong>Water Vapor</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.23</td>
<td>0.53</td>
<td>1.02×10⁻¹⁶</td>
</tr>
<tr>
<td>70</td>
<td>0.19</td>
<td>0.57</td>
<td>3.50×10⁻¹⁵</td>
</tr>
<tr>
<td>110</td>
<td>0.14</td>
<td>0.60</td>
<td>1.82×10⁻¹⁴</td>
</tr>
<tr>
<td>150</td>
<td>0.12</td>
<td>0.63</td>
<td>8.13×10⁻¹⁴</td>
</tr>
<tr>
<td>190</td>
<td>0.09</td>
<td>0.66</td>
<td>4.21×10⁻¹³</td>
</tr>
</tbody>
</table>
Table 6-2: Mott potential, Debye length and diffusion coefficient obtained from the fitting of oxidation model at different pressures for oxygen/water oxidation at 30 °C.

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>Mott potential (V)</th>
<th>Debye Length (nm)</th>
<th>Diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6x10⁻⁸</td>
<td>0.43</td>
<td>0.54</td>
<td>5.08x10⁻¹⁷</td>
</tr>
<tr>
<td>2.6x10⁻⁷</td>
<td>0.87</td>
<td>0.51</td>
<td>6.12x10⁻¹⁷</td>
</tr>
<tr>
<td>2.6x10⁻⁶</td>
<td>1.24</td>
<td>0.54</td>
<td>1.89x10⁻¹⁶</td>
</tr>
<tr>
<td>Water Vapor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6x10⁻⁸</td>
<td>0.23</td>
<td>0.53</td>
<td>1.02x10⁻¹⁶</td>
</tr>
<tr>
<td>2.6x10⁻⁷</td>
<td>0.51</td>
<td>0.54</td>
<td>5.60x10⁻¹⁶</td>
</tr>
<tr>
<td>2.6x10⁻⁶</td>
<td>0.83</td>
<td>0.56</td>
<td>1.99x10⁻¹⁶</td>
</tr>
</tbody>
</table>

The Debye length could also be deduced from the oxidation model. It is a measure of a charge carrier’s net electrostatic effect in the material. From equation 6.17, the Debye length depends on the temperature and the local charged ion concentration, which is the oxygen vacancy concentration in this case. By increasing the temperature, the Debye length increases (equation 6.17 and Figure 6-6). With larger Debye length, the electric field distribution in the oxide film will be more uniform. Therefore, the electric field strength in the rate limiting point will be stronger within the oxide that has larger Debye length. Under the same magnitude of the Mott potential, the one with a larger Debye length will have a thicker oxide formed. On the other hand, there is no clear gas pressure dependent could be observed on the Debye length (Table 6-2) for both oxygen and water oxidation of Zr (0001). This result may be attributed to the fact that, under the same temperature, the defect concentration formed in the oxide is similar despite the difference the gas pressure, or in the experimental pressure range the difference is rather small. Therefore, the Debye length will keep almost the same as changing the oxidation pressure.

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Figure 6-5: Mott potential for oxidation under different temperatures at $2.6 \times 10^{-8}$ mbar oxidant pressure. Red squares are oxygen oxidation, and blue circles are water oxidation.

Figure 6-6: Debye length for oxidation under different temperatures at $2.6 \times 10^{-8}$ mbar oxidant pressure. Red squares are oxygen oxidation, and blue cycles are water oxidation.
The diffusivity of the initial oxide form on Zr (0001) surface could also be extracted from our oxidation model. For both oxygen and water oxidation, the diffusion coefficient increases with increasing the oxidation temperature (Table 6-1). The data diffusion coefficient v.s. temperature (including the literature reported values) are plotted in Figure 6-7. For the diffusivity measured in this work (metal oxidation) (Figure 6-7 a), by increasing the temperature, the slope has a sudden change between -10°C and 30°C. The corresponding activation energy are 0.66 eV for the temperature range between 30°C and 190°C and 0.15 eV for the temperature range between -130°C and -10°C.

In the temperature range between 30°C and 190°C, the activation energy measured by oxidation measurement is quite similar to the value measured by our previous electric field driven oxygen transport measurement (Figure 6-7 b) (0.84 eV). However, there is almost 6 order of magnitude difference of the pre-exponential factor. This might be the result of difference in the defect concentration in these two systems. In our previous diffusion measurement, the sample was fully oxidized ZrO₂ thin films, the intrinsic oxygen vacancy concentration will expected to be very low. On the other hand, in our oxidation measurement, the starting material is the Zr (0001) metal, the stoichiometry of initially formed surface oxide maybe far away from the Zr dioxide. In fact, the oxygen concentration in the oxide form during the oxidation measurement is plotted in Figure 6-8. For all the oxidation temperatures, the oxide formed on the surface are quite non-stoichiometry. Given the abundance of the oxygen vacancies, the pre-exponential fact for the diffusion coefficient could be large in this case. If extrapolate our result to higher temperature, it is quite consistent with the literature values reported for doped ZrO₂, given that in these doped ZrO₂ the oxygen vacancy concentration are also very high.

In the temperature range between -130°C and 30°C, the energy barrier for the oxygen ion/vacancy diffusion is quite low, it is only 0.15 eV. This may stems from the fact that, under these oxidation temperatures, the oxide formed on the surface is extremely non- stoichiometry and there is no well-defined crystal structure for these oxide, it is amorphous in general (Figure 2-7)[25, 51]. This kinetic transition may also be a sign that the oxide starts to form crystal structures under higher oxidation temperature. Similar dependence of the oxygen diffusion activation energy on the
crystal structure was also found in other oxide systems: for amorphous Al₂O₃, the activation energy for oxygen diffusion is 1.3 eV [166], which it is 6.3–6.9 eV [167] for crystallized α-Al₂O₃: for SiO₂, the activation is 0.1–0.4 eV [168] for amorphous phase, and 2.53 eV for crystallized phase [169].

Combining the results discussed above, we could give an explanation for the decrease of the oxide limiting thickness between -130°C and -10°C, and increase between 30°C and 190°C. In temperature range between -130°C and -10°C, the effect from the decrease of the Mott potential (Figure 6-5) by increasing temperature is dominant. Even though the Debye length increases with temperature (Figure 6-6), the electric field developed at the interface still decreases with increasing the temperature (Figure 6-9 and Figure 6-10). The overall result is a decrease of the oxide thickness formed on Zr (0001) surface. At temperatures above -10°C, the effect from the increase of the Debye length becomes dominant, and the electric field strength increases with increasing the temperature (Figure 6-9 and Figure 6-10). So the oxide thickness increases with increasing the temperature. This result indicates the importance of considering the electric field distribution during the modeling of Zr initial oxidation kinetics. In addition, the diffusivity of oxygen ion/vacancy increases largely at higher temperatures than the lower temperatures, which makes the diffusion faster and facilitate the formation of a thicker oxide.
Figure 6-7: Comparison of oxygen diffusion coefficient obtained in this work with the data from the literature. (a) measured by oxidation experiment in this work, (b) oxygen vacancy diffusivity measured by electrically biasing monoclinic ZrO$_2$ thin films (Chapter 5), (c) monoclinic ZrO$_2$ [148], (d) 10 mol % Y$_2$O$_3$ stabilized cubic ZrO$_2$ [147], (e) 2.8 mol % Y$_2$O$_3$ stabilized tetragonal ZrO$_2$ [151], (f) tetragonal ZrO$_2$ [170], (g) monoclinic ZrO$_2$ [149], (h) monoclinic ZrO$_2$ [150], (i) 14.2 mol % CaO stabilized ZrO$_2$[152], (j) porous ZrO$_2$ [154], (k) 9.5 mol % Y$_2$O$_3$ stabilized cubic ZrO$_2$ [155].

Figure 6-8: Oxygen concentration in the oxide formed by oxygen oxidation on Zr (0001) at temperature range between -60°C and 190°C in $2.6 \times 10^{-8}$ mbar oxygen. The oxide formed at the surface becomes more stoichiometric with increasing temperature. The result is found from analysis of the XPS data.
Figure 6-9: The electric field strength distribution in the initial oxide films formed under different temperatures after 150 min oxygen exposure at $2.6 \times 10^{-8}$ mbar (the oxidation kinetics was shown in Figure 6-4). The x-axis is the relative position within the oxide film, $x/L=0$ is the sample surface, $x/L=1$ is the metal/oxide interface.

Figure 6-10: The electric field strength at metal-oxide interface for oxidation at different temperatures shown in Figure 6-4. (Points at $x/L=1$ in Figure 6-9)
6.6 Conclusions

The goal of this work is to characterize and model the effect of temperature, oxidant pressure and oxidant type on the initial oxidation kinetics of zirconium, and also identify the key kinetic parameter that governs the initial oxidation kinetics. The initial oxidation kinetics on Zr (0001) in dry oxygen and water vapour within the temperature range of -130°C to 190°C and pressure range of $2.6 \times 10^{-8}$ mbar to $2.6 \times 10^{-6}$ mbar was characterized by in situ synchrotron based X-ray Photoelectron Spectroscopy (XPS). For oxidation in temperature range of -130°C to -10°C at $2.6 \times 10^{-8}$ mbar, the oxide thickness decreases with increasing temperature. In temperature range of 30°C to 190°C, the oxide thickness increases with increasing temperature, and the kinetics change from self-limiting to non-self-limiting. The pressure dependence of the oxide thickness is such that the thickness increases with increasing the pressure. For different oxidants, the kinetics are pretty similar. The difference for water oxidation with respect to oxygen is that for the same oxidation conditions, the thickness of the oxide formed by water oxidation is thinner than the one by oxygen because of the effectively lower Mott potential at the surface introduced by water. A new model including the local distribution of the electric field is proposed and constructed for Zr initial oxidation. From fitting the oxidation kinetics data by this model, both the magnitude of the Mott potential and its distribution within the oxide film was found to play an important role in determining the oxidation kinetics. By increasing the oxidation temperature at the same oxidation pressure, the Mott potential decreases, which is due to the reduced surface coverage of oxygen ions. On the other hand, the increase of the temperature increases the Debye length, which in turn could provide local electric field strength. These competing effect could explain the initial decrease of oxide thickness followed by the increase of oxide thickness with increasing temperature. This finding emphasises the crucial role of the electric field during the initial metal oxidation: not only the magnitude but also the distribution matters for getting the accurate oxidation kinetic model. In addition by increasing the oxidation temperature, activation energy for the oxygen diffusion in the oxide changes between -10°C and 30°C, which indicates an intrinsic change of the oxide structure or composition during the initial oxidation.
7 Summary and Future Directions

7.1 Summary of This Thesis

In this thesis we presented a detailed framework to study the metal initial oxidation, starting from characterizing the basic chemical state and atomic structure of the initial oxide formed on the metal surface, to probing the oxygen transport properties under electric field, and finally to modelling the initial oxidation kinetics. This framework was applied to the study of initial oxidation of Zr (0001) single crystal as a model system, which is important for understanding the corrosion and protectiveness of the oxide formed on zirconium alloys in nuclear reactors.

In the first part of this study, we probed the formation of ZrO$_x$ during the early stage oxidation of the metal in oxygen gas by high resolution synchrotron x-ray photoelectron spectroscopy, which was analysed by physical modelling of the Zr 3d photoelectron spectrum. Although the average composition yields a stoichiometry of ZrO, as also observed by previous atom probe tomography measurements [9], the local chemical environments in such a ZrO$_x$ deviate from only the 4+ oxidation state of Zr and include all three Zr$^{3+}$, Zr$^{2+}$ and Zr$^{3+}$ states. The mechanisms that drive the formation of ZrO$_x$ at the metal/oxide interface under these experimental conditions could be attributed to the following two aspects: 1) the presence of a strong electric field that changes the energy landscape and modulates the red-ox processes in the oxide, and 2) the minimization of the interfacial energy by forming a ZrO$_x$ at the metal-oxide interface.

The formation conditions of this seemingly unstable (unexpected) ZrO$_x$ under electrical bias at different temperatures and oxygen partial pressures were assessed by ambient pressure, synchrotron x-ray photoelectron spectroscopy and simultaneous chronoamperometry measurements on model fully oxidized ZrO$_2$ films. The x-ray photoelectron spectra of Zr on ZrO$_2$ were found to change with time under strong electric fields, which indicates the change of chemical states in the Zr-oxide films. Consistent with the variation in the XPS signature, the chronoamperometry measurements exhibit by a momentary current increase, followed by a new steady state under bias. This typical electronic signature has also been found in other oxide systems [21, 85], which indicate the nucleation and growth of secondary phases. Then, this chronoamperometry characteristic was used to determine the ZrO$_x$ formation
conditions. The temperature, oxygen partial pressure and electric bias dependence of the ZrOₓ formation have been resolved: by increasing the strength of applied electric bias, the temperature (oxygen partial pressure) required for ZrOₓ formation decreases (increases). The mechanism of the temperature, pressure and electric bias coupling for ZrOₓ formation could be explained by the large surface electrochemical potential gradient induced by the applied electrical bias.

The second part of this thesis focuses on the study of surface structure of the initial oxide formed on Zr (0001) single crystal surface by using scanning tunneling microscopy (STM). By exposing the sample to oxygen at 2×10⁻⁸ mbar at room temperature for 1 min and annealing, the first layer of the surface oxide form a large triangle moiré pattern. Atomic resolution STM images show the surface of the triangle moiré pattern has a c-ZrO₂ (111) orientation, with an O-Zr-O trilayer structure is proposed for this triangle moiré pattern. This first oxide layer has a large concentration of oxygen vacancies. The presence of such a highly sub-stoichiometric surface oxide is consistent with the formation of reduced ZrOₓ we found in our XPS studies in the first part. The formation of the surface oxygen vacancies at 45 % is consistent with an 8% shrinkage of the lattice constant. By further oxygen exposure and annealing, a second layer of oxide grows on top of the first layer, with intermediate steps up to 95 minutes. The structure of this second oxide layer has a “row” moiré pattern. The growth of the oxide on the surface is self-limiting, which is consistent with our previous oxidation kinetic studies by XPS on the same sample. The surface of the “row” pattern has a squared lattice, which could be cubic ZrO₂ (001). A possible model for the “row” moiré pattern is proposed. The detailed atomic level structure of the initial Zr oxide presented in this work should pave the way for modelling and interpreting the oxidation properties of Zr and Zr alloys as well as the surface properties of the oxide formed on them.

In the third part, we have investigated the oxygen diffusion in the ZrO₂ thin films under electric bias was investigated by means of in situ XPS and chronoamperometry measurements. A detailed XPS spectrum analysis revealed that the electric field distribution changes with the increase of the concentration of reduced zirconium species (or equivalently by the increase of oxygen vacancies). By applying electric field to the sample surface, the oxygen vacancies are generated at the anode and are driven to the cathode side. Chronoamperometry measurements captured the increase of the film’s conductivity by increasing the bias magnitude and time. The time
needed to reach a steady state limiting current depends on the temperature and bias: the higher the temperature and bias, the shorter the threshold time. The resulting I-t (current-time) curve was fitted by using the diffusion-drift model, which considered the drift induced by the electric field and the surface oxygen exchange reaction in addition to self-diffusion. From this model, the oxygen vacancy diffusion and oxygen surface exchange coefficients could be extracted. We compared the vacancy diffusion coefficient found from our diffusion-drift model to the effective diffusion coefficient found by the Cottrell equation as described in [21]. We found that the Cottrell equation yields about two orders of magnitude greater vacancy diffusion coefficient. The difference comes from separating the self-diffusion coefficient from the effect of the electric field on ion drift and oxygen surface exchange that are all convoluted in the Cottrell approach. The experimental method and the modelling approach applied in this work could also be applied for assessing the oxygen vacancy diffusion kinetics in other oxides that function under electric field, such as thin oxide films during metal oxidation or red-ox based resistive switching oxides.

Finally, the initial oxidation kinetics of Zr (0001) was characterized by in situ synchrotron based X-ray Photoelectron Spectroscopy (XPS) and a corresponding model for Zr initial oxidation was proposed. The pressure dependence of the oxide thickness is such that the thickness increases with increasing the pressure. For different oxidants, the kinetics are pretty similar. The difference for water oxidation with respect to oxygen is that for the same oxidation conditions, the thickness of the oxide formed by water oxidation is thinner than the one by oxygen because of the effectively lower Mott potential at the surface introduced by water. The effect of temperature, oxidant pressure and oxidant type on the initial oxidation kinetics of zirconium was discussed. For oxidation from -130 °C to -10 °C and at 2×10⁻⁸ mbar of oxygen gas or water vapour, the self-limited oxide thickness decreases with increasing temperature. From 30°C to 190°C, the oxide thickness increases with increasing temperature, and the oxide growth kinetics becomes non-self-limiting. There has been no existing single model that could capture this transition in the temperature dependence of oxide thickness. A new oxidation model was proposed by considering the local electric field distribution, based on the classic Cabrera-Mott model and the Debye-Hückel theory for field distribution. From fitting the oxidation kinetics data by this model, both the magnitude of the Mott potential and its distribution within the oxide film were found to play important roles.
in determining the oxidation kinetics. By increasing the oxidation temperature at the same oxidation pressure, the Mott potential decreases, which is due to the reduced surface coverage of oxygen ions. On the other hand, the increase of the temperature increases the Debye length, which in turn could provide local electric field strength. Competition between the Mott potential, the Debye length and oxygen diffusion could explain the initial decrease of oxide thickness followed by an increase at the higher temperature range studied here. This finding emphasises the crucial role of the electric field distribution during the initial metal oxidation: not only the magnitude but also the distribution matters for getting the accurate oxidation kinetic model. In addition by increasing the oxidation temperature, activation energy for the oxygen diffusion in the oxide changes between -10°C and 30°C, which indicates an intrinsic change of the oxide structure or composition during the initial oxidation.

7.2 Future Work

7.2.1 Modelling of detailed atomic structure of the initial oxide formed on Zr (0001)

In Chapter 4, we have demonstrated the surface atomic structure of the first and second layers of oxide formed on Zr (0001) single crystal, and proposed corresponding atomic model for them. However, only from the surface images, we could not verify the validity of the exact atomic model. Further experimental and computational work should be able to provide the validity of the models. For example, the Low Energy Electron Diffraction (LEED) could provide further confirmation on the surface crystal structure of the initial oxide; Density Functional theory (DFT) calculation could be used to test stability of the proposed atomic model.

7.2.2 Application of the characterization method of oxygen transport under electrical field to other oxides

In Chapter 5, we have developed a model for the oxygen transport under electrical bias for the lateral sample geometry (both electrodes are on the top of the oxide). This model could be further modified to study other sample geometry, such as “sandwich” sample structure (electrode/oxide/electrode). In that way, it could be directly applied to other fields of studies. For example, in the red-ox based resistive switches for memory applications, the thin oxide is “sandwiched” between the two
electrodes. The resistive switching behaviour depends on the transport property of oxygen/oxygen vacancies under electric field. The ability of being able to characterize it under the operation condition could provide the possibility to get detailed understanding of the resistive switching mechanisms.

7.2.3 Application of the initial oxidation model to other metals

In Chapter 6, we have proposed a new model including the local distribution of the electric field is proposed and constructed for Zr initial oxidation. It will be interesting to assess whether this model is also applicable to oxidation of other metals and zirconium alloys. In that way, we could acquire the generality and limits of our model. For the nuclear materials applications of Zr, it would be particularly interesting for assessing the effects of alloying elements on the early-stage oxidation kinetics of Zr.
Appendix:

Appendix 1: Methods

Appendix 1.1: X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive spectroscopic technique that can quantitatively measure the chemical composition and chemical states and electronic states in the materials. The principle of XPS is based on measuring the kinetic energy and number of electrons that escape from the sample by irradiating X-ray. Since the energy of the X-ray is known, the electron binding energy of each of the emitted electrons can be deduced from the following equation:

\[ E_b = E_{\text{photon}} - E_k - \phi \]

where \( E_b \) is the binding energy (BE) of the electron, \( E_{\text{photon}} \) is the energy of X-ray, \( E_k \) is the kinetic energy of the electron escaped from the surface and detected by XPS analyzer and \( \phi \) is the work function of the sample.

Since each element has its unique electronic structure, the XPS spectrum could be used as "fingerprint" to identify the chemical species. Moreover, the shift in binding energy could provide more information about the local binding states of the element.

The accuracy of the quantitative analysis of XPS spectrum depends on the method used to subtract the background of inelastic scattering. Usually the XPS spectrum is analysed by peak fitting procedure, which would subtract a Shirley or Linear background and then fit with standard line shape (Gaussian and Lorentzian, Doniach-Sunjic, etc.). However for some transition metals, Zr for example, this approach could not give the accurate results due to the strong core-hole scattering during the photoelectron emission. The spectrum reconstruction method should be use in these cases. The details about the spectrum reconstruction method is discussed in Chapter 2.

One of the main advancements for the use of XPS is the ability to utilize synchrotron radiation based light source under near-ambient gas conditions. Since the synchrotron radiation could provide much higher brilliance and photon flux than anode-based radiation sources(typically Al Ka (1486.6 eV) or Mg Ka (1253.6 eV)), a much better signal-to-noise ratio could be achieved, which in turn could provide much better
energy resolution of the XPS spectrum. Figure 0-1 shows an example of the comparison between the Lab source XPS spectrum and synchrotron X-ray XPS spectrum. The addition feature marked as the dash line in Figure 0-1 could only be observed by using synchrotron radiation. Another advantage of using synchrotron radiation is that the wavelength of the X-ray could be tuned to a desired value. The probing depth could be changed by varying the photon energy, since the probing depth is exponentially correlated with the photoelectron kinetic energy.

![Graph showing comparison between Lab source X-ray (a) Al Kα (1486.7 eV) and Synchrotron X-ray (400 eV) (b)](image)

Figure 0-1: Zr 3d photoelectron spectra comparison between (a) Lab source X-ray Al Kα (1486.7 eV) and (b) Synchrotron X-ray (400eV). The additional feature representing Zr sub-valence state is indicated by the dash line.

In this work, all the XPS spectrum were collected by using synchrotron radiation at National Synchrotron Light Source beam line U12A (Brookhaven National Lab) and Advanced Light Source beam line 9.3.2 (Lawrence Berkeley National Lab). At beam line U12A, the radiation source was tunable, monochromatized soft x-rays in the energy range of 100-600 eV with a resolution ΔE/E of 2×10⁻²-10⁻³. The analyzer of the XPS system is VSW EAC 125. The system is in an Ultra High Vacuum (UHV) chamber with a base pressure of 2.6×10⁻¹⁰ mbar. At beam line 9.3.2, the radiation source energy could be tuned in the range of 30-850eV. The photon flux could be up to 1.5×10¹¹
Appendix 1.2: Principle of Operation of Scanning Tunnelling Microscopy

Since the invention of STM in 1981, STM has become one of the most important surface imaging techniques in many surface science studies. The basic principle of STM is based on the quantum-mechanical tunnelling of electrons through a very small vacuum gap between the sample surface and the probing tip. The schematic plot for the STM operation is shown in Figure 0-2. A atomically sharp metal probe tip, usually made of W or Pt-Ir alloy, is mounted on piezodrive, which can move in three dimensional space. By coarse approaching, the tip and sample could be brought to within a few angstroms from each other. The bias voltage, applied between the sample and tip, will cause the electron tunnelling through the vacuum, which results in detectable current.

The tunnelling current could be expressed approximately by the following equation:

\[ I \approx V \rho_s \exp[-1.025 \sqrt{\phi d}] \]

where \(d\) is the sample-tip distance; \(\phi\) is the parameter related to the energy barrier between the sample and tip; \(V\) is the bias between the sample and tip; \(\rho_s\) is the electron density of the sample.[171] Since the tunnelling current is exponentially dependent on the tip-sample distance and energy barrier for electron tunnelling through vacuum, a small change in the sample-tip distance could result in large change in tunnelling current. In the constant-current scanning mode, a constant tunnelling current is attained by adjusting the tip-sample distance \(d\) by a feedback loop, which could adjust the Z-Piezo controlled by applied voltage on a piezoelectric tube. By recording the Z-Piezo change during the lateral (x-y) scan, the surface topography of the sample could be obtained.

One of the main disadvantages of STM is that it requires the sample to be conductive. Since there will be no tunneling current could be obtained on insulating (bulk) materials. However, image of very thin insulating films on conductive substrate is still possible. Another important aspect of STM is that the image obtain does not only
depend on the topography of the sample surface, it also depends on the local electronic structure. This may lead some difficulty in understanding the obtained STM images. Nevertheless, sufficiently large scale scan could be regarded as purely topographic images.

In this work, the in-situ STM has been used to investigate the topography of initial oxide formed on Zr(0001) single crystal surface. The oxide growth over time could be captured by taking the image after every oxygen exposure. (see Chapter 4 for details) Since the oxide formed during this very early oxidation stage is very thin, the electrons could tunnel through this very thin oxide. With increasing the oxygen exposure, the tunneling voltage required to get the stable image also increases.

![Schematic plot of STM measurement](image)

**Figure 0-2:** Schematic plot of STM measurement. The bias voltage is applied between the sample and the tip and the resulting tunneling current is measured. The tunneling current will be compared with the current set point, and then the difference between them will be set as input for the feedback loop to change the distance (d) between the sample and the tip. The lateral movement of the tip with respect to the sample while record the variation of Z-Piezo could provide topographic image of the sample surface. (Figure reproduced from reference [171].)

**Appendix 1.3: Chronoamperometry measurement**

Chronoamperometry is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrode (caused by the potential step) is monitored as a function of time. Chronoamperometry generates high charging currents, which decay exponentially with time as any RC circuit. The Faradaic current—which is due to electron transfer
events and is most often the current component of interest—decays as described in the classic Cottrell equation [143].

\[ i = \frac{nFAC_j^0 \sqrt{D_j}}{\sqrt{\pi t}} \]

where \( i \) is the current, \( n \) is the number of electrons, \( F \) is the Faraday constant, \( A \) is the area of the electrode, \( c_j^0 \) is the initial concentration of the charged species, \( D_j \) is the diffusion coefficient, \( t \) is the time.

Figure 0-3: (a) Waveform for a step experiment in which species 0 is electron inactive at \( E_1 \), but is reduced at a diffusion-limited rate at \( E_2 \). (b) Concentrating profiles for various times into the experiment. (c) Current flow vs. time. (Figure reproduced from reference [143])

Figure 0-3 shows an example of chronoamperometry experiment. By applying higher negative electric field, the oxygen species in the solution could be reduced. Current flows subsequently to maintain the fully reduce condition at the electrode surface. The initial reduction has created a concentration gradient that in turn produce a continuing flux of the solvent to the electrode surface. Since this arriving material cannot coexist with the electrode at \( E_2 \), it must be eliminated by reduction. As the concentration of the reactant deplete in the reactive zone, the slope of the concentration profile at the surface declines with time, and so does the current. In Chapter 5, we discussed how to apply the chronoamperometry measure to the solid system, and how to characterize the oxygen transport in solid under electric field.
Appendix 2: Computational Methods

Appendix 2.1: Matlab implementation of XPS spectrum reconstruction

Filename: “Main.m”
para=[******];
% load raw data
load('Raw2.txt');
f=@(x)(residual(x,Raw2));
options=optimset('LargeScale','off','Display','iter','TolX',1e-3);
options=optimset(options,'Algorithm','levenberg-marquardt');
t0 = clock;
[lam,resnorm,residual,exitflag,output] = lsqnonlin(f,para,[],[],options);
execution_time = etime(clock,t0);
fprintf('Number of iterations: %g
Number of function evaluations: %g
',output.iterations, output.funcCount);
fprintf('Sum of squared residuals at solution: %g
',resnorm);
fprintf('Execution time: %g
',execution_time);

y=residual_plot(lam,Raw2);

Filename: “residual.m”
function f=residual(para,Raw)
% load raw data
Ek=Raw(:,1); %kinetic energy
Eb=Raw(:,2); %binding energy
data=Raw(:,3); %experimental data
data=data-min(data);

% reconstruction
% zero loss line 10
% basic line shape

Em=para(1);  % metal peak position
a=0.803536223;  % metal a is asymmetric factor
rm=para(10);  % metal r is FWHM of main peak
% rm=0.129560564;  % metal r is FWHM of main peak
Hm=para(2);  % Hm is the metal height of main peak
Em_split=2.389223422;% metal E_split is energy difference between two peaks
ratiom=0.626855394;  % metal ratio between 3d3 to 3d5

Eo=para(3);  % oxide peak position
% ro=0.780714232;  % oxide r is FWHM of main peak
ro=para(11);  % oxide r is FWHM of main peak
rsub1=para(12);
rsub2=para(13);
Ho=para(4);  % Hm is the oxide height of main peak
Eo_split=2.375911032;  % oxide E_split is energy difference between two peaks
Esub1=para(5);
Hsub1=para(6);
Esub2=para(7);
Hsub2=para(8);
ratioo=0.667149249;  % oxide ratio between 3d3 to 3d5
I1=core_doublet_oxide(Eb,Eo,a,ro,Ho,Eo_split,ratioo);  % oxide peak Lorentz line
Isub1=core_doublet_oxide(Eb,Esub1,a,rsub1,Hsub1,Eo_split,ratioo);  % sub oxide peak Lorentz line
Isub2=core_doublet_oxide(Eb,Esub2,a,rsub2,Hsub2,Eo_split,ratioo);  % sub oxide peak Lorentz line
IO=core_doublet(Eb,Em,a,rm,Hm,Em_split,ratiom)+Isub1+Isub2;  % metal peak DS line

% plot(Ek,Isub1);
% hold;
% plot(Ek,Isub2);
% plot(Ek,IO);
% hold off;

% X ray distribution Ix (Al)
Ex=[-20:0.05:20];
rx=0.224;  % FWHM of x ray
line_split=0.413; % split between Ka1 and Ka2
Ix=xray(Ex,rx,line_split);

% zero loss + x ray broadening
l2=conv(IO,Ix,'same');
l3=conv(I1,Ix,'same');
% plot(Ek,l2);
% hold;
% plot(Ek,l3);
% hold off;

% Intrinsic loss li

% metal
A=para(14);  % metal cross section normalize
b=0.318566569;  % metal intensity ratios of intrinsic loss peak to main peak
ri=para(15);  % metal FWHM of intrinsic loss peak
lim=in_convo(Ek,l2,A,b,ri);
l4=lim+l2;  % metal
% oxide
Ao = 0.794726319; % oxide cross section normalize
bo = 0.083233382; % oxide intensity ratios of intrinsic loss peak to main peak
rio = 5.828799982; % oxide FWHM of intrinsic loss peak
Iio = in_conv_oxide(Ek, I3, Ao, bo, rio);
I5 = Iio + I3; % oxide

% plot(Ek, I4);
% hold;
% plot(Ek, I5);
% hold off;

% Extrinsic loss surface Ies
D = para(9); % surface thicknesss
lams = 2.392; % surface IMFP
theta = 0; % detection angle relative to surface normal
Cs = 0.046; % surface atomic concentration
% fele = para(12); % loss ox peak shift
fele = 1;
Plesp = 12.48487089; % surface plasmon peak position
Ies = ex_surface(Ek, I5, D, lams, theta, Cs, Ao, fele, Plesp);

% Inten_surf = 1;
% Ies1 = ex_surface(Ek, I2, D, lam, theta, C, A);
% Factor = C.*lam.*cos(theta).*exp(-D./(lam.*cos(theta)));
% I3 = (Ies1 + Factor.*I2).*Inten_surf;

% plot(Ek, Ies);
% hold;
% plot(Ek, I3);
% hold off;

% Extrinsic loss bulk Ieb
lamb=2.543;
Cb=0.0713;
Ieb=ex_bulk(Ek,I4,Cb,D,lams,lamb,theta,A,fele);

plot(Ek,Ieb);
hold;
plot(Ek,12);
hold off;

% Spectrum of ex and in contribution
I9=Ies+Ieb;

% Total spectrum
rg=0.91;  % Gauss function FWHM
instr=instrumental(rg);
Itot=conv(I9,instr,'same');
f=Itot-data;
lent=length(f);

plot(Ek,Itot);
hold;
plot(Ek,data);
plot(Ek,f);
hold off;

f=f(40:(lent-40),1);
Ek0=Ek(40:(lent-40),1);
data0=data(40:(lent-40),1);
Itot0=Itot(40:(lent-40),1);

plot(Ek0,Itot0);
hold;
plot(Ek0,data0);
% plot(Ek0,f);
% hold off;
end

Filename: “broading.m”
function y=broadening(E,r)
y=(2./(r.*sqrt(pi))).*exp(-(E*2/r).^2);
end

Filename: “core.m”
function y=core(E,Em,a,r)
% core level zero loss peak, D-S line shape
% Em is peak position
% E is binding energy
% a is asymmetric factor
% r is FWHM
y=gamma(a)*cos(0.5*pi*(1-a)+a*atan((Em-E)*2/r))./(((Em-
E).^2+(0.5*r).^2).^(0.5*a);)
end

Filename: “core_doublet.m”
function y=core_doublet(E,Em,a,r,Hm,E_split,ratio)
% core level zero loss peak, D-S line shape, spin orbit splitting
% Em is peak position
% E is binding energy
% a is asymmetric factor
% r is FWHM
% Hm is the height of main peak
% E_split is energy difference between two peaks
y=Hm*(core(E,Em,a,r)+core(E-E_split,Em,a,r)*ratio);
end

Filename: “core_doublet_oxide.m”
function y=core_doublet_oxide(E,Em,a,r,Hm,E_split,ratio)
% core level zero loss peak, D-S line shape, spin orbit splitting
% Em is peak position
% E is binding energy
% a is asymmetric factor
% r is FWHM
% Hm is the height of main peak
% E_split is energy difference between two peaks
y=Hm*(core_oxide(E,Em,a,r)+core_oxide(E-E_split,Em,a,r)*ratio);
end

Filename: “core_oxide.m”
function y=core_oxide(E,Em,a,r)
% core level zero loss peak, Lorentz line shape
% Em is peak position
% E is binding energy
% a is asymmetric factor
% r is FWHM
y=(2./(pi*0.5*r*(1+4*((E-Em)/r).^2)));
end

Filename: “depth_distri.m”
function y=depth_distri(z,lam,theta,n)
% depth distribution function
% z is the distance from surface
% lam is inelastic mean free path
% theta is the angle relative to surface normal
% n is integer
a=z./(lam.*cos(theta));
y=(1./factorial(n)).*(a.^n).*exp(-a);
end
function y = ex_bulk(Ek, I, Cb, D, lams, lamb, theta, A, fele)
y = zeros(length(I), 1);
a = D ./ (lams .* cos(theta));
for n = 1:5
    for p = 0:n
        P = 0.25 .* Cb .* cos(theta) .* lamb .* (1 ./ factorial(n - p)) .* (a .* (n - p)) .* exp(-a);
        L = partial_loss(Ek, p, A, fele);
        temp = zeros(length(I), 1);
        for i = 2:length(I)
            for j = 1:(i - 1)
                if p == 0
                    temp = I;
                else
                    temp(i - j) = temp(i - j) + 0.05 .* (I(i) .* L(j));
                end
            end
        end
        L = partial_loss(Ek, n - p, A, fele);
        temp1 = zeros(length(I), 1);
        for i = 2:length(I)
            for j = 1:(i - 1)
                if p == n;
                    temp1 = temp;
                else
                    temp1(i - j) = temp1(i - j) + 0.05 .* (temp(i) .* L(j));
                end
            end
        end
        y = y + P .* temp1;
    end
end
% P=0.25.*Cb.*cos(theta).*exp(-a);
y=y+P.*I;
end

Filename: “ex_ox.m”
function y=ex_ox(El,E,a,fele)
% extrinsic cross section of zr
% El is energy loss
% E is the kinetic energy
% a is normalize factor

% original ox
y=ox(El,E,16.3*fele,168,5.5)+ox(El,E,4.3*fele,0.65,3)+ox(El,E,8.5*fele,5.4.5
)+ox(El,E,30*fele,5.5)+ox(El,E,38*fele,366,11.5)+ox(El,E,52*fele,33,14);
m=[0:0.05:100];
s=ox(m,E,16.3*fele,168,5.5)+ox(m,E,4.3*fele,0.65,3)+ox(m,E,8.5*fele,5.4.5)
+ox(m,E,30*fele,5.5)+ox(m,E,38*fele,366,11.5)+ox(m,E,52*fele,33,14);
s=sum(s).*0.05./a;
y=y./s;

% modified ox
% y=ox(El,E,4.3,0.65,3)+ox(El,E,9,5,4.5)+ox(El,E,30,5,5)+ox(El,E,52,33,14);
% m=[0:0.05:100];
% s=ox(m,E,4.3,0.65,3)+ox(m,E,9,5,4.5)+ox(m,E,30,5,5)+ox(m,E,52,33,14);
% s=sum(s).*0.05./a;
% y=y./s;
End

Filename: “ex_ox_surface.m”
function y=ex_ox_surface(El,E,a,fele,Plesp)
% extrinsic cross section of zr
% El is energy loss
% E is the kinetic energy
% a is normalize factor

% original ox
y = ox(E, E, Plesp, 63, 4.3) + ox(E, E, 8.5*felle, 3.3, 3.5) + ox(E, E, 20.5*felle, 37, 7)
+ ox(E, E, 26*felle, 110, 8) + ox(E, E, 34*felle, 8, 2)
+ ox(E, E, 41*felle, 270, 9) + ox(E, E, 57.5*felle, 65, 13);
m = [0:0.05:100];
s = ox(m, E, Plesp, 63, 4.3) + ox(m, E, 8.5*felle, 3.3, 3.5) + ox(m, E, 20.5*felle, 37, 7)
+ ox(m, E, 26*felle, 110, 8) + ox(m, E, 34*felle, 8, 2) + ox(m, E, 41*felle, 270, 9)
+ ox(m, E, 57.5*felle, 65, 13);
s = sum(s) .* 0.05 ./ a;
y = y ./ s;

% modified ox
% y = ox(E, E, 4.3, 0.65, 3) + ox(E, E, 9, 5, 4.5)
% m = [0:0.05:100];
% s = ox(m, E, 4.3, 0.65, 3) + ox(m, E, 9, 5, 4.5)
% s = sum(s) .* 0.05 ./ a;
% y = y ./ s;
end

Filename: "ex_surface.m"
% z is surface thickness, lam is IMFP, theta is the detection angle, n is
% the time of scatter, C is the ocncentration of element,A is ox normalize
function y = ex_surface(Ek, I, z, lam, theta, C, A, felle, Plesp)
y = zeros(length(I), 1);
for n = 1:10
    P = partial_inten(z, lam, theta, n, C);
    L = partial_loss_surface(Ek, n, A, felle, Plesp);
    temp = zeros(length(I), 1);
    for i = 2:length(I)
        ...
    end
end
for j=1:(i-1)
    temp(i-j)=temp(i-j)+0.05.*(I(i).*L(j));
end
end
y=y+temp.*P;
end
P=partial_inten(z, lam, theta, O, C);
y=y+I.*P;
end

Filename: “in_convo.m”
% E is kinetic energy, P is peak intensity, a is cross section normalize
% factor, b is intensity ratios of intrinsic loss peak to main peak
function y=in_convo(E,P,a,b,ri)
% y=0;
% for i=2:length(E)
%    s=0.05.*(i-1);
%    El=[s:-0.05:0.05];
%    temp=b.*P(i).*total_ox(El,E(i),a);
%    x=length(P)-length(temp);
%    temp(end+x)=0;
%    y=y+temp;
% end
% y=y';
% y=0.05.*y;
% end
l=length(E);
y=zeros(l,1);
El=[0.05:0.05:0.05*1];
ox=total_ox(El,E(1),a,ri);
for i=2:l
    for j=1:(i-1)
% y=y';
y=y.*b;
end

% y=y';
y=0.05.*y;
end

l=length(E);
y=zeros(l,1);
El=[0.05:0.05:0.05*1];
ox=total_oxide(El,E(1),a,ri);
for i=2:l
    for j=1:(i-1)
        y(i-j)=y(i-j)+0.05.*(P(i).*ox(j));
    end
end
% y=y';

Filename: "in_conv oxide.m"
% E is kinetic energy, P is peak intensity, a is cross section normalize
% factor, b is intensity ratios of intrinsic loss peak to main peak
function y=in_oxide(E,P,a,b,ri)
% \( \text{y} = 0 \);
% for \( \text{i} = 2 : \text{length(E)} \)
% \( \text{s} = 0.05 \cdot (\text{i} - 1) \);
% \( \text{El} = [\text{s} : 0.05 : 0.05] \);
% \( \text{temp} = \text{b} \cdot \text{P(i)} \cdot \text{total_oxide(El,E(i),a)} \);
% \( \text{x} = \text{length(P)} - \text{length(temp)} \);
% \( \text{temp(end+x)} = 0 \);
% \( \text{y} = \text{y} + \text{temp} \);
% end
% \( \text{y} = \text{y}' \);
% \( \text{y} = 0.05 \cdot \text{y} \);
% end

l=length(E);
y=zeros(l,1);
El=[0.05:0.05:0.05*1];
ox=total_oxide(El,E(1),a,ri);
for i=2:l
    for j=1:(i-1)
        y(i-j)=y(i-j)+0.05.*(P(i).*ox(j));
    end
end
% y=y';
Filename: “instrumental.m”
function y=instrumental(rg)
x=[-20:0.05:20];
y=exp(-(2*x./rg).^2)./(0.5*sqrt(pi).*rg);
end

Filename: “partial_inten.m”
% z is surface thickness, lam is IMFP, theta is the detection angle, n is
% the time of scatter, C is the concentration of element
function y=partial_inten(z, lam, theta, n, C)
x=[0:1:n];
a=z./(lam.*cos(theta));
fi=(1./factorial(x)).*(a.^x).*exp(-a);
y1=sum(fi);
y=C.*lam.*cos(theta).*((1-y1).*0.5);
if y<=0
    y=0;
end
end

Filename: “partial_inten_bulk.m”
function y=partial_inten_bulk(C, D, lam, theta, i)
l=depth_distri(D, lam, theta, i);
y=C.*lam.*cos(theta).*l;
end

Filename: “partial_loss.m”
function y=partial_loss(Ek,n,A,fele)
I=length(Ek);
El=[0.05:0.05:100];
K=ex_ox(El,Ek(1),A,fele);
if n<0
    y=0;
elseif n==0
    y(1)=20;
    y(end+l-1)=0;
else
    m(1)=1;
    for i=1:n
        m=conv(m,K);
        m=m.*0.05;
    end
    y=m(1,1:1);
    s=sum(m).*0.05;
    y=y./s.*A;
end
y=y';
end

Filename: “partial_loss_bulk.m”
function y=partial_loss_bulk(Ek,i,j,A)
L1=partial_loss(Ek,i,A);
L2=partial_loss(Ek,j,A);
l=length(Ek);
m=conv(L1,L2);
y=m(1:1,1);
% s=sum(m).*0.05;
% y=y./s.*A;
End
function y = partial_loss_surface(Ek, n, A, fele, Plesp)
    l = length(Ek);
    El = [0.05:0.05:100];
    K = ex_ox_surface(El, Ek(1), A, fele, Plesp);
    if n < 0
        y = 0;
    elseif n == 0
        y(l) = l;
        y(end + l - 1) = 0;
    else
        m(1) = 1;
        for i = 1:n
            m = conv(m, K);
            m = m .* 0.05;
        end
        y = m(1, 1:l);
        s = sum(m) .* 0.05;
        y = y / s .* A;
    end
    y = y';
end

function y = ox(El, E, Ep, A, r)
% intrinsic excitation energy loss cross section
% El energy loss, E electron kinetic energy
% Ep position of loss peak, A magnitude of loss peak, r width of loss peak
    c = (El.^4 + (r .* El).^2).^0.25;
    g = (0.5 * (1 + (El / c).^2)).^0.5;
    h = (0.5 * (1 - (El / c).^2)).^0.5;
    k1 = (sqrt(E) + sqrt(E - El)).^2;
    k2 = (sqrt(E) - sqrt(E - El)).^2;
end
% 2.2: Program for deducing surface electric potential distribution by XPS

Filename: “Efield.m”
para=[***];

load('Raw.txt');
f=@(x)(fieldp(x,Raw));

options = optimset('LargeScale','off','Display','iter','TolX',1e-3);
options = optimset(options,'Algorithm','levenberg-marquardt');
t0 = clock;
[lam,resnorm,residual,exitflag,output] = lsqnonlin(f,para,[],[],options);
execution_time = etime(clock, t0);
fprintf('
Number of iterations: %g
Number of function evaluations: %g
',output.iterations, output.funcCount);
fprintf('Sum of squared residuals at solution: %g
',resnorm);
fprintf('Execution time: %g
',execution_time);

y=residual_plot(lam,Raw2);

Filename:"fieldp.m"
function y=fieldp(para,Raw)
Ek=Raw(:, 1); %kinetic energy
Eb=Raw(:, 2); %binding energy
data=Raw(:, 3); %experimental data
data=data-min(data);
f=reconstr(para,Raw);
p=para(16:26);
y=conv(p,f)-data;
end

Appendix 2.3: Program for oxygen diffusion under electric field and oxidation
Filename:"main.m"
para=[***];
% load raw data
load('Raw.txt');
f=@(x)(model(x,Raw));

options = optimset('LargeScale','off','Display','iter','TolX',1e-3);
options = optimset(options,'Algorithm','levenberg-marquardt');
t0 = clock;
[lam,resnorm,residual,exitflag,output] = lsqnonlin(f,para,[],[],options);
execution_time = etime(clock, t0);
fprintf('Number of iterations: %g
Number of function evaluations: %g
', output.iterations, output.funcCount);
fprintf('Sum of squared residuals at solution: %g
',resnorm);
fprintf('Execution time: %g
',execution_time);

y=residual_plot(lam,Raw2);

Filename:"model.m"

function f=model(para,Raw)
d=500; %dimension of matrix
h=10; %step size

K=toeplitz([-2 1 zeros(1,d-2)]);
K(1,1)=-1;
% K(d,d)=-1;
K=K/h/h; %second order difference

m1=diag(ones(1,d-1),1);
m2=diag(-ones(1,d-1),-1);
D=m1+m2;
D(1,1)=-1;
D=D*0.5/h; %first order difference

V0=0.1;
V=zeros(d,1);
% for j=1:d
% V(j,1)=V0/d*j;
% V(j,1)=V(j,1)-V(1,1);
E = D * V;
T = 513;
Pe = 2 * sinh(E / T / 0.000086);  \% Peclet number
\% Pe = 3 / 8.6 * V / T * Pe;
\% Pe = 0.002698935;  \% Peclet number
tau = 50;  \% time interval

ex = para(1);
diff = para(2);
k = zeros(d, 1);
k(1, 1) = ex;
k(d, 1) = ex;
gas = zeros(d, 1);
gas(1, 1) = 1;

C = ones(d, 1);  \% initial condition

detac = exp(2 * V / T / 0.000086) - ones(d, 1);
\% x = C(:, 1);
\% x2 = (K * t - Pe * D * t) * tau + x;
\% C(:, 2) = x2

for i = 1:3000
x = C(:, 1);
I(i, 1) = sum(x);
R = 1 / x;
for j = 1:d
V(j, 1) = VO / sum(R) * (sum(R(1:j)) - R(1));
\% V(j, 1) = V(j, 1) - V(1, 1);
end
E = D * V;

Pe = 2 * sinh(E / T / 0.000086);

E(1) = E(2);
E(d) = E(d-1);

detac = exp(2 * V / T / 0.000086) - x;

m = diff * K * x;

n = diff * D * (Pe .* x);

m(1) = 0;

m(d) = 0;

n(1) = 0;

n(d) = 0;

C(:,1) = (m - n + detac .* k) * tau + x;

C(1,1) = 1;

f = Raw - I;

end
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