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Growth, structure and physicochemical properties of ultrathin iron and vanadium oxide films

by

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Dedicate to my loving parents, who never hesitate at any moment of supporting me to make my dream come true, and to everyone I love in this beautiful world.

Declaration

Declaration of the candidate

I hereby declare that the content of this dissertation is original research. It has been composed by me and has not been submitted for any previous degree or professional qualification. The whole experimental work was carried out by me, the members of the research group I was working in and our external collaborators, during my contract period within the First TEAM project of the Foundation for Polish Science (July 2017–June 2021), under the supervision of Prof. Dr. Mikołaj Lewandowski and Prof. Dr. Niklas Nilius. The contributions from respective Authors are provided in their Contribution Statements. The purpose of submission of this dissertation is to obtain the degree of Doctor of Philosophy in Physics at the Faculty of Physics of Adam Mickiewicz University in Poznań, Poland.

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Declaration of the supervisor

The declaration made by the candidate is, to the best of my knowledge, accurate. The dissertation is ready to be reviewed.

Prof. Dr. Mikołaj Lewandowski

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Abstract

Ultrathin transition metal oxide films grown on noble metal single-crystal supports exhibit unique electronic, magnetic and catalytic properties. These properties mainly originate from their low-dimensionality and the interaction with the underlying substrate. As an example, ultrathin iron monoxide (FeO) films were found to exhibit superior catalytic activity in oxidation reactions, which was related to the structural flexibility of their crystalline lattices, as well as substrate-mediated charge transfer processes. These films may also be characterized by thickness-dependent electronic and magnetic properties, making them promising multifunctional materials.

The aim of this work was to study the growth, structure and physicochemical properties of ultrathin iron and vanadium oxide (FeO_x and VO_x, respectively) islands and films on selected metal single-crystal supports: Ru(0001) (FeO_x and VO_x) and Ag(111) (only FeO_x). The studies were carried out under ultra-high vacuum (UHV) conditions using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) as the experimental tools.

The studies carried out on ultrathin FeO islands and films on Ru(0001) allowed determining the detailed structure of mono- and bilayer FeO species (Fe-O and Fe-O-Fe-O, respectively) and creation of the corresponding structural models. It was found that in one of the three main in-plane crystallographic directions, the oxide is characterized by slightly different atomic and Moiré periodicities compared to the other two directions, which leads to the rotation of the layer with respect to the underlying Ru(0001) support. Bilayer films were further subjected to atomic oxygen at room temperature (RT) and 700 K to mimic highly-oxidizing conditions that are typically present during catalytic oxidation reactions. Room-temperature exposure was found to lead to the transformation to oxygen-rich FeO_x (1 > x > 2) phase, which can be reverted by annealing at 800 K in UHV. Exposure at 700 K, on the other hand, leads to irreversible transformation to a Fe₂O₃like phase. The reactivity of both – pristine FeO and the O-rich phase (obtained at RT) – towards carbon monoxide (CO) at RT and 600 K was also evaluated, contributing to the understanding of catalytic properties of the films.

Ultrathin FeO films were also grown on Ag(111). Ag(111) is one of the promising substrates for iron oxide films growth, as it exhibits only 5% lattice mismatch to FeO(111) and is considered weakly-interacting. Additionally, it is not prone to oxidation, which reduces the complexity of the FeO/Ag(111) system. However, the reports published on the structure of this system are often contradictory to each other. Within the present work, two preparation procedures were used, that included Fe deposition either at RT or at 500–600 K and post-oxidation. Few different iron oxide structures were observed, including a previously unreported Moiré superstructure with a 45 Å periodicity, a structural model of which is proposed. Local work function measurements also allowed identification of reconstruction-free iron oxide species.

 VO_x islands grown on Ru(0001) were studied during the research stay at the University of Oldenburg, Germany. For the first time, a well-ordered oxide structure was obtained on this particular support. The oxide was found to be covered with periodically arranged features that were assigned to V=O (vanadyl) groups. The vanadyl species could be removed by electron-stimulated

desorption (ESD), which was achieved by applying voltage pulses with the tip of a low-temperature STM. Based on the statistical analysis, the removal of one V=O group requires two or three electrons. The possible mechanism would include resonant tunneling into the anti-bonding or out of bonding orbitals of V=O, followed by the ladder-climbing of vibrational states in the binding potential of the vanadyl group. Such an approach provides a potential route for precise surface modification and single-molecule catalysis.

In conclusion, the work broadens the existing knowledge on the growth, structure and properties of ultrathin transition metal oxide islands and films grown on noble metal single-crystal substrates, in particular iron oxides on Ru(0001) and Ag(111) and vanadium oxides on Ru(0001). The obtained results constitute the basis for further fundamental studies, especially in the field of heterogeneous catalysis. Those could include, for example, the studies of the catalytic activity of ultrathin FeO islands and films on Ru(0001) in oxidation reactions, as they exhibit superior structural flexibility when subjected to subsequent oxidizing and reducing treatments.



Streszczenie

Ultracienkie warstwy tlenków metali przejściowych wytworzone na monokrystalicznych podłożach metali szlachetnych wykazują unikatowe właściwości elektronowe, magnetyczne i katalityczne. Właściwości te wynikają głównie z ograniczonej wymiarowości warstw, jak również oddziaływania z podłożem, na którym zostały wytworzone. Dla przykładu, pokazano, że ultracienkie warstwy tlenku żelaza FeO wykazują wysoką aktywność katalityczną w reakcjach utleniania, co jest związane z elastycznością strukturalną ich sieci krystalicznej, jak również transferem ładunku elektrycznego wynikającym bezpośrednio z oddziaływania z podłożem. Warstwy te mogą również wykazywać zależne od grubości właściwości elektronowe i magnetyczne, co czyni jest obiecującymi materiałami wielofunkcyjnymi.

Celem niniejszej pracy było zbadanie wzrostu, struktury i właściwości fizykochemicznych ultracienkich wysp i warstw tlenków żelaza oraz wanadu (odpowiednio FeO_x i VO_x) wytworzonych na wybranych monokrystalicznych podłożach metalicznych: Ru(0001) (FeO_x i VO_x) oraz Ag(111) (tylko FeO_x). Badania były realizowane w wyidealizowanych warunkach ultra-wysokiej próżni (UHV) z wykorzystaniem skaningowej mikroskopii tunelowej (STM), skaningowej spektroskopii tunelowej (STS), dyfrakcji elektronów niskiej energii (LEED) oraz rentgenowskiej spektroskopii fotoelektronów (XPS) jako narzędzi badawczych.

Badania przeprowadzone dla ultracienkich wysp i warstw tlenku żelaza FeO na Ru(0001) pozwoliły na szczegółowe określenie struktury tlenku o grubości jednej i dwóch warstw (odpowiednio Fe-O i Fe-O-Fe-O) oraz stworzenie odpowiadających im modeli strukturalnych. Zauważono, że w jednym z trzech głównych kierunków krystalograficznych w płaszczyźnie podłoża, warstwy charakteryzują się nieco innymi odległościami międzyatomowymi i periodami nadstruktury Moiré w porównaniu z dwoma pozostałymi kierunkami, co skutkuje obrotem warstw o niewielki kąt względem podłoża Ru(0001). Układy dwuwarstwowe poddano następnie działaniu atomowego tlenu w temperaturze pokojowej (RT) i w 700 K w celu zasymulowania warunków panujących w trakcie katalitycznych reakcji utleniania. Ekspozycja w RT prowadziła do powstawania bogatej w tlen fazy FeO_x (1 > x > 2), przy czym proces ten mógł zostać odwrócony poprzez wygrzanie układu w temperaturze 800 K w warunkach UHV. Z kolei ekspozycja w 700 K skutkowała nieodwracalną transformacją warstw do fazy zbliżonej do tlenku żelaza Fe₂O₃. Badano również aktywność chemiczną fazy FeO oraz bogatej w tlen fazy FeO_x (otrzymanej w RT) względem molekuł tlenku węgla (CO) w RT i 600 K. Uzyskane w wyniku tych badań rezultaty stanowią podstawę do zrozumienia aktywności katalitycznej wytworzonych układów.

Ultracienkie warstwy FeO były także wytwarzane na podłożu Ag(111). Ag(111) jest obiecującym podłożem dla wzrostu FeO, ponieważ charakteryzuję się jedynie 5% niedopasowaniem stałej sieci krystalicznej względem FeO(111) i jest generalnie uważane za słabo oddziałujące podłoże. Co więcej, podłoże to jest odporne na utlenianie, co redukuje stopień skomplikowania układu FeO/Ag(111). Doniesienia literaturowe na temat struktury FeO/Ag(111) stoją jednak często w sprzeczności względem siebie. W ramach prowadzonych badań, wykorzystano dwie metody wytwarzania warstw, uwzględniające naparowanie Fe w temperaturze pokojowej lub w 500–600 K oraz następne utlenianie. Zaobserwowano kilka różnych struktur

tlenków żelaza, w tym wcześnie nie opisaną w literaturze nadstrukturę Moiré o periodzie 45 Å, dla której zaproponowano model strukturalny. Lokalne pomiary pracy wyjścia pozwoliły z kolei na zidentyfikowanie wysp tlenku żelaza nie wykazujących żadnej nadstruktury czy rekonstrukcji powierzchniowej.

Wyspy VO_x wytworzone na podłożu Ru(0001) były badane podczas pobytu badawczego na Uniwersytecie w Oldenburgu w Niemczech. Przeprowadzone badania skutkowały wytworzeniem wysoce-zorganizowanych wysp tlenku wanadu. Jest to pierwszy tego typu przypadek na tym konkretnym podłożu. Zaobserwowano, że tlenek ten jest pokryty periodycznie ułożonymi obiektami, które przypisano do grup wanadylowych (V=O). Grupy te mogły być preferencyjnie usuwane z powierzchni z wykorzystaniem desorpcji stymulowanej elektronami (ESD), co było realizowane poprzez aplikowanie pulsów napięcia przy użyciu ostrza niskotemperaturowego mikroskopu STM. W oparciu o analizę statystyczną wykazano, że usunięcie jednej grupy V=O wymaga przepływu dwóch lub trzech elektronów pomiędzy ostrzem i próbką. Prawdopodobny mechanizm uwzględniałby rezonansowe tunelowanie do wiążących/antywiążących stanów w V=O, po którym następowałoby stopniowe aktywowanie stanów wibracyjnych w potencjale wiążącym grup wanadylowych. Tego typu podejście otwiera drogą do precyzyjnej modyfikacji powierzchni przy użyciu ESD oraz przeprowadzania reakcji katalitycznych z wykorzystaniem pojedynczych molekuł.

Podsumowując, praca poszerza obecny stan wiedzy na temat ultracienkich wysp i warstw tlenków metali przejściowych wytworzonych na monokrystalicznych podłożach metali szlachetnych, w szczególności tlenków żelaza na podłożach Ru(0001) i Ag(111) oraz tlenków wanadu na Ru(0001). Otrzymane wyniki stanowią podstawę do dalszych badań podstawowych, szczególnie w dziedzinie katalizy heterogenicznej. Badania te mogą uwzględniać, między innymi, ocenę aktywności katalitycznej ultracienkich wysp i warstw FeO na Ru(0001) w reakcjach utleniania, ponieważ – jak wykazano – struktury te poddane naprzemiennemu działaniu warunków utleniających i redukujących, charakteryzują się wyjątkową elastycznością strukturalną.

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1. Introduction

1.1. The motivation and scope of the studies

Two-dimensional (2D) materials rapidly gained interest after the discovery of graphene due to its extraordinary properties^[1]. Among all the 2D materials, oxides constitute a broad family of materials and have not yet been widely studied, especially for their fundamental properties and possible prospects. Therefore, understanding the relations between confined 2D oxide structures and properties is critical for potential applications, from catalysis to electronic, magnetic, photonic, etc. The scientific history of well-ordered ultrathin oxide film supported by single-crystal substrate has attracted much attention, thanks to their unique properties compared to their corresponding bulk forms. These unique properties are generally attributed to the low-dimensionality and the strong interaction with the underlying support^[2]. The growth of oxide film highly depends on the supporting substrate, preparation methods and film thickness. Due to the absence of the neighboring atomic layer, the interatomic forces within the surface layer differ from the ones in the bulk. These forces can induce surface stress, which further determines the growth mode and surface morphology of oxide films. Very often, rearrangement of surface atoms (extension, compression, relaxation, etc.) can be observed^[3].

Single crystals are generally used as a metal substrate for ordered ultrathin oxide film growth, since the epitaxial growth has to adopt the substrate's surface arrangement. Iron oxide is one of the well-known ultrathin oxides that can be prepared on many metal substrates, such as on Au(111)^[4], Mo(100)^[5], etc. When it grows on Pt(111)^[85], the surface exhibits a characteristic superstructure with a long-range periodicity of ~ 25 Å, which is known as the Moiré superstructure. Such coincident structure formation originates from approximately 10% lattice mismatch between FeO and Pt substrate. Indeed, different characteristic periodicity of Moiré superstructure can be expected in different system, while for FeO/Ru(0001), the periodicity is determined to be 21.6 Å^[25], and a Moiré-free structure can be obtained for FeO/Ag(111)^[293].

The preparation condition also determines the morphology and composition of the oxide film. For example, depending on the oxygen pressure, iron oxide may grow as a monolayer form, bilayer form, or coexistence of both forms^[26]. The deposition temperatures of iron also play a critical role in forming various oxide structures on Ag(111)^{[96][15]}. Defects often appear during the film growth due to unexpected surface corrugation, contamination, or non-uniform surface strain. Notably, these defects are not always undesired and, in fact, many specific properties could have arisen through them^[6]. Moreover, the overoxidized phase of iron oxide on metallic support could be obtained by strong oxidation (i.e. high oxygen pressure^[29], atomic oxygen^[7], etc.) – suggesting a promising catalyst for the oxidation process. Due to the less complexity and finite size, such models are ideal for understanding the catalytic mechanism.

Thin oxide films are considered as an excellent catalytic model system to study at an atomic scale^[8]. The reaction kinetics is related to surface geometry and electronic structures, as shown

experimentally and theoretically in Ref. [9]. Apart from having a general picture of the catalytic efficiency of a model system, it is also essential to learn which species are responsible for the reaction enhancement. As one of the most well-studied systems, iron oxide on Pt(111) is an ideal model for promoting low-temperature CO oxidation. The active sites for CO oxidation at RT are the coordinatively unsaturated ferrous (CUF) centers at the edges of oxide islands^{[241][267]}. The catalytic activity is also highly related to the high-symmetry region within the Moiré^[29], as well as the perimeter length (total length of edges) of the oxide islands^[79]. Another example, vanadium oxide, as one of the very first catalysts^[10], was actively studied in more recent times as a preliminary model (sometimes with metal adatoms or in a mixed metal oxide form) to understand the mechanism of heterogeneous CO oxidation at the atomic scale^{[11][123]}.

Moreover, connect the structural parameters to properties of oxide film is an essential topic in many surface science research. For example, the magnetic properties of FeO(111)/Pt(111) is highlz dependent on the number of iron oxide layers in the stack^[22]. A few types of iron oxide prepared on Pt(111) react differently towards CO oxidation, which is highly related to oxygen binding energy within the oxide film^[12]. The same oxide grown on different metal support exhibits various reaction efficiency, mainly generated by the different reaction mechanisms^[19]. Therefore, oxide film grown on a metal substrate is of great potential for model studies. In this work, I will focus on the relation between preparation condition, surface structure, as well as the catalytic and electronic properties. In particular, the structure and catalytic properties of various ultrathin iron oxide films grown on Ag(111) and Ru(0001) were explored, as well as the vanadium oxide prepared on Ru(0001). Different systems allow us to fine-tune the Moiré periodicity, islands perimeter length, islands thickness, etc. – towards obtaining the most efficient catalyst.

This dissertation composes of seven chapters. A literature review of relevant topics is discussed in Chapter 1. The materials and methods are described in Chapter 2, starting from a short introduction of the necessary ultra-high vacuum (UHV) facilities for sample cleaning, preparation, structure and properties determination. Standard UHV measuring techniques are described in detail in separate sections, including scanning tunneling microscopy (STM, section 2.2.1), scanning tunneling spectroscopy (STS, section 2.2.2), low energy electron diffraction (LEED, section 2.2.3), and X-ray photoelectron spectroscopy (XPS, section 2.2.4). At the end of the chapter, a typical UHV cleaning process for single crystals is briefly described.

Chapters 3–6 describe the results of my original research. Chapters 3 and 4 mainly concern the growth and catalytic properties of ultrathin iron oxide films grown on Ru(0001). Detailed structure studies of pristine FeO and the structural transformation upon exposure to atomic oxygen is introduced in Chapter 3. The catalytic activity towards CO oxidation is shown in Chapter 4. Ru(0001) is a substrate with high oxygen affinity, making it ideal for model catalytic studies. In particular, the detailed structure of pristine FeO/Ru(0001) is studied in section 3.1 and the oxygen-rich oxide phase formed by exposure to atomic oxygen at RT or 700 K is shown in section 3.2. The results of a few series of experiments of CO reaction on pristine iron oxide and on oxygen-rich iron oxide (formed by exposing atomic oxygen at RT) is presented in section 4.1.1. and 4.1.2, respectively.

Chapter 5 concerns the growth and structure of iron oxides on Ag(111). The structural feature of iron oxide prepared under different preparation conditions is systematically studied, i.e. depositing iron at RT (section 5.1.1) or at elevated substrate temperature (section 5.1.2). By carefully analyzing experimental results, a structure model of a new unreported oxide structure is proposed. Another structure called reconstruction-free oxide can be distinguished from Ag substrate by atomically resolved STM image (section 5.1.2) and STS measurement (section 5.2.1). Further confirmation by theoretical calculation is shown in section 5.2.2.

Chapter 6 reports the surface structure, electronic and potential catalytic properties at the atomic scale of vanadium oxide grown on Ru(0001). Detailed structural analysis, atomic model and thermal stability are presented in section 6.1. The top layer, which is composed of vanadyl groups, can be removed in a controllable way by tunneling electrons with a certain energy exceed the threshold. This is known as STM tip-induced electron-induced desorption (ESD) for single-molecule desorption. Different parameters such as bias and tunneling current are essential for a successful event (removal of single vanadyl group). Based on hundreds of statistics, the correlations were determined and presented in section 6.2.

The thesis ends with a summary section – Chapter 7. This chapter presents a general discussion about the most exciting results regarding the whole work and provides some supplementary information. The presented results provide the basic idea of the growth mechanism, the relation between the structure (morphology, thickness, etc.) and properties, showing that these oxide/metal systems are of great potential for model studies in the future.

1.2. Ultrathin iron oxide films

As a metal element, iron and its compounds can be used to make magnets, medicines, inks, etc. Iron is one of the so-called 'ferrous metals' since its surface is often covered with a layer of black tetroxide. Iron in its oxide form has various states, where 2+ and 3+ states are the most common ones, making the naturally-formed iron oxides are, i.e. FeO (wüstite), Fe₃O₄ (magnetite) and α -Fe₂O₃ (hematite)^[13], the corresponding crystal structures are shown in Figures 1.2.1 (a - c). FeO adopts the cubic, rock-salt structure, and it is constructed in a way that iron cations are octahedrally coordinated by oxygen anions and the oxygen anions octahedrally coordinated by iron atoms. The bulk form of FeO usually exists as black (powder) solid, which can be easily oxidized to magnetite when heated in the air. Fe₃O₄ is crystallized in a cubic inverse spinel group structure. In Fe₃O₄, iron contains both valence states with ratio of Fe²⁺ : Fe²⁺ =1:2. Fe₃O₄ can be represented as a compound composed of FeO and Fe₂O₃. It is constructed by a cubic close-packed array of oxide ions where all Fe^{2+} ions occupy half of the octahedral sites, while the Fe^{3+} is distributed evenly on the other half of the octahedral sites and the tetrahedral sites. The bulk form of Fe_3O_4 presents as a black crystal, which can be easily oxidized to Fe₂O₃ in the moist air. α -Fe₂O₃ has a rhombohedral corundum structure, which is constructed by nearly hexagonal close-packed oxygen anions, where the Fe^{3+} species in the interstitials are arranged in distorted octahedra and form two sublayers. α -Fe₂O₃ is often used as catalyst and raw material for crude iron by reacting to CO or H₂

at high temperatures (HT).



Figure 1.2.1. Crystal structure of bulk (a) FeO(111); (b) $Fe_3O_4(111)$; (c) $Fe_2O_3(0001)$, with Fe termination (Figure 1 from [14]). Simplified side view of (d) bulk FeO structure and (e) ultrathin FeO film grown on Pt(111), with O termination. Pt atoms are represented by grey balls, while iron and oxygen ions are represented by yellow and blue balls. The surface layers are marked by red rectangles.

Due to low dimensionality and strong interaction with the underlying support, ultrathin films exhibit different structural parameters, as shown in **Figures 1.2.1 (d)** and **(e)**. While the lattice constant of bulk FeO is 3.06 Å^[15], the ultrathin FeO layer grown on Pt(111) is extended to 3.11 Å^[16]. The in-plane strain can result in a reduction of Fe-O interlayer spacing from 1.25 Å (bulk) to 0.65 Å (ultrathin film grown on Pt(111) substrate)^[17]. Moreover, some interesting physicochemical properties arise within the ultrathin form, which is not observed for their bulk counterparts. As mentioned before, ultrathin FeO films on Pt(111) exhibit not only high catalytic activity towards CO oxidation^{[18][19]}, but also unique electronic and magnetic properties^{[20][21][22]}. The catalytic activity is strongly connect to the transformation of the oxide to an O-rich "FeO₂" phase under strongly oxidizing conditions^{[27][267]}.

1.2.1. Ultrathin iron oxide films on Ru(0001)

The structure of iron oxides grown on Ru(0001) has been studied and characterized by a few groups. Depending on the growth method, small variation of iron oxide structures and phases can be obtained. One of the growth methods for FeO(111)/Ru(0001) is Fe deposition followed by oxidation under moderate oxygen pressure ($5 \times 10^{-7} \sim 1 \times 10^{-6}$ mbar) between 800 and 900 K^{[23][24][25]}. An alternative preparation method is to deposit Fe in an oxygen ambient onto a heated substrate^[26]. A typical LEED pattern of FeO on Ru(0001) is shown in **Figure 1.2.2 (e)**. Sharp and intense (1×1) spots originate from the Ru(0001) substrate, the (2×2) spots arise from O atoms adsorbed on the exposed substrate regions or, at higher iron oxide coverages(Fe amount exceeds 4 MLs), form Fe₃O₄(111)^[24]. The first-order diffraction spots of FeO(111) and Fe₃O₄(111) are indicated by triangles and circles. The distances to the main Ru(0001) beams are inversely proportional to the oxides lattice constants (bulk FeO(111): 3.06 Å; bulk Fe₃O₄(111): 6 Å). Reflexes



originating from multiple scattering due to the lattice mismatch between the Ru(0001) and FeO(111) are marked by crosses^[25].

Figure 1.2.2. Structure of ultrathin FeO(111) films grown on Ru(0001). (a) Large-scale STM image of 0.3 ML FeO (I = 0.3 nA, V = + 0.5 V, 300 × 300 nm²) and (b) the corresponding LEED pattern (60 eV). (c) Large-scale STM image of 0.8 ML FeO (I = 0.5 nA, V = + 0.5 V, 300 × 300 nm²) and (d) the corresponding LEED pattern (60 eV) (Figures 5(a)-(d) from [25]). (e) LEED pattern of a mixed FeO(111)/Fe₃O₄(111) film on Ru(0001) and the schematic rpresentation of beam contributions from different surface phases (Figure 3 from [25]). (f) Atomic resolution STM image of FeO(111) (I = 0.35 nA, V = - 0.1 V, 5 × 10 nm²). (g) STM image of FeO(111) Moiré superstructure (I = 0.3 nA, V = + 0.2 V, 1.6 × 3.5 nm) ((f) and (g) are Figures 11(b,c) from [25]). (h) A schematic model of FeO(111) on Ru(0001) showing the "7 on 8" coincidence structure (Figure 4 from [25]).

The STM images and LEED patterns of submonolayer FeO on Ru(0001) are shown in **Figures 1.2.2 (a - d)**. At a coverage of 0.3 ML, FeO forms hexagonally-shaped islands. When the coverage increases to 0.8 ML, the size of the islands increases and some of them coalesce. Due to the lattice mismatch between FeO and Ru, a Moiré superstructure with a periodicity of 21.6 Å is formed, as can be seen in Figure 1.2.2 (g). The surface lattice constant of FeO, measured on atomically-resolved STM images (Figure 1.2.2 (f)), is about 3.08 Å. This lattice constant is slightly expended with respect to bulk FeO (3.06 Å), which is caused by the adaptation of the oxide to the substrate

within a "7 on 8" unit cell (the coincidence of 7 FeO units on 8 Ru atoms), the corresponding model is shown in **Figure 1.2.2 (h)**^{[24][25]}. The LEED patterns of 0.3 ML and 0.8 ML FeO(111)/Ru(0001) are shown in **Figures 1.2.2 (b)** and **(d)**. The LEED patterns are usually used as a quick check for the oxide coverage. Only beyond 0.5 ML, the intensity of FeO spots and multiple scattering reflexes is high enough to be observed^[25].

The iron oxide prepared by the other method (depositing Fe in an oxygen ambient onto a heated substrate) may slightly modify the morphology of the surface structure. The obtained results are presented in **Figure 1.2.3**. Noticeably, by this approach, the oxygen pressure plays a crucial role in oxide growth. For example, the oxide will grow as a Fe-O monolayer (see **Figure 1.2.3 (a)**) when low oxygen pressure ($< 6.7 \times 10^{-8}$ mbar) is used, while the threshold pressure value for purely-bilayer growth is 9.3×10^{-7} mbar (see **Figure 1.2.3 (b)**)^[26]. If the pressure is within an intermediate-range, for example, 1.33×10^{-7} mbar, the islands will firstly grow in the form of a bilayer, but transfer to single-layer form when they expand. Other parameters, such as oxidation temperature, can lead to the formation of fewer but larger islands if it is high enough (> 910 K). Indeed, another approach (less commonly discussed) was also applied for iron oxide growth on Ru(0001), which is to use infrared pulsed laser desorption (IR-PLD) with an α -Fe₂O₃ target^[278]. The main advantage of this approach is that the films can grow up to 8 nm while still preserving the "FeO" stoichiometry.



Figure 1.2.3. STM images of ultrathin FeO films grown on Ru(0001) under two different O₂ pressures. (a) Monolayer FeO grown under low O₂ pressure of 6.7×10^{-8} mbar (I = 1.2 nA, V = + 1.6 V, 50 × 30 nm). (b) Bilayer FeO formed under moderate O₂ pressure of 9.3×10^{-7} mbar (I = 1.0 nA, V = + 2 V, 50 × 30 nm). The green dashed lines indicate the step edges of the Ru(0001) substrate. The white lines mark the height profiles shown below the images (Figure 5 from [26]).

1.2.2. FeO to FeO₂ transformation

As already mentioned, it has been demonstrated that monolayer FeO(111) film can grow in a well-ordered structure on Pt(111). The morphology of pristine FeO/Pt(111) is shown in **Figure 1.2.4 (a)**, revealing the presence of a Moiré superstructure with a periodicity of 25 Å (due to the ~9% lattice mismatch between FeO and Pt). The inset shows the corresponding LEED pattern with sharp reflexes, indicating a well-ordered structure. FeO/Pt(111) exhibits superior catalytic activity in low-temperature CO oxidation compare to bare Pt(111)^{[18][27]}. After 20 mbar O₂ exposure at 470

K for 10 min, a new oxide phase is obtained, as shown in **Figure 1.2.4 (c)**. The phase exhibits a $(\sqrt{3} \times \sqrt{3})$ R30° structure with respect to the initial FeO phase. A less intense LEED pattern is observed of this structure due to higher corrugation and lower degree of order^[29]. Moreover, adsorbates could be observed on the surface, which confirms the higher reactivity of this phase. **Figure 1.2.4 (b)** shows the comparison of CO₂ production curves for CO and O₂ ratios ranging from 0 to 5 at 450 K^[12]. From this figure, it is evident that the reactivity increases with increasing O₂ amount. It was proposed both experimentally^[18] and theoretically^[27] that the corresponding reaction mechanism is based on the initial structural transformation of FeO into an O₂-rich phase, which has a trilayer O-Fe-O/Pt structure with stoichiometry roughly denoted as FeO₂^{[28][29]}. The obtained O₂ desorption curves of the new O-rich phase is shown in **Figure 1.2.4 (d)**. Two strong desorption signals were found at around 840 K and 1190 K, where the latter is also observed for the FeO phase. Therefore, the desorption peak at 840 K is related to the surface O layer, which is responsible for the high catalytic activity in CO oxidation^[12].



Figure 1.2.4. Ultrathin iron oxide films on Pt(111). (a) STM image and LEED pattern (inset, 60 eV) of FeO/Pt(111) (I = 0.7 nA, V = + 0.5 V, 150 × 150 nm²) (Figure 1(a) from [29]). (b) CO₂ production over FeO/Pt(111) and clean Pt(111) at 450 K as function of the CO to O₂ ratio (Figure 1(a) from [12]). (c) STM image (I = 0.7 nA, V = + 1.0 V, 150 × 150 nm²) and LEED pattern (inset, 60 eV) of FeO₂/Pt(111) – formed by oxidation of sample prepared in (a) by exposing 20 mbar O₂ at 470 K for 10 min (Figure 1(b) from [29]). (d) Thermal desorption spectra of O₂ obtained for FeO and FeO₂ films, as well as the schematic models of the two oxide structures (Figure 1 (b) from [12]).

Similar oxide phase can also be obtained when exposing FeO film to NO^[30], NO₂ or atomic oxygen^[85]. The morphology of the new oxide phase is very similar to the one obtained by high-pressure molecular oxygen, by comparing **Figure 1.2.5 (a)** (atomic oxygen at RT)^[85] and **(b)** (high

pressure of molecular oxygen at elevated temperature)^[29]. A similar $\sqrt{3}$ structure along with the Moiré cells is observed. The spectroscopic comparison of NO₂-treated film to the one formed by high-pressure O₂ is shown in **Figures 1.2.5 (c-e)**. Four different components are fitted to O 1s: (I) metal oxide, as observed for pristine FeO; (II) OH groups (bright protrusions on STM images); (III) the O layer between Pt and Fe in the FeO₂ trilayer; (IV) surface O in FeO₂^[85]. The results reveal that there is no obvious composition variation of FeO₂ films obtained by different methods.



Figure 1.2.5. Ultrathin FeO₂ films obtained using different strong oxidants. (a) STM image of the FeO₂ trilayer formed by exposing FeO to atomic oxygen at RT and then flashing to 500 K (I = 0.2 nA, V = + 2.0 V, 10 × 10 nm²) (Figure 4 (b) from [85]). (b) STM image of FeO₂ trilayer formed by oxidizing FeO in 0.5 mbar O₂ at 350 K for 10 min (I = 0.7 nA, V = + 0.1 V, 50 × 50 nm²) (Figure 2 (b) from [29]). (c) XPS O1s spectra of FeO₂ obtained by oxidizing FeO in 0.6 mbar O₂ at 500 K (Figure 2 from [85]). (d) XPS O 1s spectra of FeO₂ obtained by exposing FeO to 550 L of NO₂ at RT (Figure 3 from [85]). (e) XPS O 1s spectra of a FeO film (Figure 3 from [85]).

When it comes to O-rich iron oxide on Ru(0001), very limited publication describe the structure following strong-oxidizing treatment^[31]. The pristine FeO is prepared by Fe deposition in 5×10^{-7} mbar O₂ onto a Ru(0001) substrate heated to 900 K. The low energy electron microscopy (LEEM) results show that following the completion of the FeO layer, triangular islands representing a different iron oxide phase start growing. Such an island can be seen in **Figure 1.2.6 (a)-A**, with the LEED pattern presented in **Figure 1.2.6 (a)-C**. The additional weak (2 × 2) spots and different satellite patterns indicate the possible formation of Fe₃O₄ (magnetite)^[32]. This is further confirmed by XPS, which shows a higher Fe³⁺/Fe²⁺ ratio (**Figure 1.2.6 (b)-B**). The wetting layer around the triangular island exhibits a satellite pattern as shown in **Figure 1.2.6 (a)-B**, which may originate from the Moiré superstructure of FeO (wüstite) on Ru(0001). The XPS spectrum is also virtually identical to that of FeO (**Figure 1.2.6 (b)-A**). The system was further oxidized by exposing 1×10^{-8} to 5×10^{-7} mbar of NO₂ at 500 K. New iron oxide phases appear after this oxidation, as shown in **Figure 1.2.6 (a)-D**. The LEED patterns of the wetting layer are shown in **Figure 1.2.6 (a)-E** and islands in **Figure 1.2.6 (a)-F**. Broader LEED beams indicate lower crystalline order. The wetting

layer shows a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ pattern, while the islands preserve the (2×2) feature but with additional $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ structure. XPS spectra indicate that in both cases, i.e. the wetting layer (**Figure 1.2.6 (b)-C**) and islands (**Figure 1.2.6 (b)-D**), NO₂ treatment leads to the appearance of iron mostly in Fe³⁺ states. Combined with other measurements, the triangular magnetite islands evolve to γ -Fe₂O₃ (maghemite), and the surrounding layer is converted to α -Fe₂O₃ (hematite).



Figure 1.2.6. Ultrathin iron oxide film grown on Ru(0001) before and after low pressure NO₂ exposure $(1 \times 10^{-8} \text{ to } 5 \times 10^{-7} \text{ mbar})$ at 500 K. (a) Real space LEEM image of iron oxide before (A) and after (D) NO₂ exposure (Energy: 3 eV and 19 eV, respectively). (B,C) show LEED patterns of wetting layer (B) and islands (C) taken from (A) (48 eV); (E,F) show LEED patterns of wetting layer (E) and islands (F) taken from (D) (30 eV). The field of view (FOV) is 4 µm (Figure 3 from [31]). (b) XPS Fe 2p spectra of wetting layer (A) and islands (B) before NO₂ oxidation; (C) wetting layer and (D) island after NO₂ oxidation (Figure 4 from [31])

1.3. Catalytic activity of ultrathin iron oxide films in CO oxidation

CO is an odorless toxic gas. It can be easily produced by imperfect combustion of carbon compounds and is one of the main environmental pollutants causing health problems^{[33][34]}. The gas can be neutralized through catalytic oxidation to CO₂. As CO oxidation is one of the simplest oxidation reactions, it is also used as a model reaction for testing catalytic materials that could find application in more complex oxidation reactions.

The most commonly used oxidation catalysts nowadays are noble metals^[35]. Due to this, noble metal single-crystals were intensively studied over the years, which was aimed at getting an understanding of the fundamental steps of catalytic oxidation reactions, and the key structural features of the catalyst that are important from the point of view of the reaction. CO oxidation was studied, for example, on Rh(111)^{[36][37][38][39]}, Au(111)^{[40][41][42][43][44]}, Ru(0001)^{[45][46][47][48]} and

 $Pt(111)^{[49][50][51][52][53]}$, etc. These studies focused on the reactivity dependence on the noble metal, the crystal facet, the CO and O₂ pressure, as well as the reaction temperature. However, using noble metals as catalysts in practical technologies is not only economically unjustified, but usually also requires relatively high temperatures (> 423 K for CO reduction^[54]).

In the past decade, it was shown that ultrathin iron oxide islands and films grown on metal single-crystal substrates exhibit much higher catalytic efficiency in the CO oxidation reaction than noble metals, with the well-studied systems being $FeO_x/Pt(111)^{[55][56][18][57][58][59][60][61][62]}$ and $FeO_x/Au(111)^{[63][19][64]}$. The reactivity relates to the structural flexibility of ultrathin iron oxides species, which may undergo reversible transformations under certain reaction conditions. It also depends on the single-crystal substrate used for oxide growth, as it defines their structure and electronic properties, as well as allows gases adsorption on its exposed areas. Even though there are several published works reporting the growth and structure of ultrathin FeO islands and films on $Ru(0001)^{[24][25][26]}$, there are no direct research on the catalytic activity of CO oxidation on $FeO_x/Ru(0001)$ system.

1.3.1. CO oxidation over different metal single-crystal substrates

As mentioned above, CO oxidation effectively occurs on several noble metals. In this section, I focus on the studies on CO oxidation on Pt(111), Au(111), Rh(111) and Ru(0001). The overview is aimed at determining the differences in reactions mechanisms. Information on the processes occurring on metal single-crystals, e.g., CO adsorption and diffusion or oxidation of the substrate under reactions conditions, contributes to the determination of the reaction mechanisms taking place in the case of metal oxide islands and films supported on these single-crystal substrates.

1. CO oxidation over Pt(111)

Exposing Pt(111) to molecular oxygen leads to O₂ dissociation, resulting in two weakly bound O atoms. The saturation coverage of O can reach 0.5 ML on Pt(111) at 400–600 K; however, only 0.25 ML is present at the surface and the rest in the subsurface region^[49]. When CO molecules – either also adsorbed or present in the gas phase - approach these oxygen atoms, react and form $CO_2^{[53]}$. Low-temperature CO adsorption can reach 0.5 ML coverage with a constant sticking coefficient. The coefficient significantly drops at higher coverages due to the decrease of chemisorbed energy of the compressed CO layer^[50]. In the case of co-adsorption, surface diffusion is another critical parameter, as CO molecules diffuse much slower on Pt(111) than, for example, on Rh(111) or Ru(0001)^[52]. The temperature of the substrate plays a key role in this reaction: higher temperature, on the one hand, reduces the sticking probability of CO and O2; on the other hand, increases the desorption rate of produced CO₂. The temperature programmed reaction (TPR) spectra in Figures 1.3.1 (a-c) shows the reaction of CO on O pre-adsorbed Pt(111) at various temperatures: from RT to 700 K. In the case of the RT exposure, all CO was found to react to CO₂. However, for the 700 K exposure, part of the CO was desorbed instead of forming CO₂. This means O and CO adsorbed on Pt substrate are not reacting to each other at high temperatures. Such abnormal behavior indicates that part of O is not involved in CO reaction at elevated temperature. Therefore, it is believed that these additional O atoms are stored underneath the Pt top layer^[49]. Another report also shows that different condition towards a O-covered Pt(111)can vary the

reactivity towards CO oxidation. The O 1s XPS spectra of the p (2 × 2) O structure in **Figures 1.3.1** (d) and (e) show the main peak located at 529.88 eV. After CO dosing at low temperature and pressure (100 K, $P_{CO} = 4.4 \times 10^{-9}$ mbar), only a small peak at 532.88 eV arises, which corresponds to CO adsorption at on-top positions^[65]. For the case of higher temperature and pressure (275 K, $P_{CO} = 1.3 \times 10^{-6}$ mbar), the main O 1s peak decreases (indicating reaction) and a third peak arises at 530.93 eV (CO bridge site adsorption)^[66]. No clear peak at 530.93 eV at lower temperature is observed, indicating the O block the adsorption of CO on bridge site. The reduction of O-related peak indicates CO oxidation in the latter case. More systematic studies show that the reaction temperatures are between 275 K to 305 K (higher temperature is not tested). Within the temperature scale, a sudden drop of the O coverage and fast increase of CO on bridge sites can be observed after the CO exposure at high pressure (> 1.3 × 10^{-6} mbar)^[66].



Figure 1.3.1. TPR measurements of (a) O₂ (thin line: without CO; bald line: with CO); (b) CO₂; (c) CO. Heating rate: 4 K/s. (Figure 6 from [49]). (d) XPS O 1s spectra obtained during the reaction at 100 K, $P_{CO} = 4.4 \times 10^{-9}$ mbar, the time difference between neighboring spectra: 13 s; (e) O 1s spectra recorded during the reaction at 275 K, $P_{CO} = 1.3 \times 10^{-6}$ mbar, the time difference between neighboring spectra: 5 s. Bald line: pure O(2 × 2) adlayer on Pt(111) (Figure 1 from [66]).

2. CO oxidation over Au(111)

It was shown that CO oxidation can occur at low temperatures on an O-covered Au(111) surface, and the CO₂ production highly depends on the O coverage. The infrared spectra show no vibrational modes related to CO adsorption, indicating that CO reacts directly with adsorbed atomic oxygen and forms $CO_2^{[44]}$. The CO₂ production rate for CO reacting with O atoms on Au(111) adsorbed at 200 and 400 K is shown in **Figure 1.3.2 (a)**. For both temperatures, the reaction rate increases with increasing O coverage up to 0.5 ML, with the sample stay at 200 K having higher reactivity than the 400 K one. This is related to the formation of a chemisorbed O at low coverage at 200 K, which exhibits high reactivity towards CO. Higher coverage results in increased contribution from bulk gold oxide, which is inert towards reaction with CO. At 400 K, the formation of large gold oxide islands suppresses the reactivity^[43]. O₂ exposure at 77 K leads to similar results as the 200 K, with the critical coverage of 0.5 ML^[40] (**Figure 1.3.2 (b)**). Additionally, water can act as a promoter of CO oxidation on Au(111)^{[41][42]}.



Figure 1.3.2. (a) CO_2 desorption rate (normalized to the total area of CO_2 desorption profile from mass spectrometer during 300 s) as a function of oxygen coverage. The oxygen exposure was carried out at two different temperatures: 200 and 400 K (Figure 2 from [40]). (b) Quadrupole mass spectrometer (QMS) of CO_2 signal recorded when exposing samples with various O coverages (formed by exposing Au(111) to O_2 at 77 K) to CO (Figure 2 from [43]).

3. CO oxidation over Rh(111)

The reaction of CO with O_2 on Rh(111) critically depends on the reaction temperature. Using low dosage (60 L) at RT, O_2 dissociatively adsorbs on Rh(111), forming (2 × 1) domains rotated with respect to each other by 120° (Figure 1.3.3 (a)). This arrangement corresponds to a coverage of 0.5 ML. Following the exposure to 2 L of CO at 220 K, a new structure - denoted as (2×2) -2O+CO – is formed (Figure 1.3.3 (b)). In that structure, CO molecules are incorporated into the O domains, forming a (2×2) structure (the bright features visible on STM images are assigned to adsorbed CO molecules)^{[67][68]}. Annealing of such a system at 325 K in UHV leads to the lowering of the concentration of bright features (Figure 1.3.3 (c)), indicating the decrease in CO coverage^[36]. The XPS O 1s spectra, obtained after exposure of Rh(111) to pure CO and O_2 at RT, or to mixtures of both gases at higher temperatures, are displayed in Figure 1.3.3 (d). After O_2 adsorption, a peak centered at 528.7 eV appears, while for CO, the position is 530.8 eV. The studies revealed that the structure formed by chemisorbed O atoms is critical for reactivity. For the preadsorbed (2×1) -O adlayer (0.5 ML), the residual oxygen coverage and CO₂ yield does not change significantly with increasing CO exposure (at both 300 K and 350 K), as shown in Figures 1.3.3 (e) and $(f)^{[36]}$. This indicates that the reactive O species or sites for CO oxidation are fully consumed by 5 L of CO, with the rest of oxygen stay in some other or mixed phase^[36]. Moreover, CO can be oxidized by (9×9) -O reconstruction^[69], surface RhO₂^[70] and other surface oxygen species on Rh(111)^[71]. Therefore, the coverage-dependent surface structure/oxide phase, together with the reaction temperature, determine the reactivity of Rh(111) towards CO oxidation.



Figure 1.3.3. STM image of (a) (2×1) –O structure on Rh(111) formed by exposing the surface to 60 L of O₂ at 300 K (I = -0.61 nA, V = -0.108 V, 15×15 nm²), (b) (2×2) –2O + CO formed after exposing (2×1) –O/Rh(111) to 2 L of CO at 220 K (I = 0.18 nA, V = +0.84 V, 15×15 nm²), and (c) after additional annealing at 325 K in UHV (I = 0.256 nA, V = +0.69 V, 15×15 nm²) ((a), (b), (c) are Figures 5 (A), (B), (C) from [36]). (d) XPS O 1s spectra of clean Rh(111) at 300 K, after exposure to 1.33×10^{-7} mbar of CO and O₂, and after exposure to 6.65×10^{-8} mbar CO and 1.33×10^{-8} mbar O₂ at various temperatures (Figure 4 from [37]). (e) Residual oxygen coverage after CO exposures at 300 K and 350 K. (f) CO₂ yield after CO exposures at 300 K and 350 K ((e) and (f) are Figures 4(C) and (D) from [36]).

4. CO oxidation over Ru(0001)

On Ru(0001), dissociated O atoms may form different structures depending on the coverage^[72]. At low O₂ pressures, the p(2 × 2) phase is formed (corresponding to a coverage of 0.25 ML)^[73]. At intermediate pressure, the (2 × 1)–O structure with three domains (rotated by 120° with respect to each other) appears (0.5 ML coverage)^[47]. Strong oxidation will initially lead to the formation of a (2 × 2)–3O structure (0.75 ML coverage)^[74] and eventually to a (1 × 1)–O adlayer (1 ML, higher coverage in the subsurface region also show (1 × 1) symmetry)^[47]. The oxygen desorption spectra taken after exposing 10⁴ L CO to (2 × 1)–O and the (1 × 1)–O adlayer structures at various temperatures on Ru(0001) are shown in **Figures 1.3.4 (a)** and **(b)**. Obviously, less oxygen is left by increased sample temperature^[47], indicating the mean probability of CO₂ production increase with the temperature. Exposing the (2 × 1)–O structure to CO at temperatures lower than 400 K will only result in CO adsorption on Ru(0001) and no reaction with O atoms to form CO₂^[75]. In the case of the (1 × 1) phase, the reaction already occurs at 275 K. CO molecules adsorb at the vacancies in

the (1×1) -O network and react with O atoms. The removal of O leaves more vacancies for CO molecules and thus, the reaction proceeds. Notably, the temperature should be optimized by allowing sufficient residence time of CO, as well as to overcome the activation barrier of the reaction at the same time^[47]. Figure 1.3.4 (c) shows the reactivity towards CO oxidation on both (2×1) -O and (1×1) -O structures. Below 450 K, the reaction probabilities are almost identical for both structures, this might indicate the defects (independent from O coverage and O-Ru bonds) on the surface are critical for low-temperature CO oxidation. Above 500 K, (1×1) -O exhibits higher reactivity, the drop at 750 K is believed to be the depletion of the overall oxygen by heating.



Figure 1.3.4. Thermal desorption spectra of oxygen taken after exposing 10^4 L CO at various temperature on (a) (2×1) –O covered Ru(0001) surface (formed by 30 L O₂ exposure) (Figure 2 from [47]) and (b) (1×1) –O pre-covered Ru(0001) surface (formed by additional 15 L NO₂) (Figure 3 from [47]). (c) Integral CO reaction rates in terms of the averaged CO/CO₂ conversion probabilities for the (2×1) –O and (1×1) –O precovered Ru(0001) surfaces as function of the sample temperature. (d) PEEM images showing the evolution of the (1×1) –O covered Ru(0001) (stripes, $0\Delta t$) during exposure to 10^{-6} mbar CO at 600 K for $4\Delta t$ and $8\Delta t$ ($\Delta t = 33$ s). (e) Intensity profiles taken across the region marked A-A' in (d) Normalized CO₂ yield as a function of the reaction temperature. (f) Integral intensity of the stripes as a function of the CO exposure ((d - f) are Figure 4 from [48]).

More intense oxidation can lead to the coexistence of (1×1) –O structure with oxygen incorporated into the subsurface region of the substrate, which later acts as nucleation centers for surface Ru_xO_y that appear as hexagonal stripes on photoemission electron microscopy (PEEM) images (**Figure 1.3.4 (d)**). By introducing CO at elevated temperature, the amount of oxygen incorporated in the stripe structure can be depleted, as can be seen from the series of images, as well as the intensity profiles taken across one of the stripes (**Figure 1.3.4 (e)**). This indicates that the reaction homogeneously depletes the stripes. **Figure 1.3.4 (f)** shows the change integral

intensity of a particular stripe during CO exposure time. The initial increase is due to the resident time of CO, and soon a steep depletion indicating the reaction. Above 150 L CO exposure, the depletion speed slows down due to the low O coverage. Therefore, the Ru_xO_y phase contains active oxygen species to promote CO oxidation^[48]. Very similar results were reported in Ref. [45], the oxygen-rich film was formed by introducing very-high O₂ pressure (10⁻² mbar). It was found that during the transition phase, the boundary of two oxygen species – amorphous surface oxide (formed below 500 K) and ordered RuO_2 (formed above 500 K, while near 500 K starts with nucleation) – are the most reactive region, since the temperature for highest CO oxidation rate for the structure lies between 500 – 600 K.

1.3.2. CO oxidation over ultrathin iron oxide islands and films

Transition metal oxides (TMOs) are one of the most important materials in the catalytic field, especially when it comes to oxidation catalysis. Many catalytic systems rely on noble metal particles supported on TMO, with the oxide either playing a purely stabilizing role or taking part in the process. One of the effects that may appear in such systems is the so-called strong metalsupport interaction (SMSI)^[76], which manifests itself by encapsulation of supported noble metal nanoparticles with a reduced phase of supporting oxide under reaction conditions. The process usually suppresses the catalytic activity of the system, however, in some cases, the oxide species appearing on metal particles may take part in the reaction. Such systems, characterized by active oxide nanoparticles on metals, are called the "inverse" catalysts due to the inverse configuration compared to conventional catalysts^[77]. In model catalytic studies, the structure of conventional catalysts can be mimicked by depositing noble metal nanoparticles onto oxide support (usually a thin oxide film grown on a metal single-crystal substrate). "Inverse" catalysts, on the other hand, are usually modeled by growing metal-oxide species on metal single-crystal substrates. However, unlike metal deposits on oxide supports, TMO deposits on metal substrates usually grow in the form of islands/flakes (mono- or bilayer) instead of nanoparticles/clusters^[78]. Thus, the catalytic properties may be influenced by the size of the islands and their surface coverage. At present, model studies on "inverse" catalysts constitute a very active research field. Here, I only briefly review the studies performed on ultrathin iron oxide islands and films, as these constitute the basis for the interpretation of the obtained results.

1. CO oxidation over FeO_x/Pt(111)

FeO(111) films grown on Pt(111) exhibit superior catalytic activity in the low-temperature CO oxidation reaction compared to clean Pt(111)^{[18][27]}. The activity is related to the transition of chemically-inert FeO layer to an O-rich phase with an O-Fe-O structure (denoted as FeO₂, FeO_{2-x}, FeO_x in the literature – here I use FeO₂ for clarity) under strongly-oxidizing conditions (millibar O₂ pressure), followed by the reaction of CO with weakly-bound O atoms (as described previously). In submonolayer FeO coverage, CO₂ production is mainly assigned to the reaction at the oxide/support boundary, with the highest production rate observed for 0.4 ML FeO coverage^[55]. Interestingly, the experiments performed at low temperatures (5 and 78 K) showed that CO molecules bind strongly to exposed Pt(111) at 5 K but do not absorb on FeO. They become mobile at 78 K and react with O atoms present at the FeO_x edges^[58]. A similar conclusion was drawn from theoretical calculation, which confirmed that the Pt-Fe species present at the perimeter of FeO

islands act as active sites for CO oxidation and H₂O dissociation^[56]. A more recent study showed that under reaction conditions, the reaction takes place at the interface between the FeO/Pt or FeO₂/Pt phases^{[55][57][79]}, and Pt only promotes the formation of such boundaries instead of being involved directly in the reaction. To better understand the mechanisms, one may separate the procedure of exposing the catalyst to a CO + O₂ mixture to the subsequent exposure to each of these gases.

The structure of the FeO_2 is shown in Figure 1.3.5 (a). The surface layer is composed of regularly-arranged patches, which is related to the difference in FeO \rightarrow FeO₂ transformation probability in different high-symmetry regions of the Moiré superstructure of FeO/Pt(111)^{[85][80]}. Inset to (a) displays a zoom-in image of a single FeO_2 island, revealing that these patches are incomplete at the island edges^[57]. STM images obtained after exposure to CO at 450 K, shown in Figure 1.3.5 (b) and inset to the figure, reveal that the CO-induced reduction of the patches takes place from the edge of the island, transforming the structure back to a FeO(111)-like (with the interior region of the island remains intact). The percentage of regions representing the FeO₂ phase decreases with increasing CO reaction time, as shown in Figure 1.3.5 (c). DFT calculations indicate that the FeO/Pt boundaries, where O₂ dissociation takes place, host weakly bounded oxygen (WBO). However, oxygen is even more weakly bound at the FeO_2/FeO interface^[12]. In Ref. [57], the authors suggest a CO reaction pathway: (i) CO adsorbs on Pt(111), diffuses to the edge of the FeO/Pt islands, takes O away and desorb as CO₂; (ii) Fe atoms then relax and bind to Pt, terminates the reaction pathway of CO/Pt(111); (iii) new (main) reaction pathway now includes CO reaction with O atoms at the FeO₂/FeO interface. The XPS Fe $2p_{3/2}$ and O 1s spectra, shown in Figures 1.3.5 (d) and (e), confirms that the catalytic cycle maybe then continued by reoxidation (III, V) and repeat CO reaction (IV, VI).



Figure 1.3.5. (a) STM image showing FeO₂ islands on Pt(111) (I = 0.1 nA, V = -3 V, 150 × 150 nm²). The corresponding schematic of the structure is shown below (side view; Figure 1(a) from [57]). (b) STM image of sample prepared in (a) after exposure to 10⁻⁶ mbar CO at 450 K for 2 min (I = 0.1 nA, V = -3 V, 150 × 150 nm²) (Figure 1(b) from [57]). (c) The dependence of the amount of FeO₂ phase on the CO exposure time (Figure 1(e) from [57]). (d) XPS Fe 2p3/2 and (e) O 1s spectra obtained for (I) clean Pt(111), (II) 0.5 ML FeO/Pt(111), (III) after high pressure O₂ reaction at 563 K and (IV) after CO reduction at 450 K. (V) and (VI) correspond to the repeated steps (III) and (IV) (Figure 6(a) and (b) from [59]).

2. CO oxidation over FeO_x/Au(111)

FeO islands grown on Au(111) also exhibit enhanced catalytic activity in low-temperature CO oxidation. Similarly to FeO/Pt(111), the activity is related to the transition of pristine FeO to an oxygen-rich "FeO₂" phase. The STM images of both phases are shown in **Figures 1.3.6 (a)** and **(d)**, respectively. Well-defined FeO(111) islands on Au(111) are usually characterized by hexagonal shapes with alternating long and short edges. Upon strong oxidation, dislocation lines appear at the surface, which is accompanied by the formation of domains that appear bright on STM images^[81]. The LEED pattern obtained for the pristine sample (**Figure 1.3.6 (b**)) displays FeO(111) – (1×1) spots, as well as satellites reflexes related to the presence of a Moiré superstructure. Following the oxidation, weaker and broader spots can be observed (**Figure 1.3.6 (e**)). The spacing between the Au spots and the iron oxide spots slightly decreases (see the insets to figures **(b)** and **(e)**). This indicates smaller lattice constant of the FeO₂ phase compared to pristine FeO^[19].

The reactivity curves obtained for FeO-covered Au(111) are shown in **Figure 1.3.6 (c)**. Clearly, the promotional effect of the oxide slows down after a certain time/CO amount. When taking into consideration only the initial stage of the reaction, it was found that 1.0 ML FeO shows much higher CO_2 production^[19]. Fe₂O₃ islands on Au(111) was also studied and the highest activity was obtained at the coverage of 0.4 ML^[82]. In order to compare the reactivity of different iron oxides, they plotted the activity of FeO/Au(111), Fe₃O₄/Au(111), and Fe₂O₃/Au(111) – all with 0.4 ML coverage (**Figure 1.3.6 (f)**). At the initial stage of the reaction, FeO exhibits the highest catalytic activity, however, it partially converts to Fe₃O₄ in the course of the reaction. DFT calculations show that Fe₂O₃ is not stable under reaction conditions and undergoes reduction (in contrast to FeO, which undergoes oxidation). Therefore, Fe₃O₄/Au(111) seems to be the only active phase that is stable under reaction conditions. This is related to the strong interaction between Fe₃O₄ and the Au(111) substrate^[63]. Notably, compared to Pt(111), Au(111) exhibits very weak CO adsorption^[83]. Thus, the results reveal that even an oxide grown on "inert" metal support may promote the reaction through internal structural transformations^[19]. Due to the limited number of studies, the exact mechanism of CO oxidation over iron oxide islands on Au(111) is still under debate.



Figure 1.3.6. (a) STM image showing FeO islands grown on Au(111) ($40 \times 40 \text{ nm}^2$) (Figure 2(a) from [81]). (b) LEED pattern of 1.0 ML FeO(111)/Au(111) sample (60 eV) (Figure 3(a) from [19]).

(c) CO₂ production curves obtained for pristine FeO(111)/Au(111) and clean Au(111) (50 mbar O₂ and 10 mbar CO at 480 K; Figure 2(a) from [19]). (d) STM image of sample (a) after oxidation in 10^{-3} mbar O₂ at RT (40 × 40 nm²) (Figure 2(b) from [81]). (e) LEED pattern of sample (b) after exposure to 20 mbar O₂ at 480 K for 10 min (60 eV) (Figure 3(b) from [19]). (f) Initial reaction rate for CO oxidation over 0.4 ML FeO/Au(111), Fe₃O₄/Au(111) and Fe₂O₃/Au(111) (6.65 mbar CO and 6.65 mbar O₂ at 575 K; Figure 3 from [63]).

3. CO oxidation over FeO/Ru(0001)

Up to now, there are no studies on CO oxidation over FeO/Ru(0001). There is only one theoretical publication concerning CO adsorption on Au adatoms on FeO/Ru(0001)^[84]. As the structure of FeO on Ru(0001) is different from the one on Pt(111) and Au(111), studies on this particular support could shed more light on the crucial structural parameter that drives the reactivity of supported ultrathin iron oxide islands.

1.4. Iron oxide films grown on Ag substrates

Ultrathin iron oxide layers can grow on Ag(100) (and the equivalent facet Ag(001)) and Ag(111). Where the mismatch between FeO (3.06 Å) and Pt (2.77 Å) is 9%, resulting in a coincident structure with a periodicity of about 25 Å^[85], which significantly increases the structural complexity. For Ag(111) substrate, the small mismatch (Ag: 2.89 Å) can promote iron oxide growth and reduce the structure complexity.

The structure of iron oxide grown Ag(100) exhibits a few forms depending on different preparation conditions^{[86][87][88]}. As shown in Figure 1.4.1, the structure becomes more complicated if the coverage increases. Monolayer of FeO(111) on Ag(100) was prepared by depositing Fe in 2 \times 10⁻⁷ mbar O₂ pressure at 373 K, followed by UHV annealing at 673 K for 2 min. Within this coverage regime, the surface features are shown in Figure 1.4.1 (a), line defects appear along domain boundaries, and FeO(100) also grows in the form of few-atomic-rows islands. Those islands integrate into small islands at the 2 ML coverage (by depositing 2 ML Fe in 2×10^{-7} mbar O₂ pressure at 638 K), as shown in Figure 1.4.1 (b). Multilayer starts forming on small islands at higher coverage at 3 ML (by depositing Fe in 2×10^{-7} mbar O₂ pressure at 623 K), the obtained STM image is shown in Figure 1.4.1 (c). In particular, the oxidation temperature of 573 K is the key to grow a well-defined FeO(100) and FeO(111) structure. However, high temperatures above 673 K can result in a very rough surface which might be caused by Ag diffusion^[87]. Noticeably, at low temperatures like 373 K, FeO(100) is unlikely to be formed even the coverage is higher than 2 ML^[88]. Moreover, higher oxygen pressure can significantly promote multilayer formation even at low coverage (0.5 ML)^[88]. For oxide grows in a few monolayer regimes^{[87][88]}, a few types of structures can be observed: (i) FeO(111) monolayer; (ii) line defects, with four symmetrically equivalent domains; (iii) rectangular FeO(100) islands; (iv) multilayers of iron oxide denoted as FeO_x or Fe₂O₃-like structure. For thicker layers, well-defined bulk-like FeO or Fe₃O₄ species can be observed on the surface, and the ratio of FeO/Fe₃O₄ depends on the coverage and condition^[86].



Figure 1.4.1. STM images of iron oxides grown on Ag(100). (a) A nearly complete FeO(111) monolayer with visible domain boundaries (I = 0.5 nA, V = + 0.1 V, $130 \times 130 \text{ nm}^2$) (Figure 3(a) from [88]). (b) Coexistence of FeO(111) islands and smaller distribution of rectangular FeO(100) pits and islands, with domain boundaries (I = 1.0 nA, V = + 1.5 V, $200 \times 200 \text{ nm}^2$) (Figure 8(a) from [88]). (c) A few iron oxide phases including FeO(111), FeO(100), domain boundaries and multilayer Fe₂O₃-like structure ($170 \times 170 \text{ nm}^2$) (edited from Figure 4.3 from [87]),

The structures of iron oxide grown on equivalent facet Ag(001) shows similar relation as on Ag(100)^{[89][90][91][92]}. For thick layers (22 monolayers in the reported paper), a well-defined FeO(001) is formed with a small concentration of Fe₃O₄ grown underneath^[89]. At relative thin film regime, where iron oxide was prepared by iron deposition (0.5 ML for **Figure 1.4.2 (a)** and 2 ML for **Figure 1.4.2 (b)**) in 1×10^{-5} mbar O₂ pressure at 573 K. Both multilayer and reconstructed Fe₃O₄ structure start forming at higher coverage^[90], resulting in the coexistence. While FeO(001) is still resolvable at 3 ML coverage, poorly-ordered Fe₃O₄ only appears at higher coverage^[92] or using stronger oxidation condition^[90]. Iron oxide prepared by depositing Fe at RT, followed by two steps of oxidation process is shown in **Figure 1.4.2 (c)** (1ML) and **(d)** (5ML). In principle, the first approach (depositing iron in oxygen pressure) can form a more ordered oxide structure compare to the latter case (depositing iron with post oxidation), and there is a small contradictory structure analysis between the work of ^{[90][91]} and ^[92] regarding the final Fe₃O₄ structure.



Figure 1.4.2. STM images of iron oxide grown on Ag(001) by different approaches. (a) 0.5 ML FeO(111) consists of two domains indicated by A and B with 90° rotation with respect to each other, D represents some defects and domain boundaries labeled by DB (I = 0.4 nA, V = + 2.15 V, 120 × 120 nm²) (Figure 5 from [91]). (b) 2 ML FeO overlayer with undulations (I = 0.8 nA, V = + 1.0 V, 50 × 50 nm²) (Figure 5.45 (c1) from [90]). (c) 1ML FeO (I = 0.1 nA, V = + 2.1 V, 50 × 50 nm²) (Figure 4 (a) from [92]) (d) Wavelike-structure 5ML Fe₃O₄ with a $\sqrt{2} \times \sqrt{2}R45^{\circ}$ reconstruction (I = 0.1 nA, V = + 1.0 V, 50 × 50 nm²) (Figure 5 (a) from [92])

The reports regarding the structural studies of the FeO/Ag(111)^{[15][93][94][95][96][97]} are

sometimes contradictory to each other. In addition, only one report analyzed the detailed atomic structure by STM ^[97]. The iron oxide was generally prepared by two methods: (i) depositing iron under oxygen pressure or (ii) depositing iron in vacuum with post oxidation. Repeating cycles of (i) or (ii) are used to achieve thicker layers to obtain a more homogeneous film.

Unlike the case on Ag(001), the oxide structures formed on Ag(111) by approach (i) are often poorly ordered compared to approach (ii) for relatively thick layers^[15]. Oxidation at high temperatures may improve the ordering^[96]. Therefore, approach (ii) is applied in most studies. For relative thick layers (>10 Å)^{[15][93][94][95]}, the surface structure exhibits a mixed phase of Fe₃O₄ and Fe₂O₃, in some reports, people simply denoted the mixed-phase by FeO_x (confirmed by techniques like LEEM, XPS, etc.). Additional oxidation at higher pressure is the key to transit Fe₃O₄ to Fe₂O₃ film (Ref. [93] suggests higher temperature while Ref. [94][95] hold a different opinion of using slightly lower temperature). Fe₂O₃ can reduce back to Fe₃O₄ on Ag(111) by vacuum annealing^{[93][94][95]}. FeO(110) is also reported to grow on Ag(111) at coverage of 6 ML^[98].

Within the monolayer regime, which is of interest in this work, FeO(111) dominates but shows contradictory results^{[15][96][97]}. Compared to the LEED pattern of clean Ag(111) (**Figure 1.4.3 (a)**), the LEED pattern of 5 Å FeO grown by RT-iron deposition on Ag(111) shows a splitting feature (**Figure 1.4.3 (b)**), suggesting the small lattice difference and FeO film adopted the (111) orientation^[15]. A different structure can be obtained if the iron oxide is prepared by depositing iron onto a heated substrate in oxygen pressure, as shown in **Figures 1.4.3 (c)** and (d). While a similar splitting beam feature is observed from the LEED pattern, additional higher-order diffraction spots with less intensity appear – these satellites imply the existence of Moiré superstructure^[96]. The model of such structure is constructed based on structural parameters obtained from LEED and STM data, as shown in **Figure 1.4.3 (e)**^[97]. It suggests a $p(9 \times 9)$ coincidence structure with the FeO lattice expanded to 3.25 Å (i.e. by ~7%).



Figure 1.4.3. Iron oxide films grown on Ag(111). LEED pattern (70 eV) of (a) clean Ag(111) and (b) 5 Å FeO grown on Ag(111) (using approach (i), Figure 5(a) and (b) from [15]). (c) LEED pattern (120 eV) of monolayer FeO(111) (using approach (ii), Figure 2(a) from [96]); (d) Atomically-

resolved STM image of sample prepared in (c) and corresponding LEED pattern (40 eV) of 0.4 ML FeO(111) (I = 0.8 nA, V = -0.08 V, 5.7×5.7 nm²) (Figure 1(b) from [97]). (e) Ball models of the FeO(111) monolayer on Ag(111) based on the results obtained from (c) and (d).

1.5. Ultrathin vanadium oxide films

Vanadium is a d-transition metal with an electron configuration [Ar] $3d^34s^2$. It has five removable valence electrons and therefore it can adopt multiple oxidation states, from V²⁺ to V^{5+[99]}. Due to the complex valence structure of vanadium, it can combine with oxygen to form a variety of oxides and mixed phases. There are many types of vanadium oxide, including VO, V₂O₃, VO₂, V₂O₅, etc. VO adopts a distorted NaCl structure and forms gray powder under ambient conditions (including high temperatures). V₂O₃ has the corundum structure and exists as a gray-black crystal or powder. It slowly absorbs oxygen in the air and transforms into vanadium tetroxide (V₂O₄) and burns when heated in air^[100]. VO₂ is a dark blue crystalline powder that exhibits a distinct phase transition at 340 K. While it has a monoclinic crystal structure below the critical temperature^[101], the structure turns tetragonal above that temperature, like in rutile TiO₂^[102]. V₂O₅ has orthorhombic structure and usually exists as a red-brown crystalline powder or gray-black flakes. This type of oxide is widely used as a catalyst in chemical industry^[103].

With the development of surface science technology, various vanadium oxide nanostructures have been successfully prepared and investigated on different substrates, including single- crystals, like Pd(111)^{[104][105]}, Rh(111)^{[106][107][108]}, Pt(111)^{[109][110][111]}, Au(111)^{[112][113][114][115]} and W(110)^[116], as well as on oxide supports, such as TiO₂(110)^{[117][118][119]} and α -Al₂O₃(0001)^{[120][121]}. They exhibit many unique properties, such as metal-insulator transitions and unusual magnetic properties^[122]. Moreover, they can serve as a model system for catalytic studies, particularly when it comes to oxidation reactions, such as CO^{[123][124][125][126]} or SO₂^{[127][128][129]} oxidation.

To better understand the structure of VO_x on Ru(0001), I discuss here the literature describing similar films on other close-packed metal single-crystal substrates, in particular the fcc(111), as there are no reports on the growth of such films on hcp(0001) metal subastrates.

1. Ultrathin vanadium oxide films on Pt(111)

Vanadium oxide on Pt(111) grows in layer-by-layer mode and the surface structure is highlydependent on the coverage and preparation method^[111]. Vanadium deposited onto Pt(111) at room temperature in H₂O atmosphere (1×10^{-7} Pa) forms VO(111)-like structures^[110]. For V deposition at RT and subsequent oxidation at 623 K in O₂ pressure of 1.33×10^{-7} mbar, a (1×1) LEED pattern is observed for coverages up to 0.5 ML, as can be seen from **Figure 1.5.1 (a)**, with the film suggested to have a O=VO_x/Pt (x = 0~3) structure^[111], as shown in **Figure 1.5.1 (b)**. The model structure of **d** (isolated O=VO₃ species) in (**b**) is usually called the nanopyramid. A complete monolayer represents a well-ordered (2×2) V₂O₃ structure ^{[109][111]}, with the suggested structural model shown in **Figure 1.5.1 (b)** resembling the stacking arrangement of O-V/Pt (also called surface-V₂O₃ or s-V₂O₃). When the thickness exceeds one monolayer, more complicate structures are observed. At 2 ML, a O-V-V-O/Pt arrangement seems to be preferred (additional layer grown on s-V₂O₃ is not energetically-favorable based on DFT calculations^[130] and the obtained LEED result shows a $(3\sqrt{3} \times 6)$ pattern^[111]). Above 2 ML, the oxide is believed to be terminated by V=O species (vanadyl groups), resulting in a O=V-O-V-V-O/Pt stacking configuration. The oxidation states of vanadium in this structure are V²⁺ or V³⁺, while higher oxidation states require higher oxygen pressures and temperatures^[111].



Figure 1.5.1. (a) LEED patterns of ultrathin VO_x films on Pt(111) with different coverage (Figure 3 from [111]). **(b)** Structure models (side-view) for the VOx/Pt(111) at coverages of 0.3–0.5 ML (Figure 4 (A) from [111]). **(c)** Top and side view of a structural model of $V_2O_3/Pt(111)$ (Figure 2(c) from [109]).

2. Ultrathin vanadium oxide films on Au(111)

A similar preparation method, i.e. deposition of V at RT and post oxidation in 1×10^{-7} Torr O₂ pressure at 800-1000 K, applied to Au(111) leads to the formation of an ordered ($\sqrt{3} \times \sqrt{3}$) R30°-V₂O₃ film^[112]. The corresponding LEED pattern can be seen in **Figure 1.5.2 (a)**. Well-ordered V₂O₃(0001) films were also prepared by vanadium deposition in a background O₂ pressure of 1×10^{-7} mbar, followed by 700 K oxidation under oxygen pressure of 5×10^{-8} mbar. For thicker layers (LEED pattern of such structure is shown in **Figure 1.5.2 (b)**), the vanadium oxide film seems to feature a V=O terminated surface^[113]. Similar to the case on Pt(111), higher O₂ pressure (50 mbar) results in higher oxidation states of vanadium (V₂O₅)^{[114][115]}.



Figure 1.5.2. LEED patterns of ultrathin VO_x films on Au(111). (a) A ($\sqrt{3} \times \sqrt{3}$) R30° -V₂O₃ film, with the circles marking the Au(111) beams and crosses diffraction spots orginiating from V₂O₃

(modified Figure 3(b) from [112]). (b) well-defined $V_2O_3(0001)$ film (Figure 1(b) from [113]).

3. Ultrathin vanadium oxide films on Pd(111)

Compared to VO_x films grown on other single-crystal supports, those on Pd(111) are particularly well-studied, both experimentally and theoretically. For the vanadium oxide prepared by V deposition at substrate temperature of 523 K under 2×10^{-7} mbar O₂ and cooling down to room temperature in oxygen, multiple structures are observed. At submonolayer coverage, a hexagonal surface structure with a periodicity of ~11.0 Å and height of ~ 2.0 Å is observed, which corresponds to a (4 × 4) structure (lattice constant of Pd is 2.75 Å)^{[104][105]}. The results of DFT calculations indicate that it represents the V₅O₁₄ phase, with the simulated STM images based on the proposed model being identical to the experimentally observed ones^{[131][105]}. The (4 × 4)-V₅O₁₄ structure, shown in **Figures 1.5.3 (a - c)**, can be reduced to (2 × 2)-V₂O₃ either by vacuum annealing or H₂ pressure exposure^[104]. Such s-V₂O₃ is identical to the one observed on Pt(111).

The (2×2) –V₂O₃ can be further transformed into a zigzag stripe-like structure by vacuum annealing at 300°C, shown in **Figure 1.5.3 (d)**. Such structure exhibits a corrugation of ~ 1 Å due to the presence of bright features located at the zigzag corners (sitting on top of the corner atoms). These bright features likely represent vanadyl species^[104]. DFT calculations showed that such a structure has a V₆O₁₄ stoichiometry, which is more compared to the V₅O₁₄ phase^[131]. The proposed model is shown in **Figure 1.5.3 (f)**, while the simulated STM image is presented in the inset to **Figure 1.5.3 (e)**.



Figure 1.5.3. Ultrathin vanadium oxide structures grown on Pd(111) at submonolayer range: (a) STM image showing the coexistence of (4×4) and (2×2) structures (I = 0.02 nA, V = + 1.5 V, 20 $\times 20 \text{ nm}^2$) (Figure 1(c) from [104]). (b) An atomically resolved STM image of a (4×4) structure. The inset display the simulation image based on the model shown in (c) (Figure 2(a) from [131]). (c) shows the DFT model of the (4×4) structure – the V₅O₁₄ (Figure 2(b) from [131]). (d) STM image of the zigzag oxide stripe phase (I = 1.0 nA, V = + 0.1 V, 9 \times 9 nm², Figure 9(a) from [104]). (e) Atomically-resolved STM images of the zigzag structure. The inset shows the simulated image based on the model presented in (f) (Figure 2(c) from [131]). (f) DFT model of zigzag structure –

the V_6O_{14} (Figure 2(d) from [131]).

In the monolayer range, vanadium oxide films on Pd(111) exhibit a relatively complicate structure. As shown in Figures 1.5.4 (a) and (d), in addition to the islands representing the zigzag V₆O₁₄ structure (marked as "D" in the figure), three other structures are observed (marked as "A", "B" and "C"). Islands "A" are rectangular and grow on top of the s-V₂O₃ (2 \times 2) structure, with an overall height of 4.0 Å^[104]. The theoretically determined structural model (only the rectangular islands on top) is shown in Figure 1.5.4 (f). The composition is found to be VO_2 , with octahedral V coordination (denoted as VO₂-rect^[130]). Type "B" islands are generally flat (with negligible corrugation), having a height of about 3.0 Å. When it comes to the atomic arrangement, a hexagonal structure with a periodicity of ~2.8 Å was observed on a Fourier-transform of a STM image (not shown here), with a lattice constant similar to that of the substrate (i.e. corresponding to a (1×1) structure^[104]. The model of this structure, called VO₂-hex, is shown Figure 1.5.4 (e). The configuration is similar to the case of VO_2 -rect but with octahedral O coordination^[130]. The calculations show that the VO₂-hex is not very stable and prone to transform to the "C"-type structure, which is composed of a layer similar to s-V₂O₃ on top of VO₂-hex, with a total height of 5.0 Å. The structure of $4(VO_2-hex)/s-V_2O_3$ (V₆O₁₁ stoichiometry) is much more complex, with differently coordinated V atoms^[104]. The proposed structural model of this structure is presented in Figures 1.5.4 (b) and (c). For thicker layers, more structures appear, e.g. an ordered ($\sqrt{3} \times \sqrt{3}$) $R30^{\circ}-V_2O_3$ bulk-like phase^[104], the formation of which was also observed on Au(111)^[112].



Figure 1.5.4. Monolayer vanadium oxide films grown on Pd(111). (a) Large-scale STM image showing four structurally-different regions: A – the VO₂-rect; B – the VO₂-hex; C – the V₆O₁₁; D - the zigzag V₆O₁₄ (I = 0.7 nA, V = + 0.7 V, 40 × 40 nm²) (Figure 4 (d) from [104]). (b) and (c) show top- and side-view of the structural model of type-C islands (V₆O₁₁), respectively (Figure 3(e) from [130]). (d) STM image showing both type-A islands (VO₂-rect) and type-B islands (VO₂-hex) (I = 1.0 nA V = + 0.7 V, 20 × 20 nm²); Figure 8(a) from [130]). (e) and (f) show structural models of type-B islands (VO₂-hex) (modified Figure 3(a) from [130]) and type-A islands (VO₂-rect) (modified Figure 3(b) from [130]), respectively.

4. Ultrathin vanadium oxide films on Rh(111)

Three different preparation procedures are reported for ultrathin VO_x films on Rh(111): (i) V deposition at elevated substrate temperature in an oxygen ambient^{[106][108][126][123]}; (ii) room temperature V deposition followed by oxidation^{[106][126]} and (iii) V deposition onto a O-covered Rh(111) substrate followed by brief annealing in UHV^[107]. Both (i) and (ii) are finalized by cooling the sample down in oxygen. The most commonly used method is (i). By using higher substrate temperature (for example 673 K), a more ordered structure can be obtained. In general, vanadium oxide starts growing at the regular terrace sites and nucleate at the substrate step edges only at higher coverages^[106]. In the submonolayer regime, for coverages less or equal to 0.6 ML, two different structures, shown in Figure 1.5.5 (a), can be formed depending on the oxidation conditions^[106]: (i) higher oxygen pressure and temperature results in the formation of a $\sqrt{13} \times \sqrt{13}$ R13.8° V_6O_{18} phase, the calculated model of which is shown in Figure 1.5.5 (c); (ii) under mild oxidizing conditions, the $\sqrt{7} \times \sqrt{7}$ R19.1° V₃O₉ phase forms. Its theoretical model is presented in Figure 1.5.5 (b). Most model studies on the catalytic oxidation of CO (both theoretical and experimental^{[123][126]}) considered this model. At higher coverages, vanadium oxide islands start nucleating at the step edges of the substrate, forming a structure with a lattice constant of ~ 2.9 Å and a Moiré pattern with ~30.5 Å periodicity^[106] (corresponding to a slightly expanded VO₂-hex structure – labeled "A" in Figure 1.5.5 (d). The model of the Moiré superstructure, originating from the lattice constant mismatch between VO₂-hex and Rh (2.69 Å), is shown in Figure 1.5.5 (f). Another structure forming at the regular terrace sites, called the "oblique" phase and marked "B", is similar to the zigzag structure observed on Pd(111)^[106]. The atomically-resolved image of this phase is shown in Figure 1.5.5 (e) and the bright protruisons are assigned to vanadyl groups.



Figure 1.5.5. Ultrathin vanadium oxide structures grown on Rh(111) using method (i) (see the text for details). (a) STM image of a vanadium oxide islands (sample with 0.25 ML surface coverage) consisting of two structures: $\sqrt{7} \times \sqrt{7}$ R19.1° V₃O₉ phase and the $\sqrt{13} \times \sqrt{13}$ R13.8° V₆O₁₈ phase (I = 0.1 nA, V = + 0.69 V, 10 × 10 nm²) (Figure 4(a) from [106]). (b) Theoretical model of the $\sqrt{7} \times \sqrt{7}$ R19.1° V₃O₉ structure (Figure 7(c) from [106]). (c) Theoretical model of the $\sqrt{13} \times \sqrt{13}$ R13.8° V₆O₁₈ structure (Figure 7(d) from [106]). (d) STM image obtained for higher surface coverage (0.7 ML) showing two types of regions: the phase with a Moiré pattern (marked A) and the "oblique" oxide phase (B) (I = 0.1 nA, V = + 2.0 V, 50 × 50 nm²) (Figure 8(a) from [106]). (e) Atomically-

resolved STM image of type-B region (I = 0.1 nA, V = +2.0 V, 15 × 15 nm²) The inset displays an atomically-resolved STM image of the internal hexagonal unit-cell structure of the Moiré pattern (I = 1.5 nA, V = +0.025 V, 5 × 5 nm²) (Figure 8(b) from [106]). (f) Proposed model of the moiré structure visible on type-A regions (Figure 8(d) from [106]).

Thicker vanadium oxide films grown on Rh(111) are characterized by different surface structures. Monolayer vanadium oxide consists of four structures, as shown in Figure 1.5.6 (a): (i) (2×2) precursor of the bulk V₂O₃ structure – formed by V-O double layer on VO₂-hex; (ii) ($\sqrt{3} \times$ $\sqrt{3}$ R30° reconstruction, its atomic corrugation is superimposed on the large-scale modulation of the Moiré superstructure; (iii) the phase exhibiting a Moiré superstructure (growing at the substrate step edge); (iv) wagon-wheel structure^{[106][104]}. The atomically-resolved wagon-wheel structure is shown in Figure 1.5.6 (b), with the hexagonal unit cell consisting of a dark protrusion in the center surrounded by six bright features. The unit cell of this structure, marked as "A", can be described as (7×7) R21.8°^[106]. For much thicker vanadium oxide layers (10.0 ML, using 523 K oxidation temperature), a hexagonal bulk-like $V_2O_3(0001)$ structure is formed (Figure 1.5.6 (c)). Higher temperature either during oxidation(673 K)^[106] or vacuum post-annealing leads to the formation of a vanadyl-terminated (1×1) V₂O₃ structure^[108]. The V=O terminated film can be either oxidized to oxygen-rich vanadium using strong oxidation conditions (5 \times 10⁻⁶ mbar, 773 K), resembling a $(\sqrt{3} \times \sqrt{3})$ R30° V₂O₃ structure showed in Figure 1.5.6 (d), or reduced to vanadium-rich film by adding metallic vanadium at room temperature and flashing to 823 K. The latter phase is characterized by a flat and smooth surface^[108] (Figure 1.5.6 (f)).



Figure 1.5.6. Monolayer and thicker vanadium oxide films grown on Rh(111) using method (i) (see the text for details). (a) STM image of 1.0 ML vanadium oxide with four visible structures (I = 0.1 nA, V = + 1.8 V, 20 × 20 nm²) (Figure 10(a) from [106]). (b) Atomically-resolved imgae of the wagon-wheel structure (I = 0.1 nA, V = + 0.1 V, 10 nm²) (Figure 10(c) from [106]). (c) STM image of 10.0-ML-thick vanadium oxide film prepared in 2×10^{-7} mbar O₂ at 523 K and having a bulk-like hexagonal V₂O₃(0001) structure (I = 0.25 nA, V = + 1.25 V, 10 × 10 nm²) (Figure 11(b) from [106]). (d) STM image of a thick (~10 nm) vanadium oxide film subjected to UHV annealing at 673 K exhibiting a vanadyl-terminated (1 × 1) V₂O₃ structure (I = 0.05 nA, V = + 1.0 V, 20 nm²) (Figure
5(a) from [108]). (e) shows (d) after exposure to 1000 L of oxygen (d), which leads to the formation of an O-rich ($\sqrt{3} \times \sqrt{3}$) R30° V₂O₃ structure (I = 0.05 nA, V = + 1.0 V, 20 × 20 nm²) (Figure 5(d) from [108]). (f) presents a V-rich V₂O₃ structure obtained by depositing additional 0.6 ML V onto vanadyl-terminated (1 × 1) V₂O₃ structure, followed by short flash at 723 K (I = 0.2 nA, V = + 1.5 V, 100 × 100 nm²) (Figure 8(c) from [108]).

A completely different structure is obtained when preparation method (iii) is used. Figure 1.5.7 (a) shows a STM image of the as-prepared sample, revealing the presence of a rectangularshape ($5 \times 3\sqrt{3}$) structure. The corresponding model is presented in Figure 1.5.7 (c). The overall stoichiometry is V₁₃O₂₁, with a central VO₃ unit surrounded by six V₂O₃ groups^[107]. Such structure collapses and forms a planar flower-like structure following additional oxidation. This structure is displayed in Figure 1.5.7 (b), with an atomically-resolved image presented in Figure 1.5.7 (d). The model of this structure presented in Figure 1.5.7 (e) indicating the V₆O₁₂ symmetry. Interestingly, the oxide "flowers" can diffuse on the surface during vacuum annealing, even at relative low temperature (383 K).



Figure 1.5.7. Monolayer vanadium oxide film grown on Rh(111) using method (iii) (see the text for details). (a) STM image showing the $(5 \times 3\sqrt{3})$ -rect structure (I = 0.1 nA, V = + 2.0 V, 150×150 nm²) (Figure 1(a) from [107]). (b) shows the film from (a) after additional oxidation in 5×10^{-8} mbar O₂ at 383 K, when the structure decomposes into a 2D flower-like oxide clusters (I = 0.1 nA, V = + 1.0 V, 20 × 20 nm²) (Figure 2(a) from [107]). (c) presents the calculated model of the structure shown in (a), resembling the V₁₃O₂₁ phase (Figure 1(c) from [107]). (d) shows atomically-resolved image of the structure presented in (b) (I = 0.1 nA, V = + 0.5 V, 6.3 × 6.3 nm²). The inset shows simulated STM image based on the model shown in (e) (Figure 5(b) from [107]). (c) presents the model of structure shown in (b) and (d), resembling the V₆O₁₂ phase (Figure 5(d) from [107]).

1.6. STM induced electron stimulated desorption (ESD)

Desorption of molecular species through an electron stimulated mechanism, which is known as electron stimulated desorption (ESD), is of wide interest for surface scientists since few decades^{[132][133][134][135]}. In ESD, energetic electrons are directed towards adsorbed atoms or molecules, causing electronic excitation of these ad-species. The excitation further causes the desorption of ions, metastables or neutrals from surface^[136]. In general, ESD can provide information on the chemical and physical properties of adsorbed species, which is of importance for both fundamental studies and practical usages in many fields. By studying the nature and dynamical behaviour of the desorbed species, it is possible to determine the desorption mechanism.

The non-thermal desorption behaviour utilized in ESD can be understood as an electronadsorbate interaction and, based on the number of electrons involved in an isolated event, it can be divided into a single-electron scheme and many-electron process. The first model was developed by Menzel, Gomer and Redhead, thus it is known as the MGR mechanism^{[137][138]}. Considering an absorbate (A) and substrate (M) system, the corresponding energy diagram is schematized in Figure 1.6.1 (a). This mechanism includes a Frank-Condon transition in an adsorbate-substrate system from an initial ground state (M + A) to excited states, which including three possibilities: (i) antibonding $((M + A)^{a})$, electrons are placed into the antibonding orbitals), (ii) metastable $((M + A)^{a})$ A)*, an intermediate state within a dynamical system), and (iii) ionic ($(M^- + A^+)$, loss or gain of electrons)^[135]. A further developed model, describing the ESD of physisorbed layers and based on the MGR model, is called the Antoniewicz mechanism^{[135][139]}, the most simple case is to describe a neutral particle desorption. From the ground state (M + A) to an ionic $(M + A^{+})$ state via vertical FC transition is shown in Figure 1.6.1 (b). In this model, the adsorbate interacts with the incident electron, becomes positively ionized and attracted to the surface due to image charge potential. When the distance is smaller than the critical value, the ionized species is reneutralized by substrate electrons (higher tunneling probability), and repelled from the substrate through a Pauli repulsion as a neutral particle^[135]. This mechanism also involves a more complex two-electron process (not shown here). An alternative idea is that the energetic electrons excite the vibrational states, creating a cascading transition through a series of levels from initial to final state, which is referred to as ladder climbing of vibrational states in the binding potential^[140], as shown in Figure 1.6.1 (c). Certainly, more mechanisms can be found in the literature, also applying to field of photostimulated desorption, which finds applications in photo-chemistry and photo-catalysis^{[141][142]}.



Figure 1.6.1. (a) Schematic diagram of nuclear motion of desorbing species in the MGR picture,

crossings represent tunneling and Auger de-excitation and reneutralization process (Figure 2 from [135]). (b) Illustration of neutral-particle desorption in the Antoniewicz picture (Figure 4 from [135]). (c) Illustration representation (based on the system of O_2 on Pt(111)) showing the mechanism of vibrational excitation and dissociative attachment via electron capture. (1) FC transition from A₂ (ground state of the neutral molecule) to A₂⁻ (ionic state), and then (2) propagation of the nuclear wavepacket over the potential energy surface of the negative ion, followed (3) vibrational excitation by reneutralization or (4) dissociation (Figure 1 from [134]).

The theory of ESD was further developed when it was found that desorption of adsorbed species can be stimulated locally by electrons tunneling from the STM-tip. The main advantage of such approach is the fine control of both the location and the electron energy, which enables single adsorbates desorption. The first example found in literature is from 1995 and concerns the hydrogen desorption from the hydrogen-terminated Si(100) substrate^{[143][144][145]}, the results are shwon in Figure 6.1.2. In principle, two desorption mechanisms occur in this system. At the high energy regime (using sample bias higher than threshold bias of ~ 6 V, as shown in Figure 6.1.2 (a)), the desorption corresponds to a direct electronic transition by σ - σ ^{*} excitation of the Si-H bond. In particular, the attached electron in σ^* (Si-H) orbital will give a negative ion resonance. When electron leaves to the surface, part of its energy transfer to the Si-H bond^[144]. If the electron energy is lower than the electronic excitation threshold, as shown in Figure 6.1.2 (b), the desorption yield was several orders of magnitude lower, showing a power law relation as function of tunneling current. This dependence was explained by a vibrational excitation (heating) induced by the desorption of attached electron to σ^* (Si-H) orbital, where a few electrons were needed since one electron only provide a portion of energy to the Si-H bond. This vibrational heating effect may relate to the high current densities in STM and provides a potential way of controlling surface functionalization, such as STM induced lithography, nanofabrication, single particle reaction, etc. The STM tip-induced desorption of hydrogen from H terminated Si(100) was also observed at a negative bias^[146], where elastic tunneling of holes into Si-H 5σ induces a hole resonance, which causes inelastic scattering and further leads to vibrational heating of hydrogen. Such a desorption process is also considered as a many-electron pathway.



Figure 1.6.2. STM tip-induced desorption of H atoms from $Si(100) - (2 \times 1)$ surface. (a) H atom desorption yield as function of the sample bias with I = 0.01 nA (Figure 7 from [144]). (b) H atom desorption yields at the incident electron energies below the electronic transition threshold (~ 6.5 V). The curves predict the truncated harmonic oscillator model of multiple vibrational excitations.

The inelastic fractions f_{in} obtained from fitting to the data are given next to the curves (Figure 9 from [144]).

Certainly, STM tip-induced ESD is not limited to Si-H systems, as it was also used for a selective bond breaking in the system of chemisorbed O_2 species on oxidized Si(111)-(7×7) substrate^[147]. Excitation involves the capture of electrons and relaxation to the negative ion state, followed by emission of electrons which leads to the formation of an excited vibrational state. When the excitation exceeds the binding energy, the desorption process starts. A similar molecular excitation via ladder-climbing of vibrational states was reported to induce the dissociation of single O₂ molecules bound to Pt(111)^[148]. The dissociation rate as function of voltage and tunneling current (with one, two or three electrons being involved in the event of O_2 dissociation at 0.4, 0.3 and 0.2 V, respectively) indicates that such dissociation is induced by intermolecular vibrational excitation, which is caused by inelastic electron tunneling. Comparable experiments (desorption rate as a function of current and bias for both polarities) were also performed for chlorobenzene from Si(111)-(7×7) substrate^[149]. Accompanying DFT calculations, revealed that such desorption process is caused by the population of negative/positive ion resonance in chemisorbed species by tunneling electrons/holes. All the works described above interpreted the mechanism of STM tipinduced single adsorbate desorption either as a result of direct tunneling from bonding states or into antibonding states, or ladder climbing via inelastically tunneling electrons. A later work based on an STM study on CO desorption from Cu(111)^[150] combined these two interpretations into a twostep scheme: firstly, an electron tunnels into the CO $2\pi^*$ antibonding orbital and populates a longlived negative ion resonance. In the next step, vibrational excitations of the CO-Cu molecule are excited as the hot electron is transferred into the Cu from CO $2\pi^*$ orbital. The excitation of vibrational modes breaks the CO-Cu bond and results in CO desorption from Cu(111). This mechanism was confirmed both experimentally and theoretically.

Even though many similar ESD works were published for gas molecules on silicon and metal substrates, the process is most relevant for oxides from the viewpoint of photocatalysis. So far, only one example of STM tip-induced ESD from an oxide surface, i.e. hydrogen desorption from rutile $TiO_2(110)-(1\times1)$, has been reported^[151]. The mechanism was understood as the H atoms transfer from the TiO_2 substrate to STM tip via vibrational heating of the surface O-H group, which requires tunneling of either one or two inelastic electrons. Interestingly, the surface density and structure of adsorbed species can be controlled by the precise removal (using positive bias) and redeposition (negative bias) of H atoms.

2. Materials and methods

2.1. The basics of surface science studies

The focus of surface and thin film science is to connect the structure and physicochemical properties (electronic, magnetic, catalytic, etc.). For research purposes, it is essential to provide a stable environment for keeping surface features for a relatively long time (even small contamination may change the intrinsic properties of the films). This goal has been fulfilled since the late 1950s thanks to the new UHV technology being developed and widely used^[152]. The ultrahigh vacuum provides an ideal environment for thin film growth and maintenance. It also allowed many modern probing spectroscopes to be developed soon afterward, which provided huge progress on surface science studies.

In general, the UHV condition requires a pressure lower than 10⁻⁹ mbar. This is crucial for keeping a sample for sufficient time from contamination. The idea is based on the Hertz-Knudsen equation^[153]:

$$F = \frac{\alpha P}{\sqrt{2\pi m k_B T}} , (2.1.1)$$

where *F* is the incidence molecular flux (in m⁻²·s⁻¹), α is the sticking coefficient (from 0 to 1), *P* is the pressure (in Pa), *m* is the molecular mass (in kg·mol⁻¹), *T* is the temperature (in K) and k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K). The single crystal often used in today's UHV chamber contains about 10¹⁵ atoms at the surface (roughly estimated to 1 cm²). If the sample needs to be kept clean for 1 hour for the further experiment, by equation (2.1.1), assuming sticking coefficient as 0.1, with pure N₂ pressure at room temperate (300 K), the preferred pressure is in the range of low 10⁻⁹ mbar (1 mbar = 100 Pa).

A typical modern UHV chamber is made of stainless steel and usually consists of a few types of equipment: (i) pumping system, including different types of pumps and pressure gauges to keep and monitor vacuum pressure; (ii) manipulator (with sample stage) and wobble stick, which is used to move or transfer the sample to the desired position; (iii) temperature control system (thermocouple, PID controller, pyrometer, etc.), in order to monitor and control the heating temperature; (iv) apparatus and facilities for sample preparation and examination.

There are a few types of pumps used for the UHV chambers. The most common pumps are rough pumps, turbopumps, ion pumps and titanium sublimation pumps (TSPs). A rough pump is used to generate the pressure of around 10^{-2} mbar from the atmosphere stage. A turbopump can obtain and maintain the high vacuum regime (10^{-7} mbar). The ion pump ionizes the gas and accelerates them towards the electrode to improve the pressure. TSP is usually combined with an ion pump to improve the pumping efficiency by sublimating and coating clean titanium on the chamber wall. The pumping effect is related to the collision of the residual gas molecules with the

coated chamber wall and the formation of a stable solid compound. A critical step for reaching a good-quality vacuum (lower than 10^{-8} mbar) is the bakeout process. It involves hours or even days of baking the chamber at a temperature above 373 K, thus, the water sticks on the equipment and inner wall of the chamber will be desorbed. Depending on the chamber condition, the pressure during baking can reach 10^{-7} or lower.

To prepare thin oxide films, a few instruments are required. For sputtering, the noble gas molecules (Ar, Ne, etc.) need to be ionized through a sputter gun, and these gas ions can bombard to the surface and remove impurity residuals. For heating, A sample stage is connected to high voltage and heating power allows sample heating (electron bombardment by applying high voltage in case to reach above 1000 K). For metal deposition, the most common equipment is E-beam evaporators (metal material is bombarded by electron beam and then evaporated to a gaseous state, precipitate into the solid when reaches the cold substrate). The evaporator often works together with a quartz crystal microbalance (QCM), which measures the mass variation within unit area and time, therefore, it helps to calibrate deposition rate. For a chemical reaction, a certain amount of gas has to be introduced through gas line systems (fine-control by a leak valve). A quadrupole mass spectrometer (QMS) is often placed in the UHV chamber to monitor the gas composition. Sometimes special equipment is installed to fulfill specific experimental needs, such as oxygen (atoms) beam source (OBS), which is used for cracking O₂ to atomic oxygen within a long noble metal capillary heating to 1773 K.

The analytical tools used for checking bulk materials are not applicable in surface science due to the small surface volume ratio (a typical cubic volume of 1 cm³ solid has $\sim 10^{23}$ atoms, but only contains $\sim 10^{15}$ atoms at the surface)^[154]. It is essential to use probes that interact with solid but penetrate only a few Angstroms inside to collect information only within the ultrathin film. In other words, increase probing sensitivity to discern surface atoms from bulk ones. A few options are currently used in modern UHV techniques, such as low-energy electrons, ions, photoelectrons (electrons excited by X-rays from their occupied electronic states), and so on. The penetration depth of those probes can vary depending on the initially applied energy. Therefore, the effect of layers just below the surface layer (the so-called subsurface layers) cannot be neglected. Some most widely used UHV probing systems will be discussed in detail in section 2.2.

Last but not the least, it is vital for modern surface sciences research to perform theoretical calculations (with complex and robust computational servers) to support the experimental findings. For an unknown system, only experimental data may not be sufficient to complete the story without theoretical model calculations, and perhaps a prediction of properties. Indeed, the calculation is a quite complex work, even for crystalline solid, the surface or interface calculation can be more complicated than expected. For example, loss of symmetry in the system will increase system complexity considerably.

2.2. Instrumentation and measurement techniques

The experiments described in this thesis were conducted in two different UHV laboratories. One is located at the NanoBioMedical Centre of Adam Mickiewicz University in Poznań, Poland. All the iron oxide experiments included in this work were performed there. As shown in Figure 2.2.1, the variable-temperature STM (VT-STM, Omicron) – originally present in the laboratory – was replaced with a LT-STM (CreaTec) in 2018. Thus, the results obtained before 2018 for ultrathin iron oxide films grown on Ag(111) (Chapter 5) were measured using VT-STM at RT, using a Wtip. The results of iron oxides on Ru(0001) were mainly measured using LT-STM (Chapter 3 and 4) at around 77 K (liquid nitrogen temperature), using a Pt80Ir20 tip. The base pressure in the UHV chamber located in Poznań is 5×10^{-10} mbar. The chamber is fully equipped with standard facilities for surface science studies and consists of three interconnected chambers: preparation chamber, STM chamber, and LoadLock chamber. The preparation chamber is designed for sample cleaning (cold cathode sputter gun, e-beam heating stage), oxide thin film growth (single electron beam evaporator, gas line, atomic oxygen source (OBS 40-A; Dr. Eberl MBE Komponenten), surface reaction and structural characterization (LEED, XPS). The STM chamber is equipped with VT-STM/LT-STM. The LoadLock chamber is mainly used for transferring samples and STM tips, or for high-pressure gas reactions.



Figure 2.2.1. The UHV chamber located at NBMC AMU in Poznań, Poland: (a) Equipped with a VT-STM before the year 2018; (b) Equipped with a liquid nitrogen-cooled LT-STM after 2018.

The other UHV laboratory is located at the Physics Department of the University of Oldenburg, Germany. All the experimental work related to vanadium oxide on Ru(0001) presented in this thesis was performed there. The UHV chamber (from CreaTec) is shown in **Figure 2.2.2**. The UHV chamber in Oldenburg also maintains a base pressure of 5×10^{-10} mbar and consists of a preparation chamber, STM chamber and LoadLock chamber. The preparation chamber is equipped with a hot cathode sputter gun, e-beam heating stage, dual electron beam evaporator, gas line, QCM and LEED. The STM chamber hosts a liquid-nitrogen-cooled STM equipped with a chemically etched Au tip.



Figure 2.2.2. The UHV chamber located at the University of Oldenburg, Germany.

All the STM images presented in this work were acquired in a constant current mode and processed with Gwyddion (http://gwyddion.net/) and WSxM (http://wsxm.es/download.html^[155]) computer software. The distances (heights, atomic periodicities, Moiré patterns, etc.) on each image were calibrated in the z-direction with respect to the height of a monoatomic step height on Ru(0001) (2.14 Å^[156]) or Ag(111) (2.40 Å^[157]), while in x- and y-direction with respect to the O(2×2) on Ru(0001) (5.33 Å^[158]) or Ag(111) surface lattice constant (2.89 Å^[159]). A lock-in amplifier was used for performing STS measurements. For dI/dz experiments on iron oxides on Ag(111), the applied modulation frequency was 6.777 kHz and the amplitude was set to 60 mV (corresponding to 0.1 nm z-piezo oscillation). For dI/dV experiments on vanadium oxide on Ru(0001), a frequency of 1.145 kHz and an amplitude of 14 mV were used.

The LEED patterns were recorded for energies ranging from 30 to 255 eV (depends on the system, 60 eV, 64 eV, and 100 eV are mainly shown in this work). For XPS measurements, a setup consisting of a channeltron-based hemispherical electron energy analyzer, a non-monochromatized AlK α (results obtained on Ru(0001)) or a monochromatic AlK α X-ray source (results obtained on Ag(111)) was used. All the spectra were recorded with a pass energy of 20 eV (regions) or 50 eV (survey). All data were fitted using CasaXPS (http://www.casaxps.com/) and further processed with the OriginPro software (https://www.originlab.com/). All the spectra were calibrated with respect to the peak position of the Ru 3d5/2 peak (280.0 eV^[160]) or Ag 3d5/2 peak (368.2 eV^[161]). For the system of FeO/Ag(111)), Fe 2p spectra were fitted by a linear combination of Gauss and Lorentz functions (GL) and Shirley background subtraction were used. For the system of FeO_x/Ru(0001), a GL(60) (with a weight of 60% Lorentzian) lineshape is applied to fit Fe 3p peak based on certain physical constraints^[279]. The peak lies in the vicinity of Ru 4p line, which was also included in the fitting in order to better reproduce the background and avoid fitting artefacts. The O 1s region was fitted by a GL(30) lineshape with linear background for both systems.

2.2.1. Scanning tunneling microscopy (STM)

Introduction

STM is a widely-used microscope that can image surfaces at the atomic level by scanning with a sharp probe. Thanks to the breakthroughs of wave-particle duality hypothesis^[162] and Schrödinger's wave equation^[163] in the early 1920s, the vacuum tunneling (the wave functions overlap and, therefore, the particle tunnels through a potential barrier) was predicted in 1928 by Fowler and Nordheim^[164]. The first STM was developed by Heinrich Rohrer and Gerd Bining in 1981^{[164][165]}. In the following year, their publication^[166] showed an atomically-resolved image of Si(111)-(7×7), which soon had a significant impact on the scientific community. For the invention of STM, Rohrer and Binnig were awarded the Nobel Prize in Physics in 1986^[167]. Nowadays, variant STMs have been built worldwide, operating in air or vacuum, at RT or low temperature (liquid nitrogen or liquid helium temperature), providing reliable results in many scientific fields.

Electron tunneling

In classical mechanics, for an electron with total energy of *E*, the probability of penetrating a potential energy barrier of V(V > E) is zero. However, such a 'passing through' phenomenon can be observed with a non-zero probability in quantum mechanics. Based on the wave-particle duality, for a given electron, its state can be described as a point static mass combined with its spreading wave function $\Psi(x, t)$ in the surrounding space, where $(x, t)|^2$ is defined as the probability of finding the electron at position x (only consider one-dimensional case) and time t. Mathematically, normalizing $|\Psi(x, t)|^2$ must equal to one:

$$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1, (2.2.1)$$

The wave function $\Psi(x, t)$ of an electron with mass *m* and moving along the *x*-direction can be solved by Schrödinger equation^[168]:

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + V\psi(x,t) = E\psi(x,t), (2.2.2)$$

where \hbar is the reduced Plank constant ($\hbar = \frac{h}{2\pi}$). Rewriting the formula (2.2.2) gives:

$$\frac{d^2\psi(x,t)}{dx^2} = \frac{2m(V-E)}{\hbar^2}\psi(x,t) = k^2\psi(x,t), (2.2.3)$$

where k is the tunneling constant, which is defined as:

$$k = \frac{\sqrt{2m(V-E)}}{\hbar} . (2.2.4)$$

Since the wave function is non-zero inside the barrier, therefore, a flux of electrons of energy E initially impinging on the left side of the potential barrier has a probability to be found on the right side. A rectangular potential barrier (with a width a) is illustrated in **Figure 2.2.1**. Within the

barrier (range from 0 to *a*), a higher potential height of U(x)=V and outside the barrier U(x)=0. If ka >> 1, the transmission probability *T* for this flux of electrons is given by^[169]:

$$T = \frac{16E(V-E)}{V^2} e^{-2ka}.$$
 (2.2.5)

The probability increases rapidly if the barrier width *a* is reduced from the formula (2.2.5). In particular, a simple example of this scenario can be represented by electrons tunnel between two conducting slabs with a spacing of *a*. Therefore, the tunneling current depends exponentially on the width of the gap. At low bias, electrons tunnel between the Fermi level of one slab to the other. The value (V - E) is, thus, considered as an equivalent of an average work function Φ (also called as "effective work function") of these two slabs^[169], the tunneling current *I* is estimated as:

$$I \sim e^{-2a\frac{\sqrt{2m\phi}}{\hbar}}.(2.2.6)$$

The equation (2.2.6) is the fundamental idea for the setup of the scanning tunneling microscope (consider one slab as tip and the other as sample). The effective work function for most systems is usually a few electronvolts and varies if the surface is inhomogeneous. Assuming Φ is 4 eV, increasing the tip-surface distance *a* from 0.8 nm to 1.0 nm, the tunneling current $I_{1.0}$ decrease to less than 1/6 of the initial current $I_{0.8}$. This highly sensitive dependence constitutes the basis for STM topographic imaging.



Figure.2.2.1. Illustration of the wave function of an electron with Energy E, tunnels through a rectangular potential barrier, with a potential height of V and width a.

STM operation

A schematic drawing of a STM scan head is shown in **Figure 2.2.2**. Typically, a scanner consists of a cylindrical tube made of piezoelectric materials. The outside of the piezoelectric tube is metal-coated in four electrodes. Applying voltages applied to a pair of the electrodes, induces strain to the tube and bends it along in x or y direction to achieve scanning motion. The inside of the tube is completely metal-coated, voltage applied to the inner surface can cause the tube to expand or contract, achieving vertical motion. A very sharp conducting tip (which, in an ideal case, has only one atom at the end) is driven by the piezo-scanner very close to the surface. If the tip-sample distance is sufficiently small, the wave functions of atoms at the tip and sample surface can overlap, allowing electrons "tunnel" through. During scanning, the tip moves horizontally and any



variation in the tip-sample distance results in a large change in the tunneling current.

Figure 2.2.2. A schematic diagram of a piezoelectric tube scanner placed above the sample's surface. The vacuum gap between tip and sample surface is *a*.

There are two main operational modes of STM^[170]. The most-used one is the constant current mode, as shown in **Figure 2.2.3** (a). In this mode, the tip-sample distance is constantly adjusted by the feedback mechanism to move the tip up/down to maintain a constant value of current. More specifically, a small voltage is applied between tip and specimen, the detected tunneling current is compared to the input value. The difference is then sent to a feedback control system which adjusts the voltage to the tube scanner to move the tip along the *z*-axis. The result reflects the topography of the surface. The other operational mode is the constant height mode, as shown in **Figure 2.2.3** (b). In this mode, the tip scans the surface without a feedback mechanism and the variations in the tunneling current value are recorded. In order to avoid tip crashes on the surface, constant height mode is often used for a flat surface to learn the surface heterogeneity by monitoring the variations of the effective work function.



Figure 2.2.3. Comparison of the two commonly used STM operational modes: (a) constant current mode and (b) constant height mode.

Experimental setup

All STM instruments include a few essential parts: (i) a sharp conductive tip; (2) a piezoelectric scanner; (iii) a vibration isolation system and (iv) supplementary electronics (data acquisition and display), as shown in **Figure 2.2.4**. Several methods can be used to make sharp tips, including cutting and grinding, electrochemical etching, etc. The tip is mounted on a piezoelectric tube scanner. Many designs were tested to isolate the STM scan heads from external noise (both electronic and mechanical). More recent designs used a spring damping system^[171]. The damped spring is made of a few identical springs to hang a suspension platform (where STM sits on). To minimize the external vibration, the resonance frequency of spring is preferred to be much less compared to the minimum resonance frequency of STM. Certainly, the optimized parameters (stiffness) of the springs are determined by the construction of a particular STM.



Figure 2.2.4. Schematic view of a basic STM setup.

STM can be performed under different conditions in various environments. It can operate in a vacuum chamber, inert gas atmosphere, air or even high-pressure environment. It can also operate at different temperatures. A VT-STM can cover a range from 15 K to 500 K (additional heating or cooling elements might be needed for such purpose)^[172], while a LT-STM is usually working at either 77 K (liquid nitrogen temperature) or 5 K (liquid helium temperature). LT-STMs are usually coupled to double-stage cryostats to keep stable low temperatures.

Interpretation of STM images

Two types of images can be obtained by STM using constant-current mode. The topographic image which depicted by the tip motion (which traces out the topography of the surface) and the current image, which reflects deviations of the tunneling current from a setpoint. Many factors can contribute to STM imaging, such as surface topography, the density of states (barrier height), and tunneling parameters (current setpoint, the bias applied between tip and sample (gap voltage), feedback loop gain, etc.). To obtain more reliable topographic information and reduce the effect from other factors, one possible way is to scan with different tunneling parameters and compare the resulting images.

A lot of information can be derived from topographic STM images. For example, FeO/Ru(0001) exhibits a Moiré superstructure, where the topographic and current images are shown in **Figures 2.2.5 (a)** and **(b)**. It is easy to determine the coverage, height, orientation, and atomic periodicity, etc., by using certain software. Certainly, reliable values of structural parameters should be determined by statistical data processing.



Figure 2.2.5. STM images of a bilayer FeO film on Ru(0001), exhibiting a Moiré superstructure: (a) topography image, (b) the corresponding current image (I = 0.7 nA, V = + 0.05 V, $20 \times 20 \text{ nm}^2$).

2.2.2. Scanning tunneling spectroscopy (STS)

Introduction

Scanning tunneling spectroscopy is a frequent-used extension of STM. As mentioned in the previous section, for a flat heterogeneous sample, the effective work function varies with the position, the STM images could reveal an apparent height variation due to the local density of states (LDOS). The dependence on the electronic structure makes STS a useful tool for studying surface electronic states. The relation between the tunneling current, the density of states, and the tipsample distance were based on J. Bardeen's work from 1960^[173]. Figure 2.2.6 shows the energy diagram of the tunnel junction. E_F is the vacuum level (refers to the energy of a free stationary electron in a perfect vacuum), ϕ , E_F , and ρ represent the work function, Fermi energy, and density of states (DOS), respectively. V is the voltage applied between the tip and the sample. As mentioned before, if the tip-sample distance a is small enough, their wavefunctions start to overlap and the probability of electrons tunnel between tip and sample becomes detectable. The Fermi levels of the tip and sample move with respect to each other by applying an external bias, resulting in an energy window between the tip and sample, thus, the tunneling current starts to flow. Using the modified Bardeen transfer Hamiltonian method to the STM^{[173][174][175]}, consider an electron initially in the unoccupied states with energy δ , and include spin degeneracy (multiply 2). After some reasonable assumption and simplification, the tunneling current I can be determined by:

$$I_{t} = \left(\frac{4\pi e}{\hbar}\right) \int_{0}^{eV} \rho_{t} (E_{F}^{t} - eV + \delta) \rho_{s} (E_{F}^{s} + \delta) e^{-2ka} d\delta .$$
(2.2.7)



Figure 2.2.6. Energy diagram of a STM tunnel junction

In many cases, the expression of tunneling current can be shortened by the integration of the transition coefficient T' and electron density ρ ^{[172][175]:}

$$I \propto \int_{0}^{e_{V}} \rho_{t}(E - eV) \rho_{s}(E) T'(E, eV, a, \phi) dE \quad . (2.2.8)$$

The $\rho(E)$ is the density of states of an electron at energy *E*. *T*' is the tunneling transmission probability which depends on energy states, the bias applied between the tip and sample *V*, as well as the tip-sample distance *a*, and thus, the tip and sample work functions can be estimated from the tunneling barrier height.

Experimental setup

STS requires a very stable temperature to minimize the thermal drift and increase the energy resolution. Therefore, LT-STMs are preferred for STS measurements. The most common type of a spectroscopy measurement is I-V curve, which can be easily done by locating the tip above the sample with a feedback control loop off (fixed tip-sample distance), if one increases the bias, the tunneling current increases since more electrons on sample and more empty states on tip become available for tunneling (as can be seen from **Figure 2.2.6**). An external lock-in amplifier is added to the basic setup of STM to attenuate external noises, which are comparable to spectroscopic signals, as shown in **Figure 2.2.7**.



Figure 2.2.7. Schematic view of a basic setup of STS setup with a lock-in amplifier.

The detailed working principle of a lock-in amplifier is shown in **Figure 2.2.8**^[176]. The input signal is amplified by the signal amplifier, where a reference signal is synchronized by a voltagecontrolled oscillator (VCO). The VCO contains a phase-shifting circuit that allows phase changing from 0 to 360° range. The amplified input signal and synchronized reference signal will be multiplied through a mathematical function at the phase sensitive detector (PSD, also known as the multiplier). For the example shown in **Figure 2.2.8**, the output from PSD is calculated as:

$$A_1 A_2 \sin(\omega_1 t + \varphi_1) \sin(\omega_2 t + \varphi_2)$$
, (2.2.9)

where A is the amplitude, ω is the angular frequency, t is time and φ is the initial phase.



Figure 2.2.8. Simple block diagram of a lock-in amplifier.

Using the principle of prosthaphaeresis, formula (2.2.9) can be rewritten as:

$$\frac{1}{2}A_1A_2\{\cos[(\omega_1 - \omega_2)t + (\varphi_1 - \varphi_2)] - \cos[(\omega_1 + \omega_2)t + (\varphi_1 + \varphi_2)]\}. (2.2.10)$$

The low-pass filter removes the signal with high frequency (high-frequency cutoff), which is the second *cos* part in equation (2.2.10). The DC amplifier only allows the zero frequency (which means $\Delta \omega = 0$) signal to be amplified and exported to the output. Therefore, the lock-in amplifier "locked" undesired frequency signal (noises) and amplified the actual signal, giving the result as:

$$\frac{1}{2}A_1A_2\cos(\varphi_1 - \varphi_2). (2.2.11)$$

To employ the lock-in amplifier for STS studies, it is necessary to superimpose a sinusoidal modulation signal on the bias. A typical lock-in amplifier control panel is shown in **Figure 2.2.9**. For the modulation signal, small amplitude and high frequency are usually set. Another three critical parameters for getting reasonable spectroscopy are phase, sensitivity and time constant^[177]. Either input signal or reference signal generated by the lock-in has its own phase, from equation (2.2.10), an in-phase condition is needed to get the maximum output signal. Lock-in has an inner function to adjust the generated reference signal to match the input to get the maximum output. The "Auto Phase" shown in the panel allows one to find the current optimization phase. The sensitivity describes the gain of the AC amplifier. In principle, it is ideal to have the possible highest sensitivity without overloading the multiplier (PSD). Time constant τ is defined as the signal integration time of the lock-in amplifier and it functions in the low pass filter – which means that the signal with a higher frequency than $1/\tau$ will be filtered. Therefore, the setting principle for this value is: $1/\omega_{modulation} \ll \tau \ll 1/\omega_{signatl}$. The slope right below time constant is another cutoff parameter – a higher value means faster attenuation of signal away from the reference frequency.



Figure 2.2.9. The control panel of the lock-in amplifier used in the UHV laboratory in Poznań.

STS operational modes

For a specific tip-sample system, the tunneling process is determined by the tunneling current I, bias V and tip-sample distance a, as deduced from equation (2.2.8). STS measurements usually rely on fixing one of these three parameters and measuring the relation between the other two interconnected parameters. Therefore, three types of spectroscopy can be achieved^[172] (From here I replaced a by z to meet the common name called in the literature): (i) dI/dV curves, where keeping constant tip-surface distance z, record and make the derivation of the variation of tunneling current with the bias; (ii) dI/dz curves, where keeping the constant bias, record and make the derivation of the variation of tunneling current with the tip-sample distance; (iii) field emission resonances (FERs) curves, usually it is dz/dV mode, where keeping the constant tunneling current, record and make the derivation of the variation of the variation of tip-sample distance with the bias. However, sometimes this spectroscopy mode can be done by measuring the dI/dV curve since the z signal is directly connected to the feedback current^[178].

(1) dI/dV

The most-used STS curves are the dI/dV curves. Assuming the density of states of the tip is a constant value, as shown in **Figure 2.2.6**, the density of occupied states of surface can be obtained from the dI/dV measurements. The density of empty states of the surface can be obtained as well by reversing the bias. Based on equation (2.2.8), dI/dV can be expressed by^[172]:

$$\frac{dI}{dV} \propto \rho_s(E)T'(E, eV, z, \varphi) . (2.2.12)$$

From the above equation, the dI/dV signal is directly proportional to the local density of electronic states of the sample. Experimentally, a small modulated sinusoidal signal is added to the bias and the lock-in amplifier screens out the responding tunneling current change, with feedback



control off. Mathematically, by extracting the first harmonic using a particularly designed circuit, a corresponding dI/dV curve can be obtained^[179].

Figure 2.2.10. (a) Topographic STM image of iron oxide islands on Ag(111) (I = 0.1 nA, V = -1.0 V, 100×100 nm²). **(b)** *dI/dV* curve obtained from exposed Ag(111) regions (average of eight measured curves).

Figure 2.2.10 (b) shows an example of a dI/dV curve of Ag(111) obtained at 77 K. Ideally, for a uniform substrate, the density of states of the surface is supposed to be the same at different locations, so does the resulting dI/dV curves. However, many factors, such as adsorbents or electronic noises, can lead to significant differences. Therefore, proper statistics and data averaging are essential to get a reliable result. It is the averaged results of curves recorded at different locations of exposed Ag substrate (as the dark region labeled 'Ag' in **Figure 2.2.10 (a)**) on FeO/Ag(111) sample. A broad conductance rises from -140 mV to -10 mV appeared in the dI/dV curve in (b), which differs from a clean Ag(111) surface with a step-like rise in conductance from -70 mV to 55 mV measured at 5 K^[180]. The energy shift of electronic states might due to the charge transfer between substrate and iron oxide. A similar effect was previously found in the system of graphene/Ag(111)^[181] and AGNRs/Ag(111)^[182]. The broadening feature (multiple states) may relate to interface states, similar to those observed for silicene/Ag(111)^[183]. The shape of the curve can also be modified by temperature (for example, the bandgap of silicene decreases with increased temperature, disappears at 40 K^[184]) and condition of the tip^[180].

Apart from collecting information on the local density of states (LDOS) by point spectroscopy, STM can also generate a dI/dV signal map (differential conductance) of the scanned region at a given bias. Similarly, the mapping can be obtained by adding a small sinusoidal modulation signal on the bias and collecting the first harmonic signal through a lock-in amplifier, with the feedback control. The dI/dV map is usually recorded simultaneously to the topographic image (in constant current mode). In this case, the modulation signal must have a high frequency to avoid feedback loop response. The topographic image of the FeO/Ag(111) and its corresponding differential conductance maps at different biases are shown in **Figure 2.2.11**. The contrast variation reveals the electronic structure of the surface.



Figure 2.2.11. (a) STM topographic image (V = +1.0 V) of FeO/Ag(111) and the corresponding dI/dV maps recorded at (b) V = -1.0 V, (c) V = +0.5 V and (d) V = -0.5 V (I = 0.1 nA, 100×100 nm²).

(2) dI/dz

The dI/dz curves are used to determine the effective work function of the tip and sample system. From equation (2.2.4) and (2.2.6), at the low bias, one can deduce the effective work function Φ :

$$\frac{d\ln I}{dz} \sim -2k \sim -\frac{2\sqrt{2m\phi}}{\hbar} . (2.2.13)$$

If z is in nm and Φ in eV, the equation can be simplified to^[169]:

$$\frac{d\ln I}{dz} \sim -10.25\sqrt{\phi}$$
 . (2.2.14)

Usually, tip and sample are made of different materials, using Φ_t and Φ_s to represent the work function of the tip and sample surface. Thus, the effective work function Φ_s is usually estimated as the average work function^[185]:

$$\phi = \frac{\phi_t + \phi_s}{2} \ (2.2.15)$$

Combining equations (2.2.14) and (2.2.15), the sample's work function can be easily determined from the dlnI/dz curve (which is converted from dI/dz collected from experiments). The dI/dz can be carried out by changing tip position above the sample and recording the variation of tunneling current. Similar to the method used for recording dI/dV spectroscopy, a small modulation with the high-frequency signal is added to the spacing between tip and sample, the variation of tunneling current is measured by the lock-in amplifier^[172].

Work function is defined as the minimum energy to move an electron from the surface to the vacuum level. However, the local work function usually has a slightly different meaning for STM

techniques. For a simple one-dimensional tunnel junction, shown from formula (2.2.6), the tunneling current *I* (at bias lower than tip or surface work function) changes exponentially with tipsample distance *z*, and it is also determined by the average work function of the tip and sample. However, the influence from the electronic structure of tip and image potential of tunneling electrons cannot be ignored^{[186][187]}, which complicates the determination of local work function from *dI/dz* curve. Therefore, in many publications, the term of apparent barrier height Φ_{at} is used^[188].

It is not trivial to unveil the relation between Φ and Φ_{at} . Still, in many studies^{[189][190]}, one can reasonably consider apparent barrier height as the same value as local average work function. dI/dzmeasures the apparent barrier height, which is closely related to work function. Depending on the tip condition and the applied bias, the measured results may give a different value of apparent barrier height^[191]. In this thesis, I simplify these two concepts and consider they share the same value Φ .



Figure 2.2.12. Illustration of a tungsten (W) tip moves over the surface of Ag(111) sample. (b) Energy diagram of one-dimensional tunnel junction between Ag(111) substrate (in gray) and W tip (black). The bias voltage is small and the electron's wave function decay exponentially during tunneling through the potential barrier. (c) An example of dlnI/dz spectroscopy of Ag(111) (solid line) and its linear fit line (dashed line), inset: the original dI/dz spectroscopy. (d) Calculated work function of W tip based on a fitted slope from (c).

For data analysis, instead of plotting the dI/dz curve, it is more convenient to convert it into a logarithmic scale. One example of dlnI/dz measurement of Ag(111) is shown in Figure 2.2.12 (c), which was processed from the original dI/dz curve (in the inset of Figure 2.2.12 (c)). A Onedimensional (z-direction) energy diagram of this system is sketched in (b). The key point of the data process is that the current *I* must be positive to calculate *lnI* successfully. Based on equation (2.2.14), the apparent barrier height Φ can be estimated by:

$$\phi \approx 0.95 \left(\frac{d\ln I}{dz}\right)^2 (2.2.16).$$

Mathematically, the value of *dlnI/dz* indicates the slope of the quasi-linear line from the *dlnI/dz* plot. For the example shown in **Figure 2.2.12 (c)**, the value of the slope is roughly 2.07 Å⁻¹, which is obtained from the fitted linear line (dashed line). Thus, the apparent barrier height can be calculated at about 4.07 eV by equation (2.2.16). This value roughly equals the average work function of the W tip and Ag sample. Since the work function of the W tip is unknown (mostly lower value compared to its bulk form due to its sharp end)^[185], taking the reported value for Ag(111) of 4.26 eV^[192], the local work function of the W tip is reduced to ~ 3.88 eV (by formula (2.2.15)).

(3) FERs

In most cases, the FERs indicates the dz/dV mode. When the applied bias is larger than the work function of the tip or the sample, the electrons can be emitted from the solid to the vacuum level of the surface (field emission regime)^[193]. Image (potential) states are important surface states contributing to the dz/dV spectrum. These hydrogen-like bond states are bound to the substrate by the surface response to image charges, similarly to a Coulomb potential^[194]. On a conducting substrate, these states can be probed by STM tip, which was first shown in 1985 by Binnig et al.^[195]. In STM, a potential well exists between the tip and surface. Due to the bias applied to the tunnel junction, the electric field across the junction causes the Stark shift (shifting the spectral lines of atoms)^[196] and leads to electron transmission resonances at specific energies^[172]. These resonances are called field emission resonances (FERs). The FERs are often used, for example, to determine the local work function of the surface. The resonance energy spectrum is defined by^[172]:

$$E_n = \phi + \alpha (n - 0.25)^{2/3} F^{2/3}, (2.2.17)$$

where Φ is the surface work function, *n* is the principal quantum number, *F* is the applied electric field between the sample and the tip and α is a constant. The energy diagram of the FERs mechanism^{[172][195][197]} (with four quantum states) is shown in **Figure 2.2.13 (a)**.



Figure 2.2.13. (a) Energy diagram of FER (dz/dV) of a conducting surface. The bias V is larger than the work function of the sample. Four quantum well states are shown. **(b)** A FER (dI/dV) curve was obtained for an Ag(111) single-crystal sample.

To record FERs in constant current mode, the feedback control of the STM has to be switched on. The variations in the tip position are detected and displayed as a function of applied bias. Differentiation of as-recorded z/V curve gives the dz/dV (FER) curve. An alternative way is to record the dI/dV (also indicated as FER) curve with a closed feedback loop, which should ideally, give the identical resonance position (since tunneling current is exponentially dependent on tip-sample distance). One example of FER spectroscopy used in the dI/dV approach of Ag(111) is shown in **Figure 2.2.13 (b)**. The first resonance peak (n = 1) is located between 4.1 to 4.2 V, close to the reported value (~4.2 V)^[198]. The small position shift usually relates to tip effects^[199].

2.2.3. Low energy electron diffraction (LEED)

Introduction

Low energy electron diffraction (LEED) has been one of the most common surface science tools since the mid-1970s^[200]. The first experiment on electron diffraction was demonstrated in 1927 by Clinton Davisson and Lester Germer at the Bell Telephone Laboratories. When they were studying the rebounding behavior of electrons by shooting an electron beam to a polycrystalline nickel surface, an accident happened and they had to heat the sample to remove contamination. The temperature was high enough to create a sizeable single-crystal region. Therefore, they observed an electron diffraction pattern after the heating treatment. This "accident" started the theory of electron diffraction, which further constructed the solid base for the technique of LEED.

Electron diffraction

Based on the hypothesis published by the French physicist Louis de Broglie in 1924, every particle (electron) can also be described as a wave. For an electron with mass m ($m = 9.109 \times 10^{-31}$ kg) and velocity v, h is the Plank constant ($h = 6.626 \times 10^{-34}$ J·s), the De Broglie wavelength λ (unit of Å) can be calculated as:

$$\lambda = \frac{h}{mv} . (2.2.18)$$

Consider an ideal case that all the energy applied to the electron is converted to kinetic energy E (eV). Then, the velocity of the electron can be written as:

$$v = \sqrt{\frac{2E}{m}} . (2.2.19)$$

Combining equation (2.2.18) and (2.2.19), the λ is found to be:

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{12.25}{\sqrt{E}} . (2.2.20)$$

A crystalline surface is similar to a diffraction grating for the incident electron beam, as shown in **Figure 2.2.14 (a)**. The parallel electron beams come towards surface atoms (with the atomic distance of d_{al}), and scattered at an angle of θ with respect to the incident beam. From formula (2.2.20), for initial energy ranging from 30 to 255 eV, the electrons' De Broglie wavelength lies in the range from 2.24 Å to 0.77 Å. These values correspond to the atomic spacing, which meets the diffraction condition (the atomic spacing of the surface atoms d_{at} is larger than electron wavelength λ) and leads to the formation of a characteristic diffraction pattern. For simplicity, one can consider two neighboring scattered beams, as shown in **Figure 2.2.14 (b)**. The constructive interference (bright diffraction spot) only occurs when the path difference x is equal to the integer multiple of full wavelength:

(a)
Parallel incident electron beam in phase

$$\theta$$
 Scattered electron beam
 d_a d_a d_a θ
 x

$$x = d_a \sin \theta = n\lambda$$
 (*n* = 1,2,3,4,...). (2.2.21)

Figure 2.2.14. Model of electron diffraction from a crystalline material. (a) Electron beam scattered from two neighboring surface atoms. (b) A simplified view of two in-phase scattered beams.

Based on formulas (2.2.20) and (2.2.21), for a fixed electron diffraction setup and sample stage position, the surface structure should be readily determined by the diffraction pattern with a giving initial energy E. Another typical measurement from a LEED is the *I*-*V* curves, which measures the intensity (*I*) of diffraction spots as a function of the electron beam energy (*V*). Such curves, combined with theoretical simulations, can provide detailed information on the crystallographic structure of the surface.

Low-energy electrons in probing the surface structure

In surface science studies, the main advantages of using low-energy electrons are nondestructive and short penetration depth inside the sample. Additionally, it is relatively easy to generate electron beams with well-defined energies. Previous experiments have shown that electrons within a low energy range (10 - 100 eV) have small inelastic mean free paths in solid (less than 10 nm). **Figure 2.2.15** shows the so-called "universal curve", which should be applicable for all particles. At low energy range (below 50 eV), the inelastic mean free path of electrons in solid decreases as the electron energy increases. This mainly relates to the increasing number of inelastically scattered electrons, resulting in a higher possibility of interaction (shorter mean free path). However, when the energy is above 100 eV, the mean free paths of electrons increase with the increase of electron energy. This is due to the higher speeds (kinetic energies) of electrons, which significantly reduces the collision time with each other. In summary, the interaction between low-energy electrons and the substrate is mild, only electrons scattered from the surface or nearsurface regions with no inelastic collision can leave the solid to the vacuum. Therefore, probing solid materials with low-energy electrons only collects information from the topmost layers of the sample, making LEED a highly surface-sensitive tool.



Figure 2.2.15. The inelastic mean free path of electrons in solids versus electron energy, based on the experimental data (dots) and fitted quasi-universal dependence curve (solid line) (Figure 1 (b) from[201]).

Experimental setup

A typical low-energy electron diffraction setup consists of an electron gun, a retarding field analyzer (repeller) and a fluorescent screen (collector). Additional facilities, like optical lenses, electronic oscillators, amplifiers, recorder and a display are also needed to complete a fully functional LEED instrument (**Figure 2.2.16**). An electron gun consists of a cathode filament, a Wehnelt cylinder and a series of electrostatic lenses with different apertures. Monoenergetic electrons (20 - 300 eV) can be produced by applying a negative potential to the cathode (sample at the ground potential). Electrons pass through electrostatic lenses with apertures 1,2,3,4, where electrons are focused to a beam through apertures 2 and 3 (with intermediate potential) and then directed to the sample.

All the scattered electrons (elastically and inelastically) are collected by a retarding field analyzer (RFA), also known as a high pass filter. It is usually hemispherical to ensure the same sample-grid distance for electrons that are scattered toward the grid in different directions. It typically includes three or four grids made of small wire mesh. The front grid (indicated by "A") is at the ground potential to let electrons travel in a field-free region before reaching RFA. A negative potential is applied to the next grid (or two grids, where the additional grid makes the retarding field more stable and homogeneous) to repel electrons with less energy than the set pass energy, thus, only elastically scattered electrons are able to pass through. This grid (or two grids) is called a repeller. The last grid (indicated by "D") is at the ground potential to minimize the electron noise from the repeller and capacitance between repeller grids and collector^[154].

A fluorescent screen (collector), usually coated with a phosphorus layer^[202], is biased positively at 4–6 kV to accelerate the screened electrons from RFA. In that way, only the Bragg diffraction spots originating from high-energy electrons contribute to the diffraction pattern. The arrangement of the diffraction spots provides information on the symmetry and lattice constant of



the surface unit cell. The intensity of a certain diffraction spot is related to the multiple scattering in the top atomic layers.

Figure 2.2.16. Simplified schematic drawing of a four-grid LEED setup.

Interpretation of LEED patterns: real and reciprocal space

From equation 2.2.21, one can easily deduce that a smaller unit cell (with lattice constant d_{at}) leads to a bigger scattering angle θ (0 to $\pi/2$), and thus, the larger distance between the corresponding diffraction spots. To analyze the symmetry and size of a unit cell in real space from diffraction patterns, the concept of reciprocal space has to be introduced^[203]. For a two-dimensional case, if a_1 and a_2 are unit vectors in real space, the unit vectors of reciprocal space b_1 and b_2 are defined by the following expressions:

$$a_1 \cdot b_1 = 2\pi$$
 $a_2 \cdot b_2 = 2\pi \cdot (2.2.22)$

Mathematically, b_1 is perpendicular to a_2 , and b_2 is perpendicular to a_1 . Assuming α is the angle between a_1 and a_2 , the length of reciprocal vectors b_1 and b_2 can be expressed as:

$$b_1 = \frac{2\pi}{a_1 \sin \alpha}$$
 $b_2 = \frac{2\pi}{a_2 \sin \alpha}$ (2.2.23)

LEED is a convenient tool for determining the level of crystallinity of the surface, including a clean single crystal and a crystal with ordered overlayers on top^[204]. There are two types of notation describing a surface unit cell with respect to the substrate structure (basic unit): Woods notation and Park-Madden Matrix notation. Woods notation is used in this work owing to its simplicity and clarity. The basic pattern of a clean crystal is usually defined as a (1×1) pattern. As an example, Ru(0001) is shown in **Figure 2.2.17 (a)**. The unit cell in real space is drawn on the left, with its corresponding reciprocal unit cell in the middle and LEED pattern on the right.

Figure 2.2.17 (b) shows a different LEED pattern after oxygen adsorption on Ru(0001). The reciprocal unit cell obtained directly from the LEED pattern in reciprocal space is displayed in the middle, where the red rhombus (O unit cell) is half-sized of the blue rhombus (Ru unit cell). Based on formulas (2.2.22) and (2.2.23), the real surface unit vector of O should be twice as large as the

Ru(0001) unit vector, without rotation, as shown in the left of (b). In this case, oxygen on Ru(0001) form a p(2 × 2) structure. More complicated structures can be written in this way. For example, Pb growing on Ru(0001) will form a $(\sqrt{7} \times \sqrt{7})$ R19.1° surface structure if the coverage exceeds 4/7 monolayer (ML)^[205].



Figure 2.2.17. Schematic views of two simple surface structures in real and reciprocal space: (from left to right) (a) Ru(0001) in real space, reciprocal space and the corresponding (1×1) LEED pattern; (b) oxygen absorbed on Ru(0001) – in real space, reciprocal space and the corresponding $p(2 \times 2)$ LEED pattern. Blue balls represent the Ru atoms, while red ones the O atoms.

2.2.4. X-ray photoelectron spectroscopy (XPS)

Introduction

X-ray photoelectron spectroscopy (XPS) is a widely used tool for measuring the chemical composition of solid surfaces^[206]. The history can be traced back to the beginning of the 19th century. In 1887, the photoelectric effect was discovered by Heinrich Rudolf Hertz, which was later explained by Albert Einstein in 1905. In 1957, Kai Siegbahn and his group developed the XPS technique^[207] based on the photoelectric effect theory. Kai won his Nobel Prize in 1981 to honor his efforts establishing XPS as an analytical tool. By analyzing the XPS spectrum, one can identify the elemental composition and the chemical states of the materials.

The photoelectric effect

When an electromagnetic wave, like UV light or X-rays (high-energy photon beam), strikes a surface, electrons may escape from the surface if they adsorb enough energy. Such a phenomenon is called the photoelectric effect. An electron excited by light is called the photoelectron. From 1886 to 1900, this effect was studied in detail by Wilhelm Hallwachs and Philipp Lenard^[208]. In general, a few unexpected phenomena was observed: (i) no photoelectrons can be emitted unless the frequency of the light exceeds the threshold frequency (determined by the target material); (ii) more electrons can emit by increasing the intensity of the light (above threshold frequency); (iii) the maximum kinetic energy E_k (with mass *m* and velocity *v*) of an electron which escapes from surface

equals to the stop potential V_{sop} , and the value stays the same even though the intensity of the light is increased:

$$eV_{stop} = E_k = \frac{1}{2}mv^2$$
. (2.2.24)

Albert Einstein explained this effect by postulating that light consists of discrete small energy packages called photons. With frequency f, the energy of each incident photon E_{phoon} is defined by the following expression:

$$E_{photon} = hf . (2.2.25)$$

The energy level diagram of the photoemission process is shown in **Figure 2.2.18**. Electrons are more strongly bonded in the core levels (K and L shells in the figure). The highest occupied state (Fermi level) is populated by the solid's outermost electrons^[209]. When an electron (at K level in (a)) absorbs an X-ray photon, and the photon energy is greater than the work function Φ ($\Phi = E_{VATC} - E_F$) of the solid, the electron will gain initial kinetic energy and escape from the solid.

During the photoemission process, two "byproducts" are produced: secondary electrons and Auger electrons. The secondary electrons are generated by strong photoelectrons-electrons interactions in the solid. Those secondary electrons usually have low energies and most of them cannot escape to the vacuum. Thus, they superimpose as a continuous smooth background on the XPS spectrum^[209]. The Auger transition is slightly more complicated. As shown in **Figure 2.2.18** (b), after the photoemission process, a vacancy is left at the core level (*K*) and an electron from a higher energy level (L_1) falls to fill the hole and gives out its energy in the form of a photon. An electron at another shell ($L_{2,3}$) adsorbs this energy and escapes from the surface. This escaping electron is called the Auger electron, and the transition is called Auger $KL_1L_{2,3}$ transition^{[210][211]}. Auger electrons also contribute to the XPS spectrum, forming Auger peaks.



Figure 2.2.18. (a) Illustration of the photoemission process in energy level diagram. (b) Illustration of Auger $KL_1L_{2,3}$ transition occurring after the photoemission process shown in (a). The yellow balls represent electrons.

Experimental setup

The XPS setup mainly consists of an X-ray source, an electron energy hemispherical analyzer (spectrometer) and a photoelectron multiplier. A simple illustration of XPS instrumentation is shown in **Figure 2.2.19**. Supporting electronics and software are required as well.



Figure 2.2.19. Simplified schematic of a laboratory XPS setup.

For standard laboratory XPS equipment, high vacuum condition is required to avoid the collision of X-rays with the molecules from the air. Mostly-used materials for anode are aluminum (AlK α radiation, 1486.7 eV) and magnesium (MgK α radiation, 1253.6 eV). In 1895, Wilhelm Conrad Röntgen first demonstrated X-ray's emission. Simply speaking, it is an inverse process of the photoelectric effect. Electrons are produced by thermionic emission from the heated cathode (filament) placed at "ground" potential with respect to the anode. These electrons will gain high kinetic energy and be accelerated towards the anode by applying a high positive voltage (a few to a few dozens of kilovolts) on it. Cooling water is passing around the anodes to prevent overheating. The energy loss of electrons will be finally emitted in the form of X-rays from the surface of the anode. Typical X-ray wavelengths are 0.001 to 1 nm^[208]. However, the produced photoelectrons contain much less energy and, therefore, have a mean free path of up to a few nanometers.

When the X-ray beam illuminates the sample, photoelectrons emitted from the surface will be collected by a hemispherical analyzer. After passing through the focusing elements, those photoelectrons are retarded to the band-pass spectrometer consisting of two concentric cylinders with different radius. Depending on the negative voltage applied on the outer hemisphere and the geometric dimensions of the analyzer, only photoelectrons with specific kinetic energy (pass energy, E_{patss}) can reach the exit of the spectrometer. Making *R* the mean radius of the hemisphere and *dS* the average slit width, the energy resolution *dE* is usually defined as^[154]:

$$dE = \frac{dS \cdot E_{pass}}{2R} . (2.2.26)$$

The spectrum resolution can be improved by using either smaller slit width or reducing the pass energy of incoming photoelectrons. Once photoelectrons get through the spectrometer, the

signal is very weak and, therefore, an additional electron multiplier is necessary to amplify it. The electronics and computer software then allows the XPS spectra recording in the form of intensity as function of kinetic energy. The kinetic energy values can then transfer to binding energy using the equation:

$$E_B = E_{phoon} - E_k - \Phi.$$
 (2.2.27)

Interpretation of XPS spectra: elements identification and chemical shifts

Conventionally, quantum numbers are used to describe the atomic structure and electronic states. The principal quantum number *n* is associated with the shell, the orbital quantum number *l* corresponds to the number of subshells in each shell (l = 0, 1, 2, ..., n-l), and the spin quantum number m_s (1/2 = "spin up"; -1/2 = "spin down") describes angular momentum of an electron. The relation between quantum notation and spectroscopic notation is shown in **Table 2.2.1**.

Table 2.2.1. Quantum numbers and spectroscopic notation.

п	l	Shell	State	
1	0	Κ	1s	
2	0	L	2s	
2	1	L	2p	
3	0	Μ	35	
3	1	М	3p	
3	2	Μ	3d	
4	0	Ν	4s	
4	1	Ν	4p	

It is common to observe signals from certain shells appear as doublets in the XPS spectra (which occurs for all orbitals excepts *s*). The doublet is related to the spin-orbital coupling process, i.e. the electromagnetic interaction between the electron spin m_s and its electronic orbitals *l*, leading to an electron energy level shift. The concept of total angular momentum *J* is, therefore, introduced to describe this interaction: $J = |m_s + l|$. For instance, Ru 3d splits (l = 2, $m_s = \pm 1/2$) to 5/2 (high energy peak) and 3/2 (low energy peak). The degeneracy of these two states and the intensity (peak area) ratio of two splitting peaks can be determined from 2J+1. For example, 5/2 state results in 6 while 3/2 state gives 4, so the intensity ratio of 3d 5/2 and 3d 3/2 peaks is 3:2.

As mentioned before, there are few types of electrons that contribute to XPS spectra. The most predominant photoelectrons give the primary chemical information of the specimen. Auger electrons, triggered by the photoemission process, contribute to the Auger peaks on the spectrum. Exemplary spectra obtained for a clean Ru(0001) single crystal using Mg and Al anodes are shown in **Figures 2.2.20 (a)** and **(b)**, respectively. All the peaks are marked within the spectra. Noticeably, the positions of Auger peaks are dependent on the anode material, since the kinetic energy of Auger electrons is fixed for a given element. For example, the Ru MNN peak appears at around 978 eV when using Mg anode, as shown in **Figure 2.2.20 (a)**, while using Al, the peak position shifts to around 1211 eV.



Figure 2.2.20. XPS survey spectra of clean Ru(0001) recorded using Mg K α (**a**) and Al K α (**b**) X-ray radiation sources; (**c**) presents Fe 2p region obtained for on Fe/Ag(111) before (dashed line) and after (solid line) oxidation.

Apart from identifying different elements in the sample, XPS spectra are also used to analyze the chemical states (such as oxidation states). The variation of the chemical surrounding of atoms can shift the position and change the shape of the original photoelectron peak. The exemplary spectra, obtained for Fe deposited onto Ag(111) substrate held at 500 K (solid line) and post-oxidized in 1×10^{-6} mbar O₂ at 700 K (dashed line), are shown in **Figure 2.2.20 (c)**. Metallic iron transforms to iron oxide hosting both Fe²⁺ and Fe³⁺ components. These ions have a more positive potential than metallic Fe, therefore, their core binding energy is centered at a higher position. Noticeably, in this case, the Fe 2p signal overlaps with the Ag 3s (not shown), which also contributes to the line shape.

Analyzing XPS spectra of transition metal oxides is complicated. Considering iron oxide discussed above, the Fe 2p is a superposition of peaks originating from Fe²⁺ and Fe³⁺, both of which are in the form of doublets (1/2 and 3/2 peaks). Other than that, multiple splitting effects and satellites are also typical features in XPS spectra for oxides. Multiplet splitting^[212] of core-level peaks results from exchange interaction between the unpaired core-level electrons and unpaired valence electrons. This coupling produces final states splitting and shows multi-peaks (broadening the core-level peaks) in the photoelectron spectrum. Shake-up satellites^[213], on the other hand, occur when the ejected photoelectrons interact with the valence electrons, involving excitation of these outer shell electrons to a higher unoccupied level ("shake up" transition). Due to the loss of some kinetic energy by the emitted photoelectrons, a peak at the higher binding energy side of the primary peak appears. If the valence electrons are ejected completely ("shake-off"), a broadening feature of the main line or inelastic background can be observed.

2.3. Single-crystal substrates preparation

The cleaning method for a single crystal in UHV chamber usually consists of ion sputtering (using an inert gas, such as Ar, Ne) with subsequent vacuum annealing, and/or chemical reaction (oxygen annealing).

The ion sputtering is done by introducing a noble gas into the ion gun, which is positioned in front of the crystal surface. The ionized noble gas is firstly produced by electrons impact with noble gas, and then accelerated towards the crystal surface by a few hundred volts to a few kilovolts. The crystal surface is bombarded by an ion current (usually a few microamps). The impurities and contamination are, therefore, sputtered off from the surface.

Although puttering is an efficient way to remove contaminations, it has a big disadvantage as this process usually results in a rough surface. To flatten the surface, a subsequent annealing step is added to increase mobility of surface atoms and thus smoothen the surface. The annealing process can also increase the desorption rate of adsorbates on the surface. The annealing is often done by Ohmic heating. For higher temperatures, it is common to add a high bias on the crystal and heat it up by electron bombardment from the rear side. In some cases, an oxygen annealing (chemical reaction) step is favored to remove carbon (usual contamination, removed in the gas form to vacuum as CO or CO₂).

Since the impurities may also diffuse from the bulk to the surface during annealing, thus, additional sputtering is necessary for further cleaning. In general, the sputtering/annealing (including vacuum and O_2 annealing) cycles have to be repeated a few times to obtain a satisfactory clean surface.

The single-crystal Ag(111) and Ru(0001) used in this work were cleaned by repeating cycles of ion sputtering, oxygen annealing and vacuum annealing. The surface cleanliness is monitored by XPS/STM and the crystallographic order is determined by LEED. The cleaning procedure for each crystal used in this work is shown in **Table 2.2.2**. The temperature of the sample was monitored by an infrared pyrometer (Poznań: Land Instruments; Oldenburg: OPTRIS CTlaser).

Substrate	UHV chamber	Cleaning approach (usually several repeated cycles)		
Ag(111)	Poznań	Ar ⁺ sputtering at RT, 0.6 keV and 1 keV; O ₂ annealing at 700 K; Vacuum annealing at $T \ge 700$ K;		
Ru(0001)	Poznań	Ar ⁺ sputtering at RT, 1 keV; O ₂ annealing at 950 K; Vacuum annealing at 1450–1500 K;		
Ru(0001)	Oldenburg	Ne ⁺ sputtering at RT, 1.5 keV; Vacuum annealing at 1300 K; O ₂ annealing at 1000 K; Flash to 1300 K		

Table 2.2.2. Cleaning procedures for the single-crystal substrates used in this work.

3. Structure of ultrathin FeO_x ($1 \le x < 2$) films on Ru(0001)

The results were partially published in:

- [214] T. Ossowski*, <u>Y. Wang*</u>, G. Carraro, A. Kiejna, M. Lewandowski, Structure of monoand bilayer FeO on Ru(0001): STM and DFT study, Journal of Magnetism and Magnetic Materials (2021), DOI: 10.1016/j.jmmm.2021.168832 (* - equal contribution)
- [215] Y. Wang, G. Carraro, H. Dawczak-Dębicki, K. Synoradzki, L. Savio, M. Lewandowski, Reversible and irreversible structural changes in FeO/Ru(0 0 0 1) model catalyst subjected to atomic oxygen, Applied Surface Science 528 (2020) 1460

The chapter presents the structural studies of both pristine FeO and the oxygen-rich oxide phase FeO_x (1 < x < 2) after strong oxidation on Ru(0001). As introduced in section 1.2, FeO grows into a well-ordered surface structure. Despite numerous studies on the FeO/Ru(0001) system, some important features, such as the stacking of Fe and O layers within mono- and bilayer structures, as well as the structural parameters of a well-ordered monolayer are still under discussion. Moreover, Ru(0001) has a relative high affinity to oxygen, making it a promising substrate for obtaining oxygen-rich oxide phase. For this, the structural changes that occur in the system at highly-oxidative conditions have to be determined.

There are two sections in this chapter. In section 3.1, the detailed structural parameters of both mono- and bilayer FeO/Ru(0001) are determined from statistics, and the corresponding structural models are proposed. In section 3.2, the work concerns the phase transition by subjecting both Ru(0001) and FeO/Ru(0001) system to atomic oxygen at RT or 700 K. The surface morphology and film composition are analyzed before and after the atomic oxygen exposure. STM, LEED and XPS measurements were involved in the data analysis.

3.1. Structure of mono- and bilayer FeO on Ru(0001)

As mentioned in section 1.2.1, there are mainly two approaches used to grow ultrathin FeO films on Ru(0001): (i) Fe deposition in an O₂ ambient onto a heated substrate^[26] and (ii) Fe deposition in UHV onto a substrate held at RT and post-oxidation^[25]. In my studies, I used the (ii) approach with Fe deposition temperature of 500 K, oxidation in 1×10^{-6} mbar O₂ at 950 K and cooling down in O₂ pressure for several minutes (to avoid reduction of the film). The use of high-temperature Fe deposition leads to the formation of Fe wetting layer, while deposition at RT mostly

results in bilayer Fe islands. As can be seen from the STM image shown in **Figure 3.1.1 (a)**, oxidation of Fe deposited at 500 K results in the formation of extended FeO islands. **Figure 3.1.1 (b)**, on the other hand, reveals that oxidation of Fe deposited at RT leads to the formation of well-dispersed smaller FeO islands. In both cases, the oxide is characterized by virtually-identical atomic and Moiré structures, similar to the literature discussed in section 1.2.1. The atomically-resolved STM image of FeO(111)/Ru(0001) is shown in **Figure 3.1.1 (c)**, while the corresponding LEED pattern is displayed in **Figure 3.1.1 (d)**. The diffraction pattern is a superposition of Ru(0001) – (1 × 1) spots, FeO – (1 × 1) reflexes, satellite spots originating from the Moiré superstructure and the (2 × 2) spots related to the presence of chemisorbed O atoms on the exposed substrate regions.



Figure 3.1.1. Large-scale STM image of FeO grown by Fe deposition at (a) 500 K (I = 0.3 nA, V = + 1.0 V, 300 \times 300 nm²) and (b) RT (I = 0.4 nA, V = + 1.0 V, 300 \times 300 nm²). (c) Atomically-resolved STM image of FeO on Ru(0001) (I = 0.1 nA, V = + 0.07 V, 8 \times 8 nm²). (d) LEED (64 eV) pattern with marked Ru, FeO and O spots.

In most studies, FeO was found to grow in a bilayer (O-Fe-O-Fe) form on Ru(0001)^[25]. Such oxide species have a height of ~5.0 Å. However, under certain conditions – namely when low oxygen pressures are used – a single FeO layer (O-Fe) can be stabilized. At intermediate pressures, the oxide initially grows in a bilayer form and switches to monolayer growth as the islands expand^[26]. In my studies, I was occasionally able to observe the coexistence of mono- and bilayer FeO islands despite the higher O_2 pressure is used. The large-scale STM image showing the coexistence of single- and double-layer species, as shown in **Figure 3.1.2 (a)**. The monolayer regions are either anchored to the edges of bilayer ones (**Figure 3.1.2 (a)**) or found inside extended double-layer islands (not shown here). **Figure 3.1.2 (b)** shows the zoom-in image of the interface region marked by yellow square in **(a)**. The red and black meshes are drawn to present the Moiré arrangement of the single- and double-layer FeO, respectively. A mutual shift of the two Moiré lattice by about 1/3 of the periodicity is observed, which is related to the ABCABC growth of FeO(111). It indicates that the single-layer FeO sticks out from the second layer, which grows on

top of it. Incomplete Moiré cells at the edges of single-layer FeO regions are also observed (marked by the green circle in (b)). A height profile taken across monolayer island (marked by red arrow) and bilayer island (marked by blue arrow) is shown in **Figure 3.1.2** (d). The statistical analysis revealed that the height of the first layer is 2.66 ± 0.15 Å, while the second is 2.25 ± 0.10 Å. The total height of double-layer FeO is 4.95 ± 0.16 Å, in agreement with the value reported in previous research^[25]. The obtained value for the single-layer FeO is slightly higher than the one mentioned in Ref. [26]. The Moiré corrugations are about 0.43 ± 0.02 Å on both types of structures.



Figure 3.1.2. (a) STM image of FeO islands on Ru(0001) (I = 0.1 nA, V = + 1.0 V, $100 \times 100 \text{ nm}^2$). **(b)** A zoom-in STM image showing both single- and double-layer FeO, (I = 0.1 nA, V = + 1.0 V, $37 \times 37 \text{ nm}^2$). **(c)** Atomically-resolved STM image of double-layer FeO (left side) and the O(2 × 2) reconstruction on Ru(0001) (right side) (I = 1.0 nA, V = + 0.05 V, $100 \times 100 \text{ nm}^2$). **(d)** Height profile marked by red arrow in **(a)**. **(e)** Atomically-resolved STM image of both monolayer FeO (I = 1.0 nA, V = + 0.05 V, $5.0 \times 6.5 \text{ nm}$). (Adopted from Figure 1 in [214]).

The atomically-resolved STM image of single-layer FeO islands is shown in **Figure 3.1.2 (c)**, while **Figure 3.1.2 (c)** shows an atomically-resolved STM image of a FeO bilayer (left side) and O-covered Ru(0001) (right side). The mesh constructed by the light blue lines is drawn to fit the $O(2 \times 2)/Ru(0001)$ structure. Within the structure, three main crystallographic directions, each rotated by 120° with respect to the other two, can be distinguished (denoted as a_1 , a_2 , and a_3). Along with each orientation, the measured value of atomic and Moiré periodicities are calibrated with respect to the $O(2 \times 2)$ structure, and the final averaged results are shown in **Table 3.1.1**. A similar calibration was applied to monolayer FeO based on other STM images. The periodicity along one orientation is obviously different from the other two, which reveals an asymmetry in the Moiré cell. In contrast to previous reports, the Moiré cell (white lines in **(c)**) along with one of the directions (a_2) (see the orientation of the long edge of the white rectangle and the light blue lines), is found to be rotated by about 1° with respect to the substrate (orange lines in **(c)**).

Table 3.1.1. Comparison of structural parameters of mono- and bilayer FeO on Ru(0001).

	Orientation	Surface lattice constant [Å]	Moiré periodicity[Å]	Corrugation
1 st FeO layer	a ₁ a ₂ a ₃	3.33±0.08 3.31±0.08 3.32±0.07	21.63 ± 0.30 19.60 ± 0.47 21.32 ± 0.26	0.43±0.02
2 nd FeO layer	$egin{array}{c} a_1 \ a_2 \ a_3 \end{array}$	3.16±0.07 3.10±0.06 3.18±0.09	21.71±0.32 19.15±0.31 21.21±0.34	0.43 ± 0.02

Based on the determined structural parameters (Table 3.1.1), I proposed models of single- and double-layer FeO on Ru(0001), which are shown in Figures 3.1.3 (a) and (b), respectively. The models are constructed based on two layers of close-packed Ru atoms (lattice constant: 2.71 Å), with a perfect hexagonal structure. Using the lattice constants of 3.33 Å, 3.33 Å and 3.31 Å for the FeO monolayer, a rotation angle of about 0.12° between the iron oxide layer with respect to Ru substrate in one crystallographic direction is obtained. On the model, the single-layer FeO is represented by red ellipses with a lattice ratio of 3.32/3.31. Such arrangement will lead to a Moiré superstructure with periodicities of 21.7 Å and 19.9 Å (depending on the crystallographic direction). The Moiré unit cell is marked by the dark red parallelogram in Figure 3.1.3 (a) and corresponds to (6.5×6) FeO cell (with vectors of 21.6 Å (3.32×6.5) and 19.9 Å (3.31×6)) superimposed on (8 \times 7.33) Ru cell (with vectors of 21.7 Å (2.71 \times 8) and 19.9 Å (2.71 \times 7.33)). One of the experimental evidences for this model is the presence of incomplete Moiré cells at the edges of the 1st FeO layer. The second layer is less expanded, as it grows on top of the 1st layer which partially compensates the epitaxial strain. For the bilayer, the lattice constants are 3.16 Å, 3.18 Å and 3.10 Å in the three studied directions. The deformation of the atomic lattice causes a rotation of about 0.66° with respect to Ru substrate. In the model, the second FeO layer is represented by blue ellipses with a lattice constant ratio of 3.17/3.10. The final model, with both layers present, is shown in **Figure 3.1.3 (b).** The coincidence structure is $(7 \times 6) - \text{FeO}(111)$ on $(8 \times 7) - \text{Ru}(0001)$, as indicated by the dark blue parallelogram. Due to only 5% mismatch between the first and second FeO layer, the resulting Moiré periodicity originating from their mismatch is larger than 10 nm, thus, which is not presented on the model. The Moiré structure relates to the mismatch between the first FeO layer and the substrate (while the second oxide layer only translates it). The proposed models may explain the discrepancies observed in the literature, where the atomic spacings of FeO were reported as $3.08 \text{ Å}^{[25]}$, $3.2 \pm 0.2 \text{ Å}^{[216]}$, $3.2 \pm 0.4 \text{ Å}^{[217]}$ and $3.2 \text{ Å}^{[26]}$, with the Moiré periodicity of 21.6 Å^[25], 18.5 ± 2 Å^[216] and 18 ± 2 Å^[217]. These divergences can result in coincidence structures of either "7 on 8"^[25] or "6 on 7"^{[26][278]}.



Figure 3.1.3. Schematic models of (a) single- and (b) double-layer FeO on Ru(0001), based on the structural parameters obtained from STM images. (Adopted from Figure 2 in [214]).

In summary, FeO was grown by depositing Fe in UHV and post-oxidation. The temperature of the substrate during Fe deposition was found to affect the density of FeO islands. The oxide grows mainly in bilayer form, occasionally, monolayer-high regions were also observed in the vicinity of the bilayer ones. A detailed structural analysis of the two types of FeO islands led to the determination of their structural parameters, including height, Moiré periodicity and corrugation, atomic periodicity in three main crystallographic directions and the rotation with respect to the support. Based on these, models of both single- and double-layer FeO were constructed. The first FeO layer forms a coincidence structure of (6.5×6) FeO on (8×7.33) Ru, while the second oxide layer is constructed in the structure of (7×6) FeO on (8×7) Ru. The results explain the discrepancies observed in the literature with respect to atomic and Moiré periodicities of FeO, as well as the coincidence structures formed between the oxide and the support.

3.2. FeO/Ru(0001) subjected to atomic oxygen

Atomic oxygen treatment is one of the ways to simulate strongly-oxidizing conditions typically present during high-pressure oxidation reactions. In the case of FeO/Ru(0001), such treatment was found to reproduce the structures formed by exposing the system to millibar pressure of molecular oxygen^[29]. Therefore, studies aimed at determining the structural transformations occurring in the FeO/Ru(0001) system under strongly-oxidizing conditions were carried out.

3.2.1. Exposing Ru(0001) to atomic oxygen at RT

Firstly, I will describe a series of blank experiments performed on a clean Ru(0001) substrate, including: (i) exposition to molecular oxygen (1×10^{-6} mbar) at 950 K, which are identical conditions to those present when growing FeO; (ii) subjecting the crystal to atomic oxygen (O_{at}) at

RT.

The large-scale STM images presented in **Figures 3.2.1** (a) and (b) show the morphology of the Ru surface before and after RT-O_{at} treatment. A clean Ru(0001) after 950 K-O₂ treatment is characterized by flat terraces with straight step edges, usually covered by a mixture of $O(2 \times 1)$ (three domains rotated by 120° to each other) and (2 × 2) domains (not shown). After the RT-O_{att} treatment, the surface becomes covered with small particles/clusters. Similar clusters were also observed by the Authors of Ref. [218], however, in their case, these clusters only form at the step edges on the substrate after RT-O_{att} treatment. This may relate to much lower O_{at} dosage in their case (10 L, while I use 670 L in the experiments). A complete (1 × 1) phase can be obtained by using a dosage of more than 20 L O_{at} at RT^[219]. The lateral size of those particles is mostly less than 5 nm, and their height varies from 1 to 3 Å. The Ru step edge becomes curvy, which might be caused by the corrosion caused by atomic oxygen^[218]. These bright particles/clusters nucleate to ruthenium oxide islands (O-Ru-O trilayers), and they may further covert to RuO₂ if the critical stacking thickness is reached^[220].



Figure 3.2.1. STM image of (a) clean Ru(0001) (I = 0.1 nA, V = + 1.0 V, 500×500 nm²) and (b) Ru(0001) after RT-O_{at} treatment (I = 0.1 nA, V = + 1.0 V, 500×500 nm²). LEED pattern (64 eV) of (c) Ru after 950 K-O₂ treatment and (d) Ru after RT-O_{at} treatment. XPS O 1s spectra of (e) Ru after 950 K-O₂ treatment and (f) Ru after RT-O_{at} treatment.

The LEED patterns indicate different O coverage for two samples: a clear (2×2) structure is visible after 950 K-O₂ treatment, indicating a low coverage of chemisorbed oxygen (**Figure 3.2.1** (c)). After RT-O_{at} treatment, a diffused (1×1) pattern appears, which is believed to be related to high oxygen coverage (**Figure 3.2.1** (d)). Some early reports correlate the oxygen coverage to the diffraction pattern. On Pt(111), for example, 0.25 ML – 0.60 ML exhibits a (2×2) – O pattern, the intensity gets weaker but still visible up to 0.75 ML^[221]. Higher coverage will result in higher
background intensity and a diffused (1×1) arrangement, indicating the oxygen adlayer is not wellordered. Using atomic oxygen, up to 2.9 MLs of oxygen can be adsorbed on Pt(111)^[222]. In the case of Ru(0001) substrate, a (2 × 2) pattern corresponds to the coverage below 0.75 ML. Between 0.5 ML to 0.75 ML, the so-called 3O(2 × 2) phase starts to form, coexisting with an O(2 × 2) structure. Above 0.75 ML, the oxygen atoms will fill the holes of the 3O(2 × 2) unit cell and form a (1 × 1) structure^[223]. By exposing to high oxygen pressure, the oxygen layer on Ru(0001) will show a (1 × 1) pattern at 1.0 ML^{[224][225]} and perhaps RuO₂(110) in some extreme cases^[226].

The XPS O 1s spectra obtained after these two treatments are shown in **Figures 3.2.1 (e)** (950 K-O₂ treatment) and **(f)** (RT-O_{at} treatment). Compared to the 950 K-O₂ samples, the peak recorded for the RT-O_{at} is shifted by approx. 0.4 eV towards higher binding energy values. Such shift is caused by the O adsorption structure and coverage on the surface. A similar effect was found in the O/Rh(110)^[227]. When convert from the coexistence phase of (10×2) (0.9 - 0.95 ML) and $(2 \times 1)p2mg$ (1 ML) O structure to pure $(2 \times 1)p2mg$ phase, the main O 1s line shifts from 529.85 eV to 530. 2 eV (approx. 0.35 eV to lower binding energy, Fig. 6 in Ref. [227]). Such shift is caused by additional broaden shoulder appearing at lower binding energy at 529.4 eV, which corresponds to the (10×2) structure. Such feature also exits on different facet like on Rh(111)^[228] and Rh(100)^[229].

In summary, STM results showed that after RT-O_{at} treatment, bright particles/clusters start forming on the Ru(0001) substrate, which are most likely the precursors of ruthenium oxide. Compare to the one recorded for the sample treated with O₂ at 950 K, the maximum of the XPS O 1s signal shifts to higher binding energy values, indicating higher oxygen coverage. This is in line with the LEED results, the change from (2×2) to (1×1) pattern when going from O₂ at 950 K to O_{at} at RT, revealing higher oxygen coverage in the latter case.

3.2.2. Exposing FeO/Ru(0001) to atomic oxygen at RT

Next, the O_{at} treatment at RT on the structure of ultrathin FeO islands grown on Ru(0001) was studied. The change in morphology and composition of the oxide upon oxidation and further thermal reduction is revealed by STM, LEED and XPS. For the study, a sample consisting of 0.5 ML FeO was used.

Figures 3.2.2 (a) and **(b)** present STM images of oxide islands before and after the RT-O_{at} treatment. As expected, the pristine islands are characterized by the Moiré superstructure (inset to **Figure 3.2.2 (a)**). After the RT-O_{at} treatment, the surface becomes covered with clusters and the Moiré is no longer visible, as can be seen in **Figure 3.2.2 (b)**. In order to check the thermal stability of the system, step-wise UHV annealing at 600, 800 and 1000 K were performed. **Figures 3.2.2 (c - e)** show STM images obtained after each annealing step. Following the 600 K annealing, the surface is still rough but some clean region is visible on both oxide islands and the Ru substrate (more evident on Ru). A better comparison between the structure of the islands before and after annealing can be found in the insets to **Figures 3.2.2 (b)** and **(c)**. The dense layer of particles partially disappears. Further annealing at 800 K brings the initial islands back to the FeO-like structure, with the characteristic Moiré pattern visible in the inset of **Figure 3.2.2 (d)**, and only a

few small particles remain at the surface. Also, the Ru substrate becomes smoother. Final annealing at 1000 K results in the complete removal of particles from FeO and Ru. Thus, the results revealed that both O-rich Ru and iron oxide could be converted back to clean substrate and pristine FeO (at least from the topographical point of view).

The height profiles taken across the FeO island before (black) and after (red) the O_{at} treatment are compared in **Figure 3.2.2 (f)**, The height of pristine FeO is 5.0 ± 0.2 Å (black profile). After atomic oxygen exposure, the maximum height is larger than $7.0 \sim 9.0$ Å (red profile, precise value cannot be determined due to high surface roughness). The bright protrusions on the islands surface after RT-O_{at} treatment observed from STM images, causing the surface roughness of $1 \sim 2$ Å in height. Annealing the sample to 600 K can slightly reduce the height (not shown in the height profile), and a small fraction of islands (see dark regions in **Figure 3.2.2 (c)**) are converted back to FeO-like (determined by a height of 5.0 Å) structure. After 800 K annealing, the height of all islands converts back to a value similar to that of the initial FeO phase.



Figure 3.2.2. STM images of 0.5 ML FeO on Ru(0001) before (a) and (b) after RT-O_{at} treatment. (c - e) show post annealing in UHV for 10 min at 600, 800 and 1000 K. V = +1.0 V, I = 0.3 nA (a) or 0.1 nA (b - e), inset to (a - e)). Image size: 300×300 nm² (a - e); 5×15 nm (inset to (a), (d),

(e)); $50 \times 50 \text{ nm}^2$ (inset to (b - c)). (f) Height profiles taken across the islands in (a) (black, indicated by white arrow), (b) (red) and (d) (blue). The LEED pattern (64 eV) of pristine 0.5 ML FeO/Ru(0001) before (g) and (h) after the RT-O_{at} treatment, as well as (i) after the post UHV annealing at 1000 K for 10 min. (Partially edited from Figure 1 and Figure 2 in [215]).

The LEED patterns obtained for FeO/Ru(0001) before and after the RT-O_{at} treatment are shown in **Figures 3.2.2 (g)** and **(h)**, respectively. Apart from sharp Ru(0001) – (1×1) spots (white rhombus), the weaker (1×1) diffraction spots positioned nearby indicated the presence of a well-ordered oxide structure (yellow rhombus for pristine FeO and red rhombus for the sample treated with O_{at}). The main difference lies in the disappearance of the satellite and (2×2) spots. The former is related to the appearance of dense particles at the surface of iron oxide (invisible Moiré in **Figure 3.2.2 (b)**), while the latter can be explained as high O coverage based on blank experiments performed on clean Ru(0001). The atomic periodicity of iron oxide measured from the LEED pattern seems to compress from 3.12 ± 0.04 Å to 3.06 ± 0.05 Å. A similar FeO lattice compression, from approx. 3.19 to 3.06 Å, was also reported for FeO/Au(111) following the exposure to millibar pressures of O₂^[230]. After annealing at 1000 K, the LEED pattern (**Figure 3.2.2 (i)**) of the sample shows the (2×2) and satellite again, indicating a reversible reduction by thermal treatment.



Figure 3.2.3. XPS spectra recorded for FeO/Ru(0001) before (black) and after (red) exposure to O_{at} at RT, as well as additional UHV annealing at 600 (green), 800 (blue) and 1000 K (purple). (a) Fe 2p. (b) Fe 3p. (c) O 1s. (d) Ru 3d. (Adopted from Figure 4 in [215], all the spectra were made by Dr. Giovanni Carraro)

To get more insight into the structural transformation, a comparison of XPS Fe 2p, Fe 3p, O 1s and Ru 3d spectra was performed. The spectra were recorded for (i) 0.5 ML FeO on Ru(0001) (black); (ii) the system after RT-O_{at} treatment (red); following annealing for 10 min at (iii) 600 K (green), (iv) 800 K (blue) and (v) 1000 K (purple). Figure 3.2.3 (d) shows the Ru 3d doublets. After exposing the sample to O_{at} at RT, Ru peaks become broader, indicating the appearance of a new component. With respect to the main peak (279.9 eV), the signal assigned to the new component is centered at a higher binding energy value (located at 280.8 eV, not fitted in the spectra for better vision) and, thus, may be assigned to ruthenium oxide clusters (the position is close to

 $RuO_2^{[239]}$). The broadening feature with a new component centered at higher binding energy can also be related to the presence of highly oxygen-coordinated ruthenium atoms^[234]. Notably, the ruthenium oxide clusters may also form underneath the FeO islands, which was confirmed by a similar broadening of Ru 3d signal after applying the RT-O_{at} treatment to a full-coverage FeO on Ru(0001) (not shown). This indicates that atomic oxygen could penetrate the FeO lattice (through defects/step edge) and oxidize the substrate underneath. Therefore, the similar roughness observed on both islands and surrounding Ru substrate can be partially explained by the formation of ruthenium oxide clusters underneath the FeO. Following the annealing at 600 K in UHV, the Ru 3d lines get narrower, while higher annealing temperatures completely restore the Ru 3d spectra back to the pristine FeO/Ru(0001) state.

Due to multiple splitting effects and satellites triggered by shake-up processes^[281], as well as the surface peak^{[231][232]}, fitting Fe 2p spectra is quite complex. Therefore, a rough analysis were performed by only marking the positions correlated to Fe³⁺ (green dotted line), Fe²⁺ (reddish-brown dashed-dotted line) and metallic iron Fe⁰ (gray dashed line)^{[278][279][26][233]}, as shown in **Figure 3.2.3** (a). The contribution from Fe⁰ (signals located at 706.8 and 719.8 eV) is barely visible for all the samples. Both 2+ and 3+ iron exists in pristine FeO. The contribution from Fe²⁺ (signals positioned at 709 and 722.6 eV) decreases after RT-O_{at} treatment, while Fe³⁺ (711.0 and 724.4 eV) becomes more dominant. In particular, the Fe³⁺ satellite at 718.8 eV becomes evident. These higher oxidation state satellites disappear after vacuum annealing at 600 K, suggesting a thermal reduction of the oxygen-rich phase. Still, the sample maintains a relatively high Fe³⁺:Fe²⁺ ratio compare to pristine FeO. The Fe 3p spectra present in **Figure 3.2.3** (b) and O 1s spectra in (c) showed similar trend – ultrathin FeO islands grown on Ru(0001) undergo a transformation to an O-rich oxide phase when subjected to atomic oxygen, while high-temperature UHV annealing leads to a reduction back to pristine FeO phase.

More detailed analysis on the phase transition can be derived from the Fe 3p and O 1s spectra shown in Figures 3.2.4 (a - d). Pristine FeO phase exhibits a broad feature which is a superposition of two components originating from Fe^{2+} (53.6 eV) and Fe^{3+} (55.4 eV)^[279]. The ratio between the components is close to 1:1, as shown in Figure 3.2.4 (a). In the spectrum obtained after the RT- O_{at} treatment (Figure 3.2.4 (c)), the main peak shifts to higher binding energy and the line gets narrower, indicating the dominant Fe³⁺ contribution. The O 1s line could be fitted with five components: O(1) originates from a metal oxide, i.e. FeO (both 2+ and 3+ states), centered at 529.9 eV^{[85][231]}. It can also be assigned to the chemisorbed oxygen on Ru(0001) especially the O species forming (2×2) and (2×1) domains on Ru substrate^{[160][234]}. O(2) is related to surface hydroxide groups/OH-groups^{[85][160][235]}, located at 530.9 eV. This component is, however, insensitive by varying oxidizing and reducing conditions, suggesting that more components may be centered at similar binding energy and also contribute to the intensity. One possible component is a "satellite" which originates from the many-body screening effect of the conduction electrons of ruthenium oxide^[160]. In some early reports, this component was also assigned as originating from "nonstoichiometric surface oxygen atoms"^[236]. O(3) comes from CO contamination, centered at 532.1 $eV^{[237]}$. O(4) is assigned to adsorbed H₂O, positioned at 533.4 $eV^{[238]}$. O(5) is considered to originate from weakly bonded oxygen (WBO) species which can be formed on both Ru substrate^[239] and FeO islands^{[240][241]}, with the peak position is at 528.9 eV. These species are sometimes referred to as surface-active oxygen^{[85][227]}. The biggest difference between the sample before and after atomic oxygen treatment is the appearance of O(5) (please compare **Figures 3.3.3 (c)** and **(d)**). This WBOs usually appears under strongly oxidizing conditions and is the active species in catalytic reactions^[12].



Figure 3.2.4. Fitted Fe 3p XPS spectra for 0.5 ML FeO/Ru(0001) before (**a**) and after (**b**) exposure to O_{at} at RT. Fitted O1s XPS spectra obtained for 0.5 ML FeO/Ru(0001) before (**c**) and after (**d**) exposure to O_{at} at RT (Adopted from Figure 6 in [215], all the spectra were fitted by Dr. Giovanni Carraro).

The variation of the five oxygen species is shown in **Table 3.2.1**. The fraction of lattice oxygen decreases after RT-O_{at} treatment, while the intensity of WBOs significantly increases. The amount of other species, like hydroxyl groups, CO and H₂O remain similar. The Fe³⁺/Fe²⁺ ratio changes from 1:1 to more than 5:1, indicating that atomic oxygen strongly oxidizes the sample. For this case, the newly-formed iron oxide phase is roughly assigned as FeO_x (1 < x < 2). Vacuum annealing at 600 K decreases the amount of WBOs and partially reduces the concentration of CO and H₂O, which is not surprising since 600 K is a high temperature to desorb CO^[242] and H₂O^[243] from Ru(0001). This desorption temperature of WBOs from FeO_x/Ru(0001) is also quite comparable to iron oxide film on Pt(111) (573 K^[240]) and Au(111) (635 K^[19]). Further annealing at higher temperature shows the limited effect on the sample, which is in agreement with STM results (no further obvious morphological change).

Table 3.2.1. Contribution of different oxygen species in different samples (derived from fitted XPS O 1s spectra), including 0.5 ML FeO, the sample after the RT-O_{at} treatment and additional stepwise annealing at 600 K, 800 K and 1000 K (the values were calculated by Dr. Giovanni Carraro).

|--|

	O(1) 529.9 eV O-Fe, O-Ru	O(2) 530.9 eV OH, satellite	O(3) 532.1 eV CO	O(4) 533.4 eV H ₂ O	O(5) 528.9eV WBOs
0.5 ML FeO	69%	19%	8%	3%	1%
O _{at} at RT	55%	21%	10%	4%	10%
600 K annealing	70%	18%	8%	2%	1%
800 K annealing	69%	21%	8%	2%	0%
1000 K annealing	69%	21%	8%	2%	0%

In summary, STM results showed that RT-O_{at} treatment of FeO/Ru(0001) leads to the formation of an oxygen-rich phase exhibiting increased surface roughness, with the height of the oxide islands increasing by more than 2 Å. The obtained LEED pattern of the O_{at}-treated samples showed diffused spots in a (1 × 1) arrangement, corresponding to oxidized Ru substrate, as well as additional FeO – (1 × 1) reflexes. The increased background intensity indicated the disordering of the surface. The disappearance of satellite spots is related to the non-presence of the Moiré superstructure. The analysis of XPS results revealed a higher oxidation state of iron and broadening of the ruthenium signals after RT-O_{at} treatment. Moreover, the appearance of a new oxygen component assigned to WBOs (surface active oxygen) was noticed. The strongly oxidized sample was found to have a FeO_x (1 < x < 2) stoichiometry. Following the annealing at 600 K in UHV, the FeO_x partially transformed back to pristine FeO, while additional annealing above 800 K completely reversed the oxygen-rich phase to the initial FeO phase.

3.2.3. Exposing FeO/Ru(0001) to atomic oxygen at 700 K

In the following, the experiment was extended to a high-temperature O_{at} reaction. Up to 500 K, the structure was found to be similar to that of RT-treated samples. Therefore, for high-temperature treatment, temperatures above 700 K were used. Following the structural characterization, the thermal stability of the system was determined. Similar to the RT case, the studies were based on STM, LEED and XPS results.

Figures 3.2.5 (a - c) show the LEED patterns obtained for the 0.5 ML FeO/Ru(0001) sample subject to atomic oxygen at 550 K, 700 K and 900 K, respectively. For the 550 K treatment, the FeO spots are still visible. When 700 or 900 K was used, only diffused (1×1) spots can be observed (with a bit sharper spot for the 900 K case). Therefore, 700 K is a reasonable temperature to form a different iron oxide structure than the RT case and worth a further investigation. The oxidized sample is further denoted as 700 K-O_{at}. A blank experiment was performed on a clean Ru(0001) substrate. The LEED pattern obtained after the 700 K-O_{at} treatment on Ru(0001) is shown in **Figure 3.2.5 (d)**. Comparing the LEED patterns in **(b)** and **(d)**, the diffused spots are more likely to be attributed to Ru. Such temperature-dependence behavior is related to the incorporated oxygen. The

O-rich (1×1) films on Ru are usually poorly-ordered and form a so-called "surface oxide" (shown in the RT case in the previous section), this is identified as the precursors for O–Ru–O trilayer, which start to nucleate at temperatures above 550 K^[45]. To form ordered rutile RuO₂ structure, more intense condition is needed. Either high temperature with low dosage (1×10^{-7} mbar at 1053 K for 20 min) or low temperature but high dosage (3×10^{-5} mbar at 653 K for 120 min) is needed^[244], which is out of the scope of the studies showing in this work.



Figure 3.2.5. LEED patterns (64 eV) of 0.5 ML FeO/Ru(0001) sample subjected to O_{at} (1 × 10⁻⁶ mbar for 15 min) at (a) 550, (b) 700 and (c) 900 K. (d) Bare Ru(0001) after 700K- O_{at} treatment.

The STM image of FeO/Ru(0001) after 700 K-O_{at} treatment is shown in Figure 3.2.6 (a). Three different types of islands with different heights can be observed. The lowest flat island has a newly-formed superstructure, which is shown in detail in the inset to the figure. The superstructure has a triangular symmetry with 36 ± 0.2 Å periodicity. Figure 3.2.6 (d) shows the atomicallyresolved structure and reveals that the atomic periodicity is approx. 3.5 ± 0.15 Å. The height of this island is about 4.8 ± 0.1 Å, which is slightly lower than pristine FeO/Ru(0001) (please compare the height profiles in Figure 3.2.6 (e): black - initial FeO phase; red - a new phase of iron oxide formed after 700 K-Oat treatment). The new phase is most likely a Fe₂O₃-like structure^{[245][246][247][248][249]}. In some cases, the (1×1) terminated Fe₂O₃ may exhibit specific structural reconstruction if the iron atoms located at the interface connected to the metal substrate, thus leading to a lattice compression^[250]. The middle- and highest-level islands can be barely resolved with STM due to high roughness, with estimated heights of ~ 9 and ~ 12 Å, respectively. The nucleating clusters are mostly located on top of oxide islands. The Ru substrate, on the other hand, seems to be atomically flat. This can be explained by a complete uniform layer of chemisorbed oxygen in a (1×1) arrangement. Other possibilities, like full coverage of well-ordered RuO₂ (a rutile crystal structure), can be safely excluded, as none stripe-like structures are resolved by STM^[251].

After annealing at 800 K, the surface became rougher and some new oxide phases were obtained, as shown in **Figure 3.2.6 (b)**. Some regions, marked with a white square in the image, could be atomically resolved. Region 1 showed a slightly distorted superstructure of the one observed in (a), while region 2 transformed to a more deformed structure. The atomically-resolved STM images are shown in **Figures 3.2.6 (b**₁) and (**b**₂), while the corresponding atomic periodicities are given in the table below. The values could not be determined precisely due to high surface corrugation. The height profiles taken across different islands (an exemplary one is shown as the blue line in **Figure 3.2.6 (e**)) give different height values, but some of them are quite similar to the surface structure before annealing (red). Higher annealing temperature, 1000 K, leads to a completely disordered surface, as shown in **Figure 3.2.6 (c**).



Figure 3.2.6. STM images of (a) 0.5 ML FeO on Ru(0001) subjected to 700 K-O_{at} treatment, (b) and (c) show the structure after step-wise annealing for 10 min at 800 and 1000 K, respectively. Atomically-resolved STM images of (d) the superstructure shown in the inset to (a), and the superstructure in (b) marked by (b₁) 1 and (b₂) 2. The averaged atomic periodicities are shown in the table below. I = 0.1 nA, V = + 1.0 V ((a) and (b), inset to (a) – (b)) or V = + 0.1 V, I = 0.1 nA ((d), (b₁) and (b₂)). Image size: 300 × 300 nm² ((a) and (b)); 15 × 15 nm² (insets to (a) and (b)); 8 × 8 nm² ((d), (b₁) and (b₂)). (e) present height profiles taken across the islands in (a) (black – pristine FeO; red – the sample after 700 K-O_{at} treatment; blue – the sample after annealing at 800 K for 10 min) (Partially edited from Figure 3 in [215]).

The XPS results obtained for the sample treated with O_{at} at 700 K are shown in **Figures 3.2.7** (**a** - **d**). The Ru 3d spectra show a similar broadening feature with additional peak appearing at the high binding energy side, indicating a more uniform RuO_x structure (observed in STM) at elevated temperature. However, 800 K annealing does not bring the shape to clean Ru-like. Sharp Ru 3d signals are only observed after the sample is annealed at 1000 K. When it comes to iron oxide, the Fe³⁺:Fe²⁺ ratio dramatically increases after the 700 K-O_{at} treatment (the concentration of Fe³⁺ changes from 52% to 80%). Compared to the sample subjected to RT-O_{at} treatment, the reduction is much less pronounced upon annealing at 800 K (the Fe³⁺ still occupies 73%). However, further annealing at 1000 K leads to a significant reduction, with metallic iron Fe⁰ starting to appear (27%). It may also be noticed that the intensity of the iron signal decreases enormously upon annealing at 1000 K, which is caused by the iron sublimation or/and diffusion into the Ru substrate. Even though there was no direct research concerning the reduction of Fe₂O₃ on Ru(0001), it is known that Fe₂O₃ can be reduced to metallic iron under strongly reducing conditions based on the iron oxide phase diagram^[245]. Moreover, in the Fe₂O₃/Pt(111) system, the oxide can decompose with Fe diffusing into the Pt substrate already above 900 K^[94].



Figure 3.2.7. XPS spectra of 0.5 ML FeO on Ru(0001) before (black) and after (red) exposure to atomic oxygen at 700 K, as well as step-wise annealing at 600 (green), 800 (blue) and 1000 K (purple): (a) Fe 2p; (b) Fe 3p; (c) O 1s; (d) Ru 3d (Adopted from Figure 7 in [215], all the spectra were made by Dr. Giovanni Carraro).

Table 3.2.2 shows the change of different oxygen species fitted from O 1s spectra obtained after 700 K-O_{at} treatment. In contrast to the RT case, the O(1) component remains at the same level (from 68% to 67%) after 700 K treatment, while this value dropped to 55% after the RT exposure. Instead, the amount of surface OH groups significantly decreases and a small reduction in CO contamination is observed. This may relate to the formation and desorption of $H_2O^{[252]}$ and $CO_2^{[18]}$ from the surface during the high-temperature oxidation process. The WBOs show a similar increase (from 1% to 10%) to the RT-O_{at} case, and are partially removed after annealing at 800 K. A slight increase of lattice oxide and OH-group can be noticed. Annealing at 1000 K further reduces the WBOs, while oxygen species such as the CO and H₂O contamination increase accordingly.

Table 3.2.2. Contribution of different oxygen species fitted from the XPS O 1s spectra. Comparison of data obtained for 0.5 ML FeO, the sample exposed to atomic oxygen at 700 K and step-wise annealed at 800 and 1000 K (the values were calculated by Dr. Giovanni Carraro).

	O(1) 529.9 eV O-Fe, O-Ru	O(2) 530.9 eV OH, satellite	O(3) 532.1 eV CO	O(4) 533.4 eV H ₂ O	O(5) 533.4 eV WBOs
0.5 ML FeO	68%	20%	8%	3%	1%
O _{at} at 700 K	67%	16%	6%	3%	8%
800 K annealing	69%	18%	6%	3%	4%
1000 K annealing	70%	16%	9%	4%	1%

In summary, the obtained LEED results indicate that O_{at} exposure at 700 K leads to the formation of a new iron oxide phase. The STM images of FeO/Ru(0001) after 700 K-O_{at} treatment showed an atomically-flat Ru substrate, indicating the formation of a complete O(1 × 1) overlayer. Additionally, few types of islands were visible through different contrast (height of islands). The

lowest flat islands exhibited a triangular superstructure with 36 ± 0.2 Å periodicity, a lattice constant of 3.5 ± 0.15 Å and a height of 4.8 ± 0.1 Å. Higher islands were relatively poorly ordered. The flat islands with superstructure are assigned to Fe₂O₃-like structure. LEED did not show the corresponding pattern, which may be related to the very low coverage of the ordered regions. The XPS analysis showed that after 700 K-O_{at} treatment, the Fe³⁺ state dominates in the mixed oxide phase and the amount of WBO species significantly increases – suggesting the formation of an oxygen-rich iron oxide film. Vacuum annealing at 800 K led to the partial disordering of the Fe₂O₃-like, even though the oxidation states ratio did not change much and the WBOs was only partially reduced. Additional annealing at 1000 K resulted in a rough and disordered surface. The concentration of Fe³⁺ reduced, while metallic iron Fe⁰ started appearing, suggesting a significant reduction of the new oxygen-rich oxide phase.

3.3. Summary and discussion

In this chapter, the results concerning the structure of mono- and bilayer FeO on Ru(0001), as well as the structural transformations taking place in the FeO(111)/Ru(0001) system when subjected to Oat treatment at RT and 700 K. In addition, the thermal stability of O-rich iron oxide phases formed upon O_{at} exposure was determined through step-wise vacuum annealing. The first (interface) FeO layer was found to be about 0.4 Å higher than the second one. Both single- and double-layer FeO were found to exhibit similar Moiré periodicity along the same crystallographic, but the determined atomic spacings of the first layer are by about 5% larger than that of the second layer. Thus, the structural parameters of oxide islands highly depend on the layer thickness and the crystallographic direction. The difference in spacing along different crystallographic directions leads to the appearance of an asymmetry of atomic and Moiré cells. Models based on the determined values were proposed. The first oxide layer forms a coincidence structure of (6.5×6) -FeO on (8×7.33) -Ru. Due to the small lattice misfit of the first and second layer, the Moiré superstructure between them would be as large as 10 nm and, thus, does not appear in the system. The second FeO layer translates the Moiré structure of the first layer, with the double-layer exhibiting a coincidence structure of (7×6) -FeO/(8×7)-Ru with the substrate. Incomplete Moiré cells are often found at the edge of the single-layer FeO islands. Sometimes, a rotation of around 1º between the double FeO layers and Ru substrate can be observed.

After exposing the 0.5 ML FeO on Ru(0001) sample to O_{at} at RT, the surface became covered with clusters that significantly increased the surface roughness (both on iron oxide islands and the Ru substrate). On average, the height of the oxide islands increased by more than 2 Å. The recorded LEED pattern was in line with STM results, as only diffused Ru and FeO spots, without any signatures of the Moiré structure or chemisorbed oxygen on Ru, were observed. Also, the background intensity increased. XPS revealed a higher concentration of Fe³⁺ and an increase in the amount of WBOs. All these results confirmed the transformation of FeO into an O-rich FeO_x phase and oxidation of the Ru(0001) substrate. Noticeably, the fraction of surface hydroxyl groups, CO and H₂O slightly increased, indicating higher reactivity of the O-rich phase.

In the case of the sample subjected to 700 K-Oat treatment, few types of islands with different

heights were observed. The lowest islands were flat and had a height of 4.8 ± 0.1 Å, which is slightly lower than the height of pristine FeO. Such islands exhibit a triangular superstructure with 36 ± 0.2 Å periodicity and 3.5 ± 0.15 Å atomic periodicity. The middle height (almost double the pristine FeO height) and highest-level islands (2.5 times higher than FeO) were found to exhibit rough surfaces. LEED pattern only showed diffused (1 × 1) spots, which might have been due to the very low coverage of ordered flat islands. The XPS spectra showed an increase in the Fe³⁺:Fe²⁺ ratio, as well as the amount of WBOs. The rest of the oxygen species remained at a similar level, suggesting a less reactive surface compared to the one obtained after RT-O_{at} treatment.





Figure 3.3.1. $Fe^{2+}:Fe^{3+}$ ratios obtained from the fitted XPS Fe 3p spectra of 0.5 ML FeO on Ru(0001), the sample subjected to atomic oxygen and then reduced by step-wise UHV annealing (Top part: RT-O_{at} treatment, bottom part: 700 K-O_{at} treatment) (Adopted from Figure 5 in [215], made by Dr. Giovanni Carraro).

As far as thermal stability is concerned, vacuum annealing at 600 K can reduce the density of clusters of the sample treated with O_{at} at RT. The Fe³⁺/Fe²⁺ ratio and the concentration of WBOs decreased. Further annealing at 800 and 1000 K converted the sample back to the initial FeO phase, as confirmed by STM, LEED and XPS. Therefore, the RT-O_{at} treated sample can be reverted back to pristine FeO by thermal reduction. UHV annealing at 600–800 K of the sample treated with O_{at} at 700 K led to a more complex structural transformation. The low-level flat islands became disordered. The oxidation state of Fe did not change significantly and the WBOs was only partially removed. The sample surface became completely disordered after annealing at 1000 K. Although there is a significant Fe³⁺ reduction, the appearance of metallic iron Fe⁰ indicates that the transformation to an O-rich phase by exposing FeO/Ru(0001) to atomic oxygen at 700 K is irreversible. The reversible transformation of FeO/Ru(0001) to an O-rich phase at T < 550 K showed that the system has potential as an oxidation catalyst.

4. Catalytic properties of ultrathin iron oxide films on Ru(0001)

The chapter presents preliminary results concerning the catalytic activity of FeO/Ru(0001) and FeO_x/Ru(0001) (1 < x < 2) in the low temperature CO oxidation reaction. Even though further studies are needed to elucidate the reaction mechanisms, the presented data provide hints on the structural transformations taking place in both systems upon CO exposure. For catalytic studies, bilayer FeO islands covering 50% of the substrate (0.5 ML coverage) were prepared by depositing Fe onto a Ru(0001) substrate preheated to 500 K or held at RT and oxidation in 1×10^{-6} mbar O₂ at 950 K. As discussed in the section 1.3, the O-covered Ru(0001) is a reactive surface for CO adsorption. To better understand the role of the substrate, blank experiments on the CO adsorption on Ru(0001) were performed.

There are two sections in this chapter. In section 4.1.1, the structure and chemical composition of FeO/Ru(0001) before and after CO exposure at RT, is discussed. In section 4.1.2, the results on the interaction of CO with the FeO/Ru(0001) sample subjected to RT-O_{at} treatment, denoted as FeO_x/Ru(0001), are presented. The surface morphology and film composition are analyzed before and after the CO exposure, both at RT and 600 K. STM, LEED and XPS measurements were involved in the data analysis.

4.1.1. CO interaction with Ru(0001) and FeO/Ru(0001)

The catalytic oxidation of CO at platinum-group metal surfaces is probably the most extensively studied reaction under UHV condition, as was introduced in section 1.3.1. Various adsorption structures were described in the literature for CO/Ru(0001), depending on the coverage and temperature, the observed pattern can be ascribed to $(\sqrt{3} \times \sqrt{3})$ –R30°(<0.33 ML, usually formed at 200 – 400 K^{[253][254]}), $(2\sqrt{3} \times 2\sqrt{3})$ –R30°(0.58 ML, usually below 200 K^[255]), etc. The maximum adsorption coverage of CO on Ru(0001) at RT is about 0.54 ML^[256]. Around (and below) room temperatures, oxygen atoms become mobile enough to arrange themselves into a honeycomb structure in the presence of coadsorbed CO molecules, leading to an ordered $p(2 \times 2)$ –(O + CO) overlayer structure^[47] (0.25 ML, see Figure 1 in Ref. [257] and Figure 2 in Ref. [258] for the structure model), or $p(2 \times 1)$ –(2O + CO) overlayer structure (0.5 ML, see Figure 4 in Ref. [259] for the structure model). In the $p(2 \times 2)$ –(O + CO) phase, the O atoms occupy hcp sites as the pure (2 × 2)O phase to open top sites for CO to chemisorb on. Notably, the CO molecules are tilted alternately in one of the three orientations by ~ 13°^{[257][258]}.

A few blank experiments were performed on bare Ru(0001) to evaluate the CO adsorption character. The clean Ru was firstly oxidized in 677 L O₂ (1×10^{-6} mbar for 15 min) at 950 K (the same temperature to form FeO), resulting in formation of (2×2) O network, as can be seen from the corresponding LEED patterns in **Figures 4.1.1 (a)**. The (2×2) or (2×1) arrangement is still

visible after 22.6 L (1×10^{-7} mbar for 5 min) CO exposure at RT, with the only change being the intensity of the reflexes, presenting in **Figures 4.1.1 (b)**. Additional 22.6 L O₂ exposure (1×10^{-7} mbar for 5 min) at RT was applied, no obvious change can be observed as shown in **Figures 4.1.1 (c)**. One may notice the (2×2) spots of O/Ru(0001) have similar intensity, while after CO and additional O₂ exposure, those spots are less intense and some of the reflexes appear weaker than the others. This observation confirm the formation the coadsorbed (O + CO) structure on Ru(0001) as described in the literature.



Figure 4.1.1. (a) LEED patterns (64 eV) of O(2 \times 2)/Ru, (b) CO/O(2 \times 2)/Ru (after 22.6 L CO exposure at RT) and (c) O₂/CO/O(2 \times 2)/Ru (after 22.6 L O₂ exposure at RT). XPS O1s spectra of (c) CO/O(2 \times 2)/Ru and O₂/CO/O(2 \times 2)/Ru.

To estimate the ratio of CO and O, XPS was performed for each sample. The O 1s line of $CO/(2 \times 2)O/Ru(0001)$ (light red dotted line, fitting by dark red solid line) and $O_2/CO/(2 \times 2)O/Ru(0001)$ (light blue dotted line, fitting by dark blue solid line) are shown in **Figure 4.1.1 (b**). Apparently, the main O 1s line is located at 531.7 eV after RT-CO treatment, closer to CO/Ru(0001) peak position (532.1 eV) than O/Ru(0001) (529.9 eV), suggesting the domination of CO component. Here, I checked a bit more details on the sample after CO exposure and additional O₂ treatment, the XPS O 1s spectra of these two samples is shown in **Figure 4.1.1 (c**). From the comparison, it is clear that additional low pressure O₂ at RT did not change the O intensity significantly, but with a slightly more broaden lineshape and higher shoulder at ~ 530 eV (chemisorbed oxygen on Ru) of the spectra. This is in accordance with the LEED results.

Next, similar experiments were performed on FeO/Ru(0001). The LEED pattern of pristine sample is shown in **Figure 4.1.2 (a)**, with the characteristic Ru(0001)– (1×1) , FeO(111)– (1×1) , Moiré satellite and the O(2 × 2) reflexes. The LEED pattern recorded after exposing the sample to 22.6 L CO at RT, presented in **Figure 4.1.2 (b)**, does not show obvious change. To obtain better

vision, the zoom-in pattern of (a) (blue circle) and (b) (red circle) is presented below. Two things should be mentioned here: (i) additional spots appear between the first and second order satellite spots, as marked by the yellow dotted ellipses, with weaker intensity compare to the surrounding beams. This may relate to small fraction of new reconstruction surface structure. (ii) The intensity of the elongated (2×2) beams (could also be artificial effect) becomes weaker, which agrees the results obtained above (weaker intensity of coadsorbed (O + CO)–(2×2) beams after CO RT-treatment on O-covered Ru). Subsequent oxidation (1×10^{-6} mbar O₂ at 950 K for 10 min) and repeated CO exposure at RT were applied, and the corresponding LEED pattern can be seen from **Figure 4.1.2 (c)** and (d). However, the change between these diffraction patterns is barely observed (the new-appeared spots remain on the surface after the further process).



Figure 4.1.2. LEED patterns (64 eV) of (a) 0.5 ML FeO/Ru(0001), (b) the sample after exposure to 22.6 L of CO at RT, (c) reoxidation and (d) after re-exposure to 22.6 L CO at RT.

The information obtained from LEED patterns is quite limited, therefore, the surface morphology of pristine and CO exposed samples was addressed with STM. **Figure 4.1.3 (a)** shows an STM image of pristine FeO. After exposure to 677 L of CO (1×10^{-6} mbar at RT for 15 min), some triangular protrusions and bright triangular line defects appear on top of FeO islands, as can be seen from **Figure 4.1.3 (b)**. More clear view of these features is given in the higher magnification image shown in **Figure 4.1.3 (c)**. The protrusions may be related to adsorbed CO or other contaminants (which will be discussed in section 4.2). The bright triangular species, on the other hand, could be assigned to oxygen dislocation loops^{[260][261]}. The edges of triangular defects surrounding the Moiré unit cell have a height of 0.5 - 0.7 Å with respect to the maxima of the Moiré cell. Similar structures found previously were assigned to O adatoms. These are usually found in oxygen-rich iron oxide film on single crystals. Noticeably, the atomically-resolved image, presented in **(e)**, also shows CO molecules adsorbed on Ru(0001) at a relatively low coverage. Similar structure was observed for < 0.2 ML FeO on Pt(111) pre-covered with an O(2 × 2) phase, which was found to significantly increase the CO adsorption compare to clean Pt(111) substrate^[58].



Figure 4.1.3. STM images obtained at different stages of CO exposure to FeO/Ru(0001) at RT experiment. (a) 0.5 ML FeO/Ru(0001). (b), (e) Exposure to 677 L CO at RT. (c), (f) Reoxidation by exposing 667 L O₂ at RT. (d) Re-exposure to 29775 L (2707 + 27068) of CO at RT. (a - d): I = 0.7 nA (a) or 0.1 nA (b - d), V= + 1.0 V, 100 × 100 nm². (e) and (f): I = 0.1 nA, V = + 1.0 V, 50×50 nm².

Following the RT-oxidation (using 1×10^{-6} mbar O₂ for 15 min) of the CO-exposed sample, the formation of additional O adatom dislocation loops is observed, with some of them in enlarged size. The number of bright clusters is significantly reduced, as shown in **Figure 4.1.3 (c)**. Rarely, oxygen vacancy dislocations (line defects appearing dark on STM images^{[262][263]}) can be observed (**Figure 4.1.3 (f)**), indicating the formation of oxygen-poor regions. The adsorbed CO molecules on Ru(0001) are not as visible as before reoxidation, which could be either caused by the tip condition or the coexistence of CO molecules with additional O. The second CO exposure at RT, carried out for a longer time and higher pressure (by firstly introducing 1×10^{-6} mbar CO for 60 min and then increasing the pressure to 1×10^{-5} mbar for the rest 60 min), resulted in a similar morphology to the one observed after the first-time exposure, bright protrusions and small O adatom dislocation loops appear again, only with less density compare to the first CO reaction, as shown in **Figure 4.1.3 (d)**.

In order to get more insight into the structural evolution of FeO/Ru(0001) upon subsequent CO and O₂ exposure, a series of XPS spectra was recorded. In particular, a set of data was applied for presenting the Fe 2p and O 1s XPS spectra, as shown in **Figure 4.1.4 (a)** and **(b)**. The sample named as "CORT" is prepared by subjecting FeO 22.6 L CO (1×10^{-7} mbar for 5 min) at RT, while "CORT2" used a slightly higher condition by 226 L CO dosage (1×10^{-6} mbar for 5 min) at RT. The reoxidation for both cases of "O₂_CORT" and "O₂_CORT2" are the same, where 667 L O₂ was involved in the process (1×10^{-6} mbar for 15 min) at RT. Compare to the pristine FeO, the

main line of Fe 2p obtained on the sample after subjecting to CO at RT, is shift to higher binding energy of about 1 eV. A bit higher O intensity is also found in O 1s spectra. This indicates a slightly higher overall oxidation states of iron, which can be also seen through those O dislocations shown in the STM images.

In general, if one excludes the spectra from pristine FeO, a repeatable reaction pattern can be observed. Sample after CO-RT treatment, a shoulder appears near 707.3 eV in the spectra (see the red solid arrow in **Figure 4.1.4 (a)**), indicating a reduction transition phase (the typical peak positions near this value are: 706.8 eV (metallic Fe0) and 709.0 eV (Fe²⁺) as introduced in Chapter 3). The O 1s spectra, on the other hand, a broaden feature at higher binding (see the red dotted arrow in **Figure 4.1.4 (b)**) confirms the incensement of CO component (~ 530.9 eV). Another observation probably worth mentioning here is that the intensity of Fe 2p and O 1s shows a reverse trend. In other words, compare to sample treated by O₂ (blue lines), sample subjected to CO (red lines) has higher O 1s intensity but lower Fe 2p signals. This may due to the bright clusters formed on the FeO and adsorbed CO molecules on Ru(0001) substrate (where O was present already at saturated coverage under the certain condition). More similar experiments were performed, and regardless the variation of the CO dosage (both pressure and time), this reaction pattern remains the same.



Figure 4.1.4. (a) Fe 2p and **(b)** O 1s XPS spectra of 0.5 ML FeO (black solid line) exposed to repeated CO at RT (red lines) and O_2 at RT (blue lines) (obtained from one set of data). Analysis of contribution of different chemical species to XPS Fe 3p signals **(c)** and O 1s **(d)** of pristine FeO/Ru(0001), as well as the sample exposed to cyclic CO and O_2 treatments at RT (averaged from

various set of data).

To conclude the observation in a more statistic way, the averaged contribution of different species is determined from a few deconvoluted Fe 3p (for simplicity) and O 1s XPS spectra from three types of samples: (i) pristine 0.5 ML FeO, denoted as 0.5 ML FeO; (ii) FeO/Ru(0001) exposed to a certain amount of CO at RT (some with different dosage), denoted as CORT; (iii) the samples reoxidized by 667 LO2 at RT, denoted as O2 CO RT. The obtained results for iron states are shown in Figure 4.1.4 (c). Where the ratio of Fe^{2+} : Fe^{3+} is almost 1:1 for the pristine FeO, the CO-treated sample has slightly higher ratio (but with quite big deviation), indicating a more oxidized sample than FeO. The reoxidized samples exhibit higher ratio of approx. 1.38 (1.2~1.5 considering the deviation). The oxygen species analysis is presented in Figure 4.1.4 (d). The highest fraction among all three types of samples are the lattice oxygen in metal oxide (denoted as the O(1)component in the graph; blue bar). The averaged value of this component decreases from 61.2% to 49.2% after CO exposure at RT and increases to 56.1% following the reoxidation (as a fixed trend even considering the deviation). This indicates the chemisorbed oxygen is reduced after CO treatment, which cannot be fully recovered to the initial state. Notably, the averaged value of components originating from CO (O(3); dark blue bar) increase by 3.5% (from 8.8% to 12.3%) after CO treatment, and reduce by 1.8% (from 12.3% to 10.5%) after reoxidaiton. Again, this is a fixed trend even add/minus the deviation. The other components (except WBOs), showing similar trend along the CO exposure (some with big deviation), which may be caused by the impurities in the CO gas line during the experiments.

In summary, both CO and O_2 can adsorb on Ru(0001) substrate at RT (O_2 dissociatively). The XPS analysis shows that exposing 0.5 ML FeO on Ru(0001) to CO at RT increases the concentration of CO-Ru and CO-FeO components, making the sample slightly more oxidized. Moreover, CO induces the appearance of O adatom dislocations and bright clusters on FeO islands from STM images. This may explain the change in the LEED pattern, i.e. decreasing intensity of the $O(2 \times 2)$ spots and appearing additional spots within the FeO satellites reflexes. However, the above findings only apply to the case of CO exposure to pristine FeO/Ru(0001) sample. Although it is barely seen from LEED pattern, the iron oxide becomes more oxidized after reoxidation at RT, as evidenced by the increased Fe³⁺: Fe²⁺ ratio observed with XPS and the formation of extended O adatom dislocation loops seen with STM. Applying the RT-CO treatment to the reoxidized sample results in the decrease of the number of O dislocation, and thus, reduce of the iron oxidation state (still higher than pristine FeO). Regardless the CO dosage (both pressure and exposing time), the oxidation/reduction process can be repeated for several times, and showing similar reaction pattern (exclude the pristine FeO in this case).

4.1.2. CO interaction with FeO_x/Ru(0001) ($1 \le x \le 2$)

Further experiments were performed on the O-rich iron oxide phase (FeO_x/Ru(0001)) formed by exposing FeO/Ru(0001) to O_{at} at RT. The reactivity was tested at 600 K, i.e. the temperature at which the FeO_x phase starts reducing (see section 3.2.2), and at RT (to compare with pristine FeO). Five different samples are compared: (i) 0.5 ML FeO; (ii) RT-O_{at}: after RT-O_{at} treatment (FeO_x); (iii) CORT: FeO_x exposed to CO at RT; (iv) CO600K: FeO_x exposed to CO at 600 K; (v) UHV600K: FeO_x after vacuum annealing at 600 K.

The change in morphology of the 0.5 ML sample treated with different condition were addressed with STM. **Figure 4.1.5 (a)** shows the STM image of pristine FeO islands grown on Ru(0001). After the RT-O_{at} treatment the surface becomes rougher on both the substrate and the oxide regions, as shown in **Figure 4.1.5 (b)**, indicating high O coverage on Ru and the formation of an oxygen-rich iron oxide phase. For the sample subjected to 451 L CO (1×10^{-6} mbar for 10 min) at RT, no significant change in morphology can be seen, except for the slightly reduced surface roughness, as shown in **Figure 4.1.5 (c)** – this may indicate CO reaction on FeO_x/Ru(0001) requires thermal activation.



Figure 4.1.5. STM images at different stages of CO exposure/UHV annealing to FeO_x/Ru(0001). (a) 0.5 ML FeO/Ru(0001). (b) FeO_x, formed by 667 L RT-O_{at} treatment on FeO. (c) After 451 L CO exposure to FeO_x at RT. (d) UHV annealing of FeO_x at 600 K for 10 min. (e) 1353 L CO reaction on FeO_x at 600 K. (f). Magnified images of edges and small islands of sample after CO600K treatment in (e). (a) – (f): I = 0.1 nA, V = +1.0 V. (a - e): 200×200 nm². (f): 30×30 nm².

Therefore, the experiment of 1353 L CO (1×10^{-6} mbar for 30 min) reaction at 600 K was further performed, the corresponding STM image is shown in **Figure 4.1.5** (e). Ru substrate gets cleaner with only a few bright protrusions remaining on top. The oxide islands also become less rough and a periodic distorted superstructure can be observed along the edges of the islands or sometimes the whole islands with small size (see the magnified image in **Figure 4.1.5** (f)). The Moiré-like structure formed at the vicinity of island edges after CO reaction at 600 K were further analyzed in details. The height is estimated between 5.8 - 6.5 Å (0.8 - 1.5 Å higher than the height of a double-layer FeO/Ru(0001), i.e. ~ 5.0 Å), with an irregular periodicity of about 20.8–23.8 Å (marked with white arrows in (e)). The precise values were difficult to determine due to high surface corrugation, poor structural arrangement and limited amount of regions exhibiting the

superstructure. Such structure is similar to the FeO₂ phase on Pt(111)^{[240][241]}, as the FeO₂ domains on Pt(111) exhibit a higher apparent height (~1.2 Å higher) than that of the FeO island. Based on the literature, I tend to assign the edge structure is formed by an additional O layer on top the pristine FeO at edge after CO 600 K treatment. The dark regions within the oxide islands might be reduced FeO_x islands (perhaps partially back to FeO structure), based on the range of height in between 4.7–4.9 Å.

To distinguish the effect from thermal annealing or CO reaction, an experiment was performed in which the sample was only post-annealed at 600 K in UHV for 10 min, as shown in **Figures 4.1.5 (d)**. Similar to the one shown in the previous chapter, the change in morphology of $FeO_x/Ru(0001)$ purely relate to annealing at 600 K in UHV could not be responsible for the edge structural changes observed following 600 K CO exposure.

The morphology change at the edge sites observed from STM after CO600 K are quite similar to previous research on the FeO_x/Pt(111) system. At low CO partial pressures the CO reaction proceeds from the edges of the oxygen-rich islands^[264], since CO molecules are usually adsorbed on Pt substrate and then attracted by the weakly bounded oxygen species at the oxide islands edge^[58] (More details see section 1.3.2). Thus, before going through details analysis of the FeO_x/Ru(0001), an attempt was made to identify the role of the substrate in the reaction. For this purpose, two CO exposure series were performed on 0.5 and 1.0 ML FeO_x samples.

The XPS Fe 2p and O 1s spectra of 0.5 ML FeO (solid lines, shown in the bottom of the figure) and 1.0 ML FeO (dotted lines, shown in the top of the figure) samples are shown in **Figures 4.1.6** (a) and (b), respectively. The results include before (FeO: black lines) and after 667 L RT-O_{at} treatment (RT-O_{at}: blue lines), as well as after CO reaction at 600 K (CO600K: red lines). For both 0.5 ML and 1.0 ML FeO, the lineshape is virtually identical to each other, except the variance of the intensity. The main features of Fe 2p spectra recorded after RT-O_{at} treatment (1×10^{-6} mbar for 15 min) for both FeO remain the same (FeO_x, mixed oxide in favor of Fe³⁺), since the 718 eV satellite appears while the mainlines of Fe 2p_{1/2} and Fe 2p_{3/2} located at 710 and 725 eV get narrower (Fe 2p_{1/2} peak also shifts towards higher binding energy). However, for O 1s spectra, the main peak at 529. 9 eV shift to 529.7 eV for 0.5 ML FeO and to 529.5 eV for 1.0 ML case. While the increase of WBOs (528.9 eV) is obvious for both coverage of FeO_x (higher increment in 1.0 ML case), the hydroxyl groups (530.9 eV) component grows significantly in the 0.5 ML sample (since this component often forms at the borders of FeO islands, and the FeOH was found to have stabilizing effect on FeO/Pt(111)^[85]). All the behaviors, are indicative of the formation of oxygen-rich phase (FeO_x) for both 0.5 ML and 1.0 ML FeO, where the latter case seems to be more oxidized.

After exposure to $450 \text{ L CO} (1 \times 10^{-6} \text{ mbar for } 10 \text{ min})$ at 600 K and additional cooling down in 225 L CO (1 × 10⁻⁶ mbar for 5 min). A new shoulder appears near 707.4 eV (marked by red arrow in **Figure 4.1.6 (a)**), which is also found previously for FeO after CO-RT treatment (see **Figure 4.1.4 (a)**), suggesting a reduction transition phase. Moreover, the slight shift towards higher binding energy in O 1s spectra shown in **Figure 4.1.6 (b)** confirms that some consumption of WBOs, while more CO component (530.9 eV) remains on the surface. However, for the full coverage of iron oxide, the effect of reduction is barely visible. Therefore, it can be assumed that for FeO_x/Ru(0001)



system, the CO reaction mechanism is also highly related to the submonolayer coverage (i.e. either the presence of edges of oxide islands or the exposed substrate regions).

Figure 4.1.6. Fe 2p (a) and O 1s (b) XPS spectra of 0.5 ML FeO (solid lines) and 1.0 ML FeO (dotted lines): before (FeO: black lines) and after 667 L RT-O_{at} treatment (RT-O_{at}: blue lines), as well as after CO reaction at 600 K (CO600K: red lines). (c), (e) Fe 2p and (d), (f) O 1s XPS spectra of 0.5 ML FeO (black lines), after RT-O_{at} treatment (blue lines), exposed to CO at RT (green lines) and UHV annealing at 600 K (green dotted lines).

To get insight into the chemical structure of the phase formed following the CO600 K, vacuum annealing at 600 K is analyzed for comparison. The XPS Fe 2p and O 1s signals of UHV600K sample are presented in **Figures 4.1.6 (c)** and **(d)**. Following the vacuum annealing at 600 K, the spectra (green dotted lines) look more similar to the one obtained for pristine FeO/Ru(0001) (black lines). As already mentioned in section 3.2.2, the thermal treatment at 600 K partially convert the FeO_x phase back to initial FeO structure, which also agrees with the STM results. However, compare **(a)** and **(c)** for Fe 2p spectra, the sample after subjecting the FeO_x sample to CO at 600 K, did not broadening the peak like the pure vacuum annealing does, but with only a shoulder appears near 707.4 eV. The intensity of O 1s (compare **(b)** and **(d)**) for sample after CO600 K treatment is not reduced like after UHV600 K annealing, but a tiny shift of the main peak to higher binding energy can be observed. Moreover, the analysis of Ru 3d spectra (not shown) indicates that after 600 K UHV annealing, the peak shifting and broadening features caused by RT-O_{at} treatment completely convert back to the clean Ru spectra – while in the case of CO600 K treatment, only partial reversing feature is found.

The effect of small amount (451 L) of CORT reaction (Figures 4.1.6 (d) and (e)) is quite

limited –as only the main peaks of Fe 2p are shifting slightly towards higher binding energy, with reduced O 1s intensity especially the WBOs component (528.9 eV) and the OH (530.9 eV) component. Ru 3d spectra also shows changeless spectra after CORT treatment (not shown). It is not trivial to interpret the mechanism of CORT reaction based on the limited STM and XPS data showing here, and certainly, CO reaction at RT with higher pressure or processing with longer time should be checked in the future.

To have an overview of the observation in a more statistic way, the averaged contribution of different species is determined from a few deconvoluted Fe 3p (for simplicity) and O 1s XPS spectra from samples as mentioned above. The reaction condition for CORT and CO600K may differ from each other by slightly varying the dosage. The obtained results for iron states are shown in **Figure 4.1.7 (a)**. First of all, FeO after RT-O_{at} treatment will be strongly oxidized to FeO_x phase. After careful analysis, I found the big deviation obtained for the analysis is related to the repeating cycle of reoxidation by Oat. In other words, reoxidizing the sample after CO600K/UHV600K treatments cannot fully convert back to the initial FeO_x stage – this also influence the further experiment (like the shoulder peak near 707.4 eV cannot be observed for new cycle of CO600K treatment), and therefore, the deviations for the rest treatment are big accordingly. If one only considers the averaged value, it can still be concluded that UHV600K has the strongest reduction properties, while CORT has limited effect on this perspective. The result for oxygen species analysis is presented in Figure 4.1.7 (b). The WBOs component is partially reduced by exposing the sample to CO at 600 K or annealing to 600 K, but barely changes by RT-CO exposure. Therefore, the temperature plays a critical rule to activate CO reaction. The variation of O(2) (OH-group), O(3)(CO) and O(4) (H₂O) is not so obvious due to high deviation in the data.



Figure 4.1.7. Analysis of contribution of different chemical species to XPS Fe 3p signals (a) and O 1s (b) of pristine FeO/Ru(0001), the sample treated with O_{at} at RT, exposed to CO at RT or 600 K, or annealed in UHV at 600 K.

In summary, the oxygen-rich phase $FeO_x/Ru(0001)$ was prepared by subjecting FeO/Ru(0001) to RT-O_{at} treatment. The presence of FeO island edges and/or exposed substrate regions seems to be critical for the reaction with CO, as almost limited reduction was observed for 1 ML (full-coverage) films. Also, exposing the 0.5 ML FeO_x/Ru(0001) system to small amount CO at RT has little effect on the structure. Compare to UHV annealing at 600 K, CO treatment at 600 K lead to the formation of a Moiré-like structures at the iron oxide island edges, may correspond to the

reduction transition phase found from the XPS Fe 2p spectra.

4.2. Summary and discussion

In this chapter, the interaction of CO with Ru(0001), FeO/Ru(0001) and FeO_x/Ru(0001), was studied. CO is a common "testing" molecule used for determining the catalytic activity of nanostructures at surface in oxidation reactions. It was also used for testing ultrathin oxygen-rich metal oxide films under UHV conditions, taking O from the oxide film, forming CO₂ and leaving oxygen vacancies after the reaction. However, CO also possesses oxidizing abilities, with C as a byproduct. One example is the Li₂O system, in the case of which the reaction of CO leads to the formation of graphene-like structures (Li₂O + 2CO \rightarrow C(graphene) + Li₂CO₃)^[265]. Another recent work indicates that CO can oxidize a defect-rich TiO₂ through oxygen vacancies and form unique black TiO₂ phase (TiO_x + (2-x)CO \rightarrow TiO₂ + (2-x)C (x<2))^[266]. Therefore, CO can have both oxidizing and reducing properties, which highly depends on the material structure and the reaction conditions.

In line with previous reports, the performed experiments showed that CO and O_2 can both adsorb on Ru(0001) at RT, forming (2×2) or (2×1) LEED patterns that differ by the intensity of some reflexes. RT-CO exposure applied to pristine FeO/Ru(0001) system at moderate pressure result in the appearance of CO-Ru and CO-FeO components in XPS O 1s spectra, while iron becomes slightly more oxidized (see Figure 4.1.4 (a) and (b)). From STM data, the formation of bright protrusions is observed on FeO, which presumably represents compressed CO particles^[58] or fuzzy carbon clusters^[267]. This morphology change agrees with the change of the LEED pattern, where the (2×2) spots become barely visible (covered by CO molecules), and the FeO satellite beams become weak. The appearance of new spots within satellite beams indicates small portion of new structure (need further analysis). Triangular O adatom dislocation loops also appear on the oxide surface after CO RT-exposure, which indicates that CO is more like oxidant than reducing agent on clean FeO at RT, where the decomposed CO molecules result in the formation of O adatom dislocation loops and C particles. The O loops could be formed through the surface defects and edge sites. Since no strong bonding can be formed between C and FeO at RT, these C atoms can subsequently diffuse and nucleate as clusters at the surface. The driving force for C diffusion may come from impinging CO molecules, as it is previously reported that CO can also promote the diffusion of surface adatoms. One example is that CO can promote Pd atoms mobility and lead to the formation of large Pd clusters on $Fe_3O_4(001)^{[268]}$.

The above-mentioned findings only apply to the case of CO exposure to pristine FeO/Ru(0001). Exclude the analysis from FeO, a repeatable reaction pattern can be observed. Reoxidation of CO-treated sample partially reduces the CO-related components and increases the Fe^{3+} : Fe^{2+} ratio. STM images, on the other hand, show the appearance of additional and bigger O adatom dislocation loops. Unlike the first CO-treatment (applied to pristine FeO), exposing the reoxidized sample to CO results in less dense O dislocation loops and the observed slight reduction of iron – making CO act as a reducing agent. Repeating the cycles shows quite similar pattern: the sample is oxidized by O₂ and reduced by CO at RT.

The experiments on 0.5 ML and 1.0 ML FeO_x/Ru(0001), i.e. FeO exposed to O_{at} at RT, were performed to determine the role of oxide island edges and/or exposed substrate regions on the reactivity. Both samples showed that iron is mostly in Fe³⁺ after the RT-O_{at} treatment. However, after CO reaction at 600 K, the sample with low coverage partially reduced back to pristine FeO, while the stoichiometry of the sample with full coverage barely changed after this treatment. Such effect implies that the presence of island edges and/or exposed substrate regions is critical for the CO reaction. Exposing CO to the FeO_x/Ru(0001) system at RT shows a minor change in XPS and STM. CO reaction at 600 K shows some similar effect as vacuum annealing at the same temperature, i.e. the surface roughness decreases after CO600 K treatment. The XPS shows less reducing properties of CO600K compare to UHV600K treatment, but with similar shoulder appearing at 707.4 eV, suggesting new reducing phase. Moreover, new poorly-ordered superstructure could be observed at the edges of iron oxide islands after CO600K treatment with about 1 Å higher than pristine FeO, which may be the presence as O adlayers on the surface. Three mechanisms happen simultaneously can be assumed in this case: (i) CO molecules adsorb on a strong-oxidized sample surface and react with O at elevated temperature and, in the meantime, the removal of O and desorption of CO₂ will leave vacancies at the surface; (ii) new CO molecules can fill the oxygen vacancies and decompose to O and C; (iii) both CO pressure and elevated temperature can promote the diffusion of O and C adatoms, where the O atoms start forming the on the additional layer close to the island edges, while C mostly stay within the islands and nucleate to clusters.

5. Structure and electronic properties of ultrathin iron oxide films on Ag(111)

The presented results were partially published in:

[293] M. Lewandowski, T. Pabisiak, N. Michalak, Z. Miłosz, V. Babacic, <u>Y. Wang</u>, M. Hermanowicz, K. Palotás, S. Jurga, A. Kiejna, "On the Structure of Ultrathin FeO Films on Ag(111)," Nanomaterials, vol. 8, no. 10, p. 828, Oct. 2018.

The chapter presents the structural analysis and electronic properties of FeO/Ag(111). As mentioned in section 1.4, Ag(111) is one of the most promising substrates for growing iron oxide films, as it exhibits only 5% lattice constant mismatch to FeO ($a_{Ag(111)}=2.89$ Å, $a_{FeO(111)}=3.06$ Å) and weak interaction with oxygen (not forming AgO_x under the condition of forming iron oxide). Therefore, the complexity of FeO/Ag system should be reduced. Additionally, only a few studies focused on the iron oxide growing on Ag substrate and even more limited publications upon (111) facet. However, the reported structures are sometimes contradictory to each other. Therefore, it is essential to reveal the critical relation between surface morphology and the preparation method systematically, especially for the detailed structure studies (theoretical calculations, atomic-scale characterization, etc.).

There are two sections in this chapter. In section 5.1, the growth of iron oxide prepared by different Fe deposition temperatures (RT and 550 K) is presented, the obtained structure and chemical composition of FeO/Ag(0001) are studied in details, and a structural model is proposed for an unreported Moiré superstructure. However, a new type of reconstruction-free islands was found, which shares very similar structural parameter to Ag(111) substrate. In order to identify the nature of this type of islands, the electronic properties (work function: dI/dz and conduction states: dI/dV) and theoretical calculation on this type of islands are presented in section 5.2. STM, STS, LEED and XPS measurements were involved in the data analysis.

5.1. Growth of iron oxide films on Ag(111)

The obtained results of ultrathin FeO(111) films grown on Ag(111) differ from each other by different research groups (Waddil et al.^[15] and Lundgren et al.^{[96][97]}). Noticing the film growth procedures used by these two groups are different from each other, thus, the deposition temperature of iron may cause the difference of surface structures. Therefore, several experiments to systematically study and reveal the structure of FeO/Ag(111) were performed.

The approach developed by Waddil et al. was applied in this work, due to the lack of longrange superstructures in their reported oxide film (less complex oxide structure). That is to say, the iron oxide is prepared by depositing Fe and post oxidation at elevated temperatures. Since the role of substrate temperature during iron deposition is unclear upon structure formation, Fe was deposited at RT (section 5.1.1) and at elevated temperatures (section 5.1.2). To distinguish these two types of iron oxide, I use RT-Fe/Ag(111) and RT-FeO/Ag(111) to represent iron/iron oxide prepared by depositing iron at RT; while HT-Fe/Ag(111) and HT-FeO/Ag(111) represents iron and its oxide prepared by depositing iron at high temperature.

5.1.1. RT-Fe/Ag(111) and RT-FeO/Ag(111)

Firstly, iron oxide was prepared by depositing Fe onto Ag(111) at RT, oxidizing the sample in 1×10^{-6} mbar O₂ pressure at 700 K for 15-30 min and cooling down in oxygen for a few minutes. The detailed structure morphology studies were obtained by the STM measurement. As shown in **Figure 5.1.1 (a)**, most metallic Fe agglomerates at the step edge of Ag after room temperature deposition, forming nanowire-like structures. A small portion of iron is distributed on the terrace. Step edge is usually a reactive site due to a large amount of unsaturated bonds of the edge atoms^[269]. In this case, the silver step edge is energetically preferential adsorption positions for iron nucleation at RT^[270]. In addition, the RT-Fe deposition can cause edge erosion by intermixing effect, where the diffusing adatom (in-plane hopped adatom on a close-packed surface like Ag(111)) replaces the edge atom once they reach a descending step^{[271][272]}. The growing pattern of RT-Fe on Ag(111) is connected to Volmer-Weber growth mode, suggesting iron atoms couple with each other more strongly than with silver, and preferably forming three-dimensional clusters. The dark holes in the silver terrace are vacancy islands, formed by surface etching during iron deposition. A similar surface feature could be found in other systems, such as Co/Cu(111)^[273].

Figure 5.1.1 (b) shows the STM image of RT-FeO/Ag(111) sample. The vacancy islands disappeared and resulted in a 'flattening' substrate due to high-temperature annealing during the oxidation process. The irregular iron clusters are mostly transformed to reconstructed islands with clear Moiré patterns at the step edge and hexagonal islands on the surface. A zoom-in image of the Moiré structure and the hexagonal crystallites with ill-defined surface structures on the terrace are shown in **Figures 5.1.1 (d)** and (e), respectively. The height profile taken through two islands on the terrace (white arrow from (e)) is presented in **Figure 5.1.1 (f)**, showing two different heights of approx. 5 and 7 Å. Various contrast (different thicknesses) of those islands could be observed from the STM image, therefore, these islands are assigned to multilayers (mixed-phase, denoted by FeO_x)^{[87].}



Figure 5.1.1. Large-scale STM images of (**a**) 0.5 ML RT-Fe/Ag(111), (**b**) 0.5 ML RT-FeO/Ag(111). (**c**) Zoom-in STM image of the blue square from (**a**), rotated 90° for better view. (**d**) Zoom-in STM image of the yellow square from (**b**), Moiré reconstruction of iron oxide grown at the step edge. (**e**) Zoom-in STM image of the red square from (**b**), ill-defined surface islands (multilayers). (**f**) Height profile of ill-defined islands taken from (**e**), marked by the white arrow. V = + 0.7 V, I = 1.0 nA (**b**, **d**) or I = 0.4 nA (**a**, **c**, **f**). (**a**) and (**b**): 300 × 300 nm², (**c**), (**d**), (**e**): 50 × 50 nm² (Edited from Figure 1 in [293]).

The reconstructed FeO superstructure that appeared at the step edges is shown in **Figure 5.1.2** (a). The height profile is taken across the island (marked by the red arrow) is presented in **Figure 5.1.2** (b). The measured height is about 2.1 Å with corrugation within 0.5 Å (depending on tunneling parameters), which is a characteristic height of Moiré-reconstructed islands. Comparing to the work made by Lundgren and co-workers (26 Å Moiré periodicity with FeO lattice extended to 3.25 Å, without rotation^{[96][97]}), the measured results reveal a Moiré periodicity of 45 Å, which is considerably bigger than the value from them. The lattice constant of FeO shows similar expansion behavior in the present case, and the atomic periodicity is around 3.2 Å (expends almost 5% compare to its bulk form), measured from the atomically resolved image (**Figure 5.1.2** (c)). Such differences might relate to different oxide preparation methods. This again supports the idea that the procedure order and preparation condition are critical for oxide structure formation.

Based on structural parameters obtained from experiments, a structure model for the Moiré superstructure was proposed, as in **Figure 5.1.2 (d)**. Assuming the FeO film as an O-terminated surface since it is usually chemical inert^[274]. The coincident structure is determined to be 14×14 FeO on $9\sqrt{3} \times 9\sqrt{3}$ Ag, with 30° rotation. The Moiré unit cell is, therefore, 45 Å, with a FeO lattice constant of 3.215 Å and Ag of 2.89 Å^[159]. Noticing on {111} orientated facet, the most densely packed direction is <110>, which is a characteristic orientation at the step edge^[275]. However, this

orientation is not favorable for FeO(111) growth, as the Moiré structure grows along with the $\sqrt{3}$ crystallographic directions. Similar growth behavior can be found in many systems, such as methylthiolate on Au(111), the islands grow along with one of the <112> directions^[276]. This can be one of the explanations of the rotated and expanded Moiré superstructure.



Figure 5.1.2. (a) STM image of Moiré superstructure of iron oxide. (b) Height profile marked by the red arrow in (a). (c). Atomic-resolved STM image of the reconstructed Moiré superstructure. (d) A proposed model for the Moiré superstructure, where the blue rhombus represents the Ag(111) surface cell, the red represents the FeO(111) unit cell, and the black represents the Moiré cell. V = + 0.7 V, I = 1.0 nA (a) or I = 0.4 nA (c). (a): 75 × 75 nm², (b): 20 × 20 nm² (Edited from Figure 1 in [293]).

The analysis of LEED and XPS is shown in **Figure 5.1.3**. The LEED pattern of RT-FeO/Ag(111) sample is shown in **Figure 5.1.3** (c). Without the splitting feature found from the literature $[^{15}][^{96}][^{97}]$, only a clear (1×1) pattern was observed. Combine with the observation from STM images (see **Figure 5.1.1** (b), with multiple oxide structures), the safe assumption is that the contributions from the oxide phase of FeO(111), or perhaps Fe₂O₃(0001) and Fe₃O₄(111), are too small to be detectable by LEED. The Fe 2p and O 1s XPS spectra are shown in **Figures 5.1.3** (a) and (b), respectively. Ag 3s overlaps within the Fe 2p region and is denoted by a dashed line in the

XPS spectra for better comparison. A small broad O 1s peak appears for the RT-Fe/Ag(111) sample, due to the high reactivity of ultrathin iron film. The intensity of the oxygen peak significantly increased after oxidation. More detailed Fe 2p XPS spectrum analysis (after subtracting Ag 3s components) is shown in Figure 5.1.3 (d). Two peaks located at 706.5 eV (Fe $2p_{3/2}$) and 719.9 eV (Fe $2p_{1/2}$) are found for the RT-Fe/Ag(111) sample, which correspond to the characteristic metallic iron (Fe⁰) peaks^[277]. After oxidation, the Fe 2p spectrum can be fitted into six components (three pairs as Fe 2p_{3/2} and Fe 2p_{1/2}): 710.3 eV and 724.0 eV, 713.4 eV and 726.9 eV, 716.6 eV and 731.0 eV. The core-level components of the oxidized sample chemically shift to higher binding energy values by approx. 4 eV (710.3 eV and 724.0 eV) compare to metallic iron, indicating the sample was oxidized and the main iron phase is Fe^{2+} within the mixed film^{[278][279]}. The multiple splitting peaks arising from the coupling effect between unpaired core electrons and valence electrons can broaden the core-level peaks^[212], while in the case of iron oxide, two components can be readily fitted at the positions of 713.4 eV and 726.9 eV^{[280][281]}. The last set of paired components located at 716.6 eV and 731.0 eV originate from the Fe²⁺ satellites^{[279][282]}, which arises from the excitation of outer-shell electrons by the photoelectrons to unoccupied orbitals^{[213][283]}. The position difference of satellite components and their corresponding core level peak are 6.3 eV for Fe 2p_{3/2} (716.6 eV and 710.3 eV) and 7.0 eV for Fe 2p_{3/2} (731.0 eV and 724 eV), which further confirmed the existence of Fe²⁺ ions^{[278][279][282]}. For Fe³⁺, the binding energy difference should be more than 8 eV^{[279][282]}. The little amount of Fe³⁺ indicates the dominant iron oxide compound should be FeO. The O 1s peak is fitted with a single component, centered at 529.7 eV^[284]. The ratio determined from the survey spectrum of Fe and O is around 1:1, which suggests that monolayer iron oxide grown on Ag(111) is in the stoichiometric FeO phase.



Figure 5.1.3. (a) Fe 2p XPS spectra; **(b)**. O 1s XPS spectra. For both **(a)** and **(b)**, from top to bottom: Ag(111) substrate, 1.0 ML RT-Fe/Ag(111), 1.0 ML RT-FeO/Ag(111). (c) LEED pattern (60 eV) of

0.5 ML RT-FeO/Ag(111). (d) Detailed Fe 2p XPS spectra obtained for the 1.0 ML RT-Fe/Ag(111) (red line) and 1.0 ML RT-FeO/Ag(111) samples (black line). The Ag 3s signal is subtracted from the Fe 2p line. Inset in (d) presents the O 1s XPS spectra of the oxidized sample ((c) and (d) are adopted from Figure 2 in [293], all the spectra were fitted by Natalia Michalak, Institute of Molecular Physics, Polish Academy in Sciences in Poznań).

In summary, for RT-FeO/Ag(111), a few types of structure can be observed, including: (i) illdefined islands on the surface with various heights; (ii) a 45 Å Moiré reconstructed FeO islands forming at the edge. The XPS shows the overall composition is FeO (Fe:O = 1:1). However, both the (1 × 1) LEED pattern and various surface structures observed from STM images indicate a low concentration of regular FeO and its Moiré superstructure. Instead, a mixed oxide phase with overall FeO composition is obtained for the RT-FeO sample.

5.1.2. HT-Fe/Ag(111) and HT-FeO/Ag(111)

Secondly, the iron oxide was prepared by depositing Fe onto a heated sample holding at 550-600 K and followed by oxidizing in O₂ with a partial pressure of 1×10^{-6} mbar. Various oxidation temperatures at 500 K, 600 K and 700 K were applied, and the results of preparation are shown in STM images (**Figure 5.1.4**). Differ from the 0.5 ML RT-Fe/Ag(111) sample, depositing iron at 550 K forms well-defined bcc Fe(110) crystallites, which distribute uniformly all over the substrate, as shown in **Figure 5.1.4** (d). **Figure 5.1.4** (f) shows a zoom-in image of these crystallites. It seems that iron could "embed" to the top silver layer at a temperature higher than 500 K, which is also found previously that iron can diffuse into bulk silver at high temperatures^[285]. The vacancy islands found in the RT-Fe/Ag(111) sample are not present in the case of the HT-Fe/Ag(111) sample, due to the simultaneous surface smoothing during elevated temperature deposition.

The size of these crystallites depends on the coverage. 0.5 ML HT-Fe/Ag(111) and 1.0 ML HT-Fe/Ag(111) samples were compared in **Figures 5.1.4 (d)** and **(a)**. Even sufficient amount of a full monolayer Fe is deposited onto Ag(111), the Fe preferably grows to multilayers with larger size instead of wetting the surface. As shown in the height profile (inset in **Figure 5.1.4 (a)**), those Fe islands have various heights from 6 to 11 Å, which is significantly larger than the single-layer height of bcc Fe ($\sim 2 \text{ Å}^{[286]}$). Additionally, some inclusions (not shown here) with a height between 0.6 - 1.2 Å also appear on the surface. The formation of those structures is mainly due to high atom mobility at elevated temperature, where iron incorporates into the top Ag layer and becomes nucleation centers for the crystallites.

The post oxidation temperature has little effect on the surface structure of HT-FeO/Ag(111). **Figures 5.1.4 (b), (c)** and **(e)** are the STM images of HT-Fe/Ag(111) after oxidation at 500 K, 600 K, and 700 K, respectively. The surface morphology is similar to each other. Two structures from the could be observed: (i) evenly distributed crystallites on the terrace; (ii) flat islands grown either at silver step edge or anchor to the crystallites on the terrace (indicated by red arrow). Noticeably, sometimes a small portion of small islands embedded into the silver (dark region pointed out by white circle) was found at lower coverage.



Figure 5.1.4. Iron oxide prepared by Fe deposition onto Ag(111) held at elevated temperature: (a) 1.0 ML Fe deposit at 600 K, the inset to (a) is the height profile indicated by the black arrow; (b) Post-oxidation of (a) at 500 K; (c) Post-oxidation of (a) at 600 K; (d) 0.5 ML Fe deposited at 550 K; (e) Post-oxidation of (d) at 700 K; (f) A zoom-in image of 0.5 ML Fe deposited at 550 K. (a), (b) and (c) measured by LT-STM, V = + 1.0 V, I = 0.1 nA; (d), (e) and (f) measured at RT, V = + 0.7 V, I = 1.0 nA (d) or I = 0.4 nA (e, f). (a - e): 300 ×3 00 nm², (f): 50 × 50 nm².

To make the results of HT-FeO/Ag(111) more comparable to the RT-FeO/Ag(111), additional STM experiments on the oxide film with 0.5 ML coverage were performed. More structures can be observed from STM images shown in **Figure 5.1.5**. In general, these structures can be classified as:

(1). Reconstructed FeO with a Moiré periodicity of 45 Å as described in the RT-FeO/Ag(111) case. However, the growing sites of such islands are not restricted to silver step edge. Some of those FeO islands can extend to the silver terrace. One example is labeled by (i) in Figure 5.1.5 (a), the iron oxide forming Moiré superstructure grows at the step edge and expands to the upper terrace.

②. Hexagonal iron oxide islands evenly distributed on the terrace or at the edge. The height of these islands ranges from 5 to 15 Å. Most of them are ill-defined multilayer nanocrystals, similar to those observed for the RT-FeO/Ag(111) sample. Some of those islands have a large in-plane atomic periodicity of approx. 6 Å, as shown in **Figure 5.1.5 (b)** (the zoom-in STM image of the islands labeled by (ii) in **Figure 5.1.5 (a)**). Such islands are most likely the Fe₃O₄(111) phase (atomic periodicity of 6 Å^[287]), as reported previously that Fe₃O₄(111) starts forming on Ag(111) at higher oxide film thickness (> 10 Å)^{[15][93]}.

③. Embedded iron oxide islands with line defects due to surface strain. This type of islands was mainly found on the terrace, and the defect lines aligned to surface crystallite orientation. One

example is shown in **Figure 5.1.5 (a)**, labeled by **(iii)**. The corresponding enlarged image is shown in **Figure 5.1.5 (c)**. The average atomic spacing is approx. 3.2 Å, virtually identical to the expanded lattice constant of FeO, which constructs the Moiré superstructure. The formation of such islands without Moiré might relate to the strain-induced distortion. One explanation is that iron deposits at high temperatures embed to the top silver layer, causing unequal interaction at the interface and resulting in regular line defects during further oxide formation. Another possible explanation could be the extra oxygen went underneath the interface between embedded iron and silver surface during oxidation. This 'incorporation' behavior was previously published in a few systems, taking $MgO(001)/Ag(001)^{[288][289]}$ as an example – metal deposited at high temperature (773 K) in oxygen pressure will accumulate extra oxygen at the silver subsurface between MgO and Ag. The interface O probably expands the silver lattice due to the opposite charge, and therefore, reduces the lattice mismatch between oxide film and substrate.

(4). Reconstruction-free islands. These flat islands are grown either at the step edge or on the terrace in between those hexagonal nanoislands. Examples of this types of islands are shown in **Figure 5.1.5 (d)**, and also labeled by **(iv)** in **Figure 5.1.5 (a)**. The height of the islands is roughly 2.4 - 2.5 Å. From the atomically resolved image displayed in **Figure 5.1.5 (e)**, the measured atomic distance was determined to be 2.94 ± 0.08 Å. One may consider this region as a protruding monoatomic step Ag (single step height: 2.40 Å^[157]; lattice constant: 2.89 Å^[159]). However, the appearance of two sub-lattices (represented as yellow and blue circles, the black circle represents the dark 'hole') from the image disproves the idea of assigning these flat islands to Ag.



Figure 5.1.5. STM images of HT-FeO/Ag(111) samples: (a) A gallery of various surface structures; (b) Zoom-in image of hexagonal islands labeled (ii) in (a) with atomic periodicity of ~6 Å; (c) Zoom-in image of embedded islands labeled (iii) in (a) with atomic periodicity of ~3.2 Å; (d) Atomically-flat islands, similar one is labelled (iv) in (a); (e) Atomic resolved image of (d), with atomic periodicity of ~ 2.94 Å. V = + 0.7 V (a, b, c, d) or V = + 0.7 V (e), I = 1.0 nA (a) or I = 0.4 nA (b - e). (a, d) 100 × 100 nm², (b) current image, 15 × 15 nm², (c) 10 × 10 nm², (e) 5 × 5 nm² (Edited from Figure 3 in [293]).

Due to the complexity of the HT-FeO/Ag(111) system, the sample was further characterized by LEED and XPS techniques. The LEED pattern of 0.5 ML HT-FeO/Ag(111) is shown in **Figure 5.1.6 (c)**, which is similar to that of RT-FeO/Ag(111) with a clear (1×1) pattern. The experiments were repeated several times to confirm this result. This result could be again, caused by low coverage of various species, and none of them is detectable by LEED.



Figure 5.1.6. (a) Fe 2p XPS spectra; **(b)** O 1s XPS spectra. For both **(a)** and **(b)**, from top to bottom: Ag(111) substrate, 1.0 ML HT-Fe/Ag(111), 1.0 ML HT-FeO/Ag(111). **(c)** LEED pattern (60 eV) of 0.5 ML HT-FeO/Ag(111). **(d)** Detailed Fe 2p XPS spectra obtained for the 1.0 ML HT-Fe/Ag(111) (red line) and 1.0 ML HT-FeO/Ag(111) samples (black line). The Ag 3s signal is subtracted from the Fe 2p line. Inset in **(d)** presents the O 1s XPS spectra of the oxidized sample. **((c)** and **(d)** are adopted from Figure 4 in [293], all the spectra were fitted by Natalia Michalak, Institute of Molecular Physics, Polish Academy in Sciences in Poznań).

The XPS data of Fe 2p and O 1s region for 1 ML HT-Fe/Ag(111) and HT-FeO/Ag(111) are shown in **Figures 5.1.6 (a)** and **(b)**, respectively. Similar to previous RT-case, the overlapped Ag 3s component is marked by a dashed line in the Fe 2p XPS spectra for both HT-Fe/Ag(111) and HT-FeO/Ag(111) samples. No oxygen was found in the spectra of the HT-Fe/Ag(111) sample (while a small peak was found in the RT-Fe/Ag(111) sample). A sharp O 1s peak centered at 529.8 eV appeared after oxidation. The fitted results can be found in **Figure 5.1.6 (d)** after subtracting the Ag 3s component from Fe 2p regions recorded for both samples. Two components can be fitted in the Fe 2p XPS spectrum for HT-Fe/Ag(111) sample, which centered at 706.4 and 719.6 eV, similar to RT-Fe/Ag(111), corresponding to metallic iron. Six components contribute to the spectra after oxidation: 710.2 and 724.0 eV; 712.7 and 726.9; 716.5 and 731.3 eV. Likewise, the core-level peaks located at 710.2 and 724.0 eV indicate ionized iron components. The multiple splitting peaks

positioned at 712.7 and 726.9 eV further proved the oxide formation. The components fitted at 716.5 and 731.0 eV are assigned to the satellites that originate from Fe^{2+} , as discussed in the case of RT-FeO/Ag(111). The composition ratio of Fe and O is found to be 1:1. In general, there is no obvious difference in XPS data between RT- and HT-samples. The absence or limited amount (beyond the detection sensitivity of XPS) of Fe³⁺ identifies the oxide to FeO.

The LEED and XPS results obtained for HT-samples did not provide more information regarding the reconstruction-free islands. It is still questionable if this structure is silver or iron oxide. The most accessible measurement to draw a conclusion is STS – where one can check if this region has the same electronic structure as the Ag substrate. Apart from experimental methods, our partner research group led by Prof. Dr. Adam Kiejna performed DFT calculations for this structure. Detailed results will be shown in sections 5.2.

In summary, the results obtained for the HT-FeO/Ag(111) system reveal some modifications of iron oxide structure compared to RT-samples. Except for the structures already found for the RT-FeO/Ag(111) sample (ill-defined multilayer crystallites and Moiré-reconstructed FeO islands located at the silver step edge with periodicity of 45 Å), some new structures also appear, including: (i) multilayer hexagonal iron oxide nanoislands with various heights, some of them formed the initial stage of Fe₃O₄ (atomic periodicity of ~ 6 Å); (ii) Moiré-free embedded iron oxide islands grown at steps or on the terrace, with defect lines and expanded lattice constant of 3.2 Å; (iii) reconstruction-free islands with a height of 2.4 – 2.5 Å and lattice constant of 2.94 ± 0.08 Å. The formation of various surface species might relate to the uniform iron distribution and partial implantation of iron into the top silver layer during high-temperature deposition before oxidation.

5.2. Reconstruction-free islands grown on HT-FeO/Ag(111)

In order to understand the nature of the observed reconstructed-free islands, STS measurements on the islands and silver substrate were performed and the obtained results were further compared. The STS experiments were performed with a lock-in amplifier. For dI/dz curves, we used a modulation voltage of 60 mV with a frequency of 6.777 kHz, measured by STM at RT. For dI/dV curves, a modulation voltage of 40 mV at a frequency of 727 Hz was applied, measured by LT-STM at 77 K. The time constant is kept at 10 ms.

Besides the experimental perspective, our partner research group performed DFT calculation for the structure determination. The DFT calculation used the Vienna ab initio simulation package (VASP, version 5.4.4, Vienna, Austria)^{[290][291][292]}, the FeO was modeled using a 1×1 unit cell to adopt the lattice constant of the Ag(111) substrate, which means a slight compression of FeO(111) lattice during relaxation. Since the DFT calculation is out of this thesis's scope, more parameters and configuration details could be found in Ref. [293] and its supplementary material.

5.2.1. Determination of electronic properties with STS

The local apparent barrier height of the Ag substrate and the reconstruction-free islands are measured by dI/dz spectroscopy (0.5 ML HT-FeO/Ag(111) sample). The recorded dI/dz curves are presented in **Figure 5.2.1 (a)**. For better comparison, Pt(111) was added as another reference sample. The obtained results clearly show the reconstruction-free islands have a different work function value than silver – with a bigger slope, indicating the local work function is higher than Ag(111), but lower than Pt(111). In this sense, these islands may be assigned to iron oxide species and use FeO to represent them. From previous reports, the values of the work function of Ag are $4.2 \sim 4.5 \text{ eV}^{[198][192][294][295]}$ and $6.08 \sim 6.4 \text{ eV}$ for Pt^{[296][297][298][299]}. Using the method introduced in section 2.2.2, the curve was plotted in logarithmic scale to determine the slope (smaller range in *z* for better view), which is for average work function calculation, as shown in **Figure 5.2.1 (b)**. The measured slope is around 2.26 Å⁻¹, and thus the value of the average work function is 4.88 eV (use equation (2.2.16)). Therefore, based on equation (2.2.15), using the calibrated work function of W tip of 3.88 eV (shown in section 2.2.2). The work function of the reconstructed-free iron oxide island is around 5.7 eV.



Figure 5.2.1. Local barrier height (work function) measurement: (a) averaged dI/dz curves obtained on Ag(111), Pt(111) and reconstruction-free iron oxide islands; (b) logarithmic scale in a smaller range of (a) (Adopted Figure 5 from [293]).

Additionally, dI/dV measurements were performed on both reconstructed-free islands and Ag substrate. The results are shown in **Figure 5.2.2 (a)**. Multiple additional conducting states appear near + 0.6 V, + 0.4 V, + 0.2 V, - 0.2 V and - 0.8 V were found for this type of iron oxide species (thin red curve) compare to the one obtained on Ag substrate (thin black curve), which further confirmed the existence of FeO. Noticeably, the calculated PDOS of 1ML FeO on Ag(111) is shown in **Figure 5.2.2 (b)**, and a very similar peaks distribution can be observed. Both experimental results and theoretical calculated states slightly shifted to higher bias in both polarities compare to the experimental ones, such behavior is related to Fermi level shift. As the temperature increases (the experimental measurements were obtained at 77 K while the calculation result is hypothesized at 0 K), free electrons and holes can be generated, which results in the decrease of Fermi level accordingly.



Figure 5.2.2. (a) dI/dV curves obtained on 1 ML FeO/Ag(111) sample. The black curve was obtained from Ag(111) and the red curve was obtained on reconstruction-free FeO islands. (b) Partial densities of electronic states (PDOS) of 1 ML FeO/Ag(111), calculated by Dr. Tomasz Pabisiak and Prof. Dr. Adam Kiejna, edited from Figure 8 (a) in [293]. (c) Comparison between theoretical and experimental curves.

In summary, the STS indicates the reconstruction-free islands are different species than the Ag substrate by electronic characteristics. Therefore, I assign these islands to FeO. Compare to Ag substrate, the work function of this type of is determined by dI/dz curves FeO, with a value about 5.7 eV. The dI/dV curves also show additional conduction states on FeO compare to Ag substrate. Moreover, the consistency of the experimental dI/dV and calculated PDOS indicates quasi-ideal measurement conditions performed for this system.

5.2.2. Structure determination by DFT calculation

Theoretical calculations supporting the experimental findings were performed by Dr. Tomasz Pabisiak and Prof. Dr. Adam Kiejna from University of Wrocław. The most energetically-favored configuration of these islands is found to be O-terminated with Fe in threefold coordinated fcc sites; O sits in the hcp hollow sites. As can be seen from **Figure 5.2.3 (e)**, the Fe-Ag distance is 2.35 Å for 1-ML-FeO/Ag(111) configuration due to enhanced adhesive bond strength with 0.91 eV per Fe atom. A reduction of Fe-O interlayer spacing of 0.82 Å is obtained (1.25 Å in bulk FeO^[17]). The overall film height is 3.17 Å.

The double-layer iron oxide form is shown in **Figure 5.2.3 (f)**. It was modeled by placing an additional monolayer of FeO(111) on top of the FeO(111)/Ag(111) slab. In the first oxide layer, Fe atoms over surface Ag atoms and O atoms over Fe atoms in the fcc positions. The next oxide layer (Fe and O atoms) stays in the same configuration. Upon structural optimization, the atoms only relaxed vertically. They increased the Fe1-O1 distance in the first layer to 1.29 Å (Ag-Fe distance slightly reduced to 2.23 Å), making the total first layer height expand to 3.52 Å. However, the second layer was found to have a thickness of 2.30 Å with an interface surface O1-Fe2 distance of 1.44 Å and surface Fe2-O2 distance of 0.86 Å.



Figure 5.2.3. (a) Atomically-resolved STM image of reconstruction-free island (HT-FeO/Ag sample) (I = 0.4 nA, V = + 0.1 V,1.73 × 1.73 nm²). (b) Simulated STM image of 1-ML FeO(111)/Ag(111). (c) Simulated STM image of 2-MLs FeO(111)/Ag(111). (Simulation of (b) and (c) based on DFT calculations and the Tersoff-Hamann method^[300]). (d) Calculated work function values for different FeO(111)/Ag(111) configurations. (e) Side view of calculated 1 ML FeO(111)/Ag(111). (f) Side view of calculated of 2 ML FeO(111)/Ag(111) (Combined Figure 6 and Figure 7 from [293], the work function table is taken from SM 5 in the supplementary document in [293]. (b - f) were calculated by Dr. Tomasz Pabisiak and Prof. Dr. Adam Kiejna et al., Institute of Experimental Physics, University of Wrocław).

To make better comparison to atomically-resolved STM image, as shown in **Figure 5.2.3** (a), the simulated STM images based on these configurations are presented in **Figure 5.2.3** (b) and (c), corresponding to 1-ML FeO/Ag(111) and 2-MLs FeO/Ag(111), respectively. The difference of simulated STM images between 1 ML and 2 MLs is simply the contrast; in other words, the FeO(111) (1×1) unit cell (marked by the white rhombus in the figure) stays the same. Therefore, both cases are applicable to the reconstruction-free islands. Different geometries of antiferromagnetic (AFM) and ferromagnetic (FM) superstructures of 1-ML FeO/Ag(111) are also simulated (not shown here), and their calculated work function are shown in the table (**Figure 5.2.3** (d)), 6.56 eV for 1ML and 6.67 eV for 2-MLs FeO/Ag(111).

Additionally, PDOS were calculated for the surface FeO layer (only the top layer) of three systems: 1-ML FeO/Ag(111), 2-MLs FeO/Ag(111) and 3-MLs free-standing FeO(111) slab. The obtained results are shown in **Figures 5.2.4 (a - c)**. In general, the main electronic structure of all three systems is similar to each other, especially for the second layer on 2-MLs FeO/Ag(111) system and the free-standing FeO slab. This implies the interaction with Ag(111) substrate has a limited effect on the density of states – in other words, the surface FeO layer mainly determines the
electronic structure. Notably, the calculation also suggests the underlying FeO is important for giving an energy gap in the top FeO layer. These calculations indicate the second FeO layer on 2-MLs FeO/Ag(111) has a "free-standing" character.



Figure 5.2.4. (a) PDOS of topmost FeO layer of: (a) 1ML FeO(111)/Ag(111); (b) 2 MLs FeO(111)/Ag(111); (c) free-standing 3 MLs thick FeO(111) slab, resulting from PBE+U calculations (Adopted Figure 8 from [293], (a - c) was calculated by Dr. Tomasz Pabisiak and Prof. Dr. Adam Kiejna, Institute of Experimental Physics, University of Wrocław).

In summary, theoretical calculations show that simulated STM images of both 1-ML and 2-MLs FeO fit the experimental one well. Moreover, 1 ML FeO/Ag(111) with a height of 3.17 Å, with work function from 5.87 eV to 6.56 eV, 2 MLs FeO/Ag(111) has a first layer height of 3.52 Å and a second layer height of 2.30 Å, with work function around 6.7 eV. The second layer of the 2 MLs FeO/Ag(111) has 'free-standing' characteristics, which makes the system a promising candidate for model studies.

5.3. Summary and discussion

In this chapter, I have shown different growth methods for preparing iron oxide on Ag(111). RT-FeO/Ag(111) sample was prepared by room temperature iron deposition followed by oxidation in 1×10^{-6} mbar O₂ pressure at 700 K. HT-FeO/Ag(111) sample was prepared by iron deposition at 550 – 600 K, post oxidation in 1×10^{-6} mbar O₂ pressure at 700 K. In general, the amount of iron deposited onto the heated silver substrate is less due to the higher iron mobility and partial sublimation and/or diffusion into the Ag bulk

Both RT-FeO/Ag(111) and HT-FeO/Ag(111) show a (1×1) LEED pattern, and the overall Fe:O ratios obtained from the XPS spectra are roughly 1:1. The fitted components suggested that after oxidation, Fe²⁺ is the dominant oxidation state in both samples. In general, LEED and XPS results for both samples are quite similar to each other. However, various types of iron oxide species were observed on STM images. The most probable reason for getting similar results of iron oxide regardless of preparation methods could be the small contribution of each surface species, and therefore, it is hard to identify precisely by XPS and LEED.

The STM images show some difference of RT-Fe/Ag(111) and HT-Fe/Ag(111) samples. Fe deposited at RT will result in a nanowire-like structure formed by iron nucleates at the Ag step edge, where is energetically favored sticking sites for iron at RT. Only small distribution could be observed on the silver terrace. Additional edge erosion and surface etching behavior was found, forming vacancy islands on the surface. For the HT-Fe sample, well-defined bcc Fe(110) crystallites were distributed uniformly on the silver terrace as well as the steps. Some iron can even diffuse into the top layer of silver at elevated temperature (>500 K). The vacancy islands found for RT-Fe/Ag(111) sample are not present due to the thermal diffusion of the surface atoms.

Subsequent oxidation showed even more complex results. RT-FeO/Ag(111) sample mainly consists of two types of species: (i) ill-defined islands with various heights on terrace, corresponding to multilayer iron oxide; (ii) reconstructed structure with big Moiré periodicity of 45 Å at the step edge. The lattice constant of FeO expanded to 3.2 Å. Based on the structural parameters, a structure model is developed. The Moiré unit cell includes 14×14 FeO on $9\sqrt{3} \times 9\sqrt{3}$ Ag, with 30° rotation. The rotation and lattice expansion might be caused by the unfavorable orientation at the step edge for FeO(111) growth. HT-FeO/Ag(111) sample shows a few more new features: (i) some of those multilayer oxides (similar to RT-sample) can be atomic-resolved with the periodicity of ~ 6 Å, which could be the initial stage of Fe₃O₄; (ii) the same type of Moiré-free islands grown on the Ag surface with similar FeO lattice expansion (~3.2 Å), with line defects along with surface orientation. The Moiré-free islands are usually anchored to multilayer crystallites; (iv) Reconstruction-free islands with a height of 2.4 – 2.5 Å and a lattice constant of 2.94 ± 0.08 Å. Although these values are very close to those of Ag(111), the atomically resolved STM images clearly show two sublattices.

To confirm the nature of the reconstruction-free islands, different STS were applied on both Ag substrate and reconstruction-free species. The results show the islands hold different electronic characteristics compared to Ag, with a bigger work function of 5.7 eV than Ag (4.26 eV), and additional conductance states. Further DFT calculation and simulation of reconstruction-free iron oxide indicate in a 2 MLs FeO/Ag(111) system, the top layer of FeO on Ag(111) with a height of 2.30 Å has a 'free-standing' character. This tunable property is dependent on its thickness (interaction with Ag substrate only applies to monolayer thickness), making the FeO(111)/Ag(111) a good model system for electronic, magnetic and catalytic studies.

6. Structure of ultrathin vanadium oxide films on Ru(0001) and electron-stimulated desorption of V=O species

The presented results were partially published in:

[327] <u>Y. Wang</u>*, P. I. Wemhoff*, M. Lewandowski, and N. Nilius, "Electron stimulated desorption of vanadyl-groups from vanadium oxide thin films on Ru(0001) probed with STM" Phys. Chem. Chem. Phys., vol. 23, p. 8439–84445. (* - equal contribution)

The chapter describe the structure and unique properties of ultrathin vanadium oxide prepared on Ru(0001). Vanadium is a d-transition metal with five removable valence electrons, therefore, it can adopt multiple oxidation states. Owing to the bonding flexibility of vanadium^[301], vanadium oxide presents as a model system for many studies, such as photooxidation of hydrocarbons^[302], catalytic oxidation of $CO^{[303]}$ or the production of sulfuric acid^[304]. Ru(0001) is chosen to be the substrate due to its oxygen affinity (prone to oxygen adsorption even at RT) and catalytic properties of CO adsorption and oxidation^{[305][306][307]}, as well as in the growth of ultrathin oxide films, including FeO(111)^{[24][25][26]} and CeO₂(111)^{[308][309]}.Most importantly, such VO_x/Ru(0001) system has never been reported before. Thanks to the detailed studies of vanadium oxide grown on other single crystals (details were described in section 1.5), making it easier for the starting point of vanadium oxide preparation on Ru(0001).

The ESD, as introduced in section 1.6, was proved to be a highly-reliable and atomicallyprecise method for stimulating local desorption of atomic species, e.g. H from Si(001) ^{[310][311]} and Si(111) ^[312] or Br from Si(111)-7×7 surface ^[313]. One of the most-know potential application of this technique is high-precision nanolithography^[314]. However, the lack of STM-ESD experiments on oxide materials motivates such studies. A sufficiently good approach for studying oxide surfaces is to grow thin oxide films on metal single-crystal substrates to limit the charging effects^{[315][316]}. It is known that many vanadium oxide surfaces, for example V₂O₃(0001), exhibit high sensitivity towards electron stimulated modifications. For example, the vanadyl terminated V₂O₃(0001) shows little reactivity towards carbon dioxide, however, it becomes chemically active if the vanadyl layer is removed by electron bombardment^[317]. Even though this phenomenon was found long time ago, it was never studied at the atomic scale. Removal of surface vanadyl (V=O) groups in an ESD-type process should lead to a highly-reactive vanadium termination^[318].

There are two sections in this chapter. In section 6.1, the structure, electronic and thermal

stability of ultrathin vanadium oxide films on Ru(0001) is presented. A structural model based on the atomic-resolved STM image is proposed (vanadyl-terminated structure). In section 6.2, the removal of vanadyl units from oxide surface by high-bias scanning was observed, and further single vanadyl desorption through STM tip-stimulated approach is explored. By applying different tunneling condition, the obtained results, which give the fundamental insight into the nature of the desorption mechanism, is discussed.

6.1. Structural studies on vanadium oxide islands

The submonolayer vanadium oxide is prepared by depositing vanadium on a preheated Ru(0001) single crystal at 573 - 673 K with oxygen pressure of 5×10^{-7} mbar, followed by post oxidation at the same condition for 5 minutes and cooling down in oxygen for a few more minutes. In a last step, final vacuum annealing was performed at 673 K for 5 minutes. The obtained oxide structural parameters and proposed model based on the structure are presented in section 6.1.1. The electronic properties of this film are discussed in section 6.1.2. Additional 10 min annealing steps at 773, 873 and 973 K were applied to check the thermal stability of the obtained oxide film (section 6.1.3). The structure of vanadium oxide was measured by STM, LEED and its electronic properties were characterized by dI/dV and FER spectra (dz/dV).

6.1.1. Ultrathin vanadium oxide films on Ru(0001)

The morphology of vanadium oxide islands that develop both on the terraces and along step edge is very homogenous. The post vacuum annealing could slightly improve the surface quality (good quality is defined as clean substrate with uniform termination of oxide islands). As can be seen from **Figures 6.1.1 (a)** and **(b)**, the morphology of oxide islands is cleaner and exhibits a more complete termination (constructed by six bright spots arranged in kagome positions) after UHV annealing at 673 K. The inset in **Figure 6.1.1 (a)** is a zoom-in image of a surface with an incomplete top layer. In general, too low substrate temperature causes inefficient oxidation (not shown here), while too high temperature applied on Ru(0001) can result in the formation of metal deposits, e.g. due to oxide reduction (see red arrows). Moreover, higher substrate temperature during deposition can lower the oxide coverage, as can be seen by comparing **Figures 6.1.1 (b)** and **(c)**. The optimized method to prepare well-ordered vanadium oxide film is depositing vanadium onto a preheated Ru(0001) substrate hold at 573 K under oxygen pressure of 5×10^{-7} mbar, post oxidation under the same condition for additional 5 min, cooling down in oxygen for a few minutes, and finally vacuum annealing at 673 K for 5 min.



Figure 6.1.1. STM images of vanadium oxide on Ru(0001) fabricated with different preparation methods. 0.3 ML vanadium deposition at preheated sample which was held at: (a) 673 K, without final vacuum annealing. (I = 1.1 nA, V = + 1.5 V). Inset: zoom-in images of indicated region; (b) 673 K with final vacuum annealing at 673 K. (I = 0.05 nA, V = + 2.0 V); (c) 573 K with final vacuum annealing at 673 K. (I = 0.3 nA, V = + 2.0 V). (a - c): $100 \times 100 \text{ nm}^2$

The large-scale STM image of well-ordered vanadium oxide prepared by the optimized method is shown in **Figure 6.1.2 (a)**. The oxide grows as flat layer islands with a triangular-like shape. Due to the adoption of the atomic hexagonal structure of Ru hcp $(0001)^{[23]}$, these triangular oxide islands present a 180° rotation when moving from one terrace of the Ru substrate to an adjacent one (the rotation is indicated by the white triangles). More detailed surface feature can be observed from **Figure 6.1.2 (b)**. The oxide film consists of two height levels: (i) the top layer consists of bright features arranged in a honeycomb structure (edge - sharing); (ii) the underneath layer grows in a flat network with nearly triangular shape and $20 \sim 50$ nm edge length (marked by white triangles in (a)). The height profile taken for both structures marked by white arrow is shown in **Figure 6.1.2 (c)**. The measured height of the flat layer is around 3.1 Å, and the top structure is approx. 1.6 Å high. Note that the corrugation of the bottom layer is ~ 0.6 Å. All the obtained values are calibrated to the Ru step height (2.14 Å).



Figure 6.1.2. STM images of vanadium oxide on Ru(0001): (a) I = 0.3 nA, V = + 1.5 V, 200 × 200 nm²; (b) I = 0.3 nA, V = + 2.0 V, 20 × 20 nm². (c) Height profiles taken from (b), marked by white arrow.

The atomic structure was studied with the help of STM images and LEED patterns to understand the construction of the oxide lattice. Figures 6.1.3 (a - d) presents atomically resolved images of the surface from STM using different tunneling parameters. The surface features remain the same, suggesting that the contrast is of topographic and not electronic nature. Only some

contrast modifications are detected, which might relate to the effect of a variable LDOS. Occasionally, domain boundaries with distinct mirror symmetry can be observed in the oxide adlayer. As shown in (a - d), such mirror domains can be found inside oxide islands regardless where they locate. This is formed by two isolated domains with 180° growth direction coming together and forming a combined island. Sometimes, a middle transition phase can also be observed, as marked by the red rectangular in **Figure 6.1.6 (a)**.

The statistics of height (measured from large scale STM image) of the underneath vanadium oxide layer are shown in **Figure 6.1.3 (e)**. Except of very low bias (+ 0.55 V with a measured height of 2.8 Å), the average height is within 3.15~3.28 Å. In general, the variation of tunneling parameters has limited effect on the structural characteristics. The oxide films exhibit sharp (2 × 2) LEED spots overlaid by a weaker (4 × 4) pattern, as shown in **Figure 6.1.3 (f)**. While the (2 × 2) diffraction spots are assigned to O/Ru(0001)^[319] structure, some (2 × 2) s-V₂O₃ film structures might exist as well, as they were found on both Pd(111)^[104] and Rh(111)^[106]. The (4 × 4) reflexes are exclusively diffracted by the vanadia overlayer.



Figure 6.1.3. STM image of vanadium oxide on Ru(0001) using different tunneling parameters: (a) I = 0.5 nA, V = + 0.3 V; (b) I = 0.5 nA, V = + 0.5 V; (c) I = 0.5 nA, V = + 1.2 V; (d) I = 0.2 nA, V = + 0.5 V. (e) Height statistics of the underneath vanadium oxide layer measured at different bias. (f) LEED pattern (100 eV), the Ru unit cell, (2 × 2) and (4 × 4) structures are labeled by the white, yellow and green rhombus, respectively. (a - d): 10 × 10 nm².

The atomic structure of the vanadium oxide was determined by the following steps. First, all types of the atomic maxima resolved in the lower plane (assigned as V cations since their states are typically better accessed at positive bias in STM) were labeled by green and blue triangles (with one V-ion at each corner), as shown in **Figure 6.1.4 (a)**. The underneath vanadium oxide layer is constructed on a kagome network. The V-ions marked by green triangles only appear every third

blue triangles in a line (in three orientations), showing an additional trifold feature. Each kagome unit cell holds one bright protrusion with their distinct threefold symmetry, sitting on top of all the three-cation group (blue triangle), forming a honeycomb-like structure. The spacing between top layer feature, as marked by the rhombic unit cell, is about 10.9 Å. This value is 4 times the lattice constant of Ru(0001), explaining the (4×4) structure observed in LEED.



Figure 6.1.4. (a) Atomically resolved STM image of vanadium oxide on Ru(0001) (I = 0.5 nA, V = + 0.5 V, 4 × 4 nm²). The black parallelogram marks the (4 × 4) unit cell of the lattice. The blue and green triangles indicate all the atomic resolved maxima by STM. (b) The same image as in (a) with the hexagonal structure of additional protrusions. (c) Complete structural model of the vanadium oxide film based on (b), with added oxygen.

Based on the structural parameters obtained from atomically resolved STM images, a complete model of this vanadium oxide is shown in the **Figure 6.1.4 (c)**. The small contrast observed for the atomic corrugation could arise from different binding sites for vanadium, on top (corners of blue triangle) or in hollow site (corners of green triangle), denoted as V_{top} and V_{hollow} , respectively. First, placing the blue balls representing the V_{hollow} ions on Ru(0001) inside the kagome frame, and then putting V_{hollow} ions depicted by green balls in every third kagome structure, as discussed above. However, an unreasonable large spacing appears in this model, while a maximum is visible at this position from STM image, indicated by blue arrow in **Figure 6.1.4 (b)**. To bridge the large gap, one extra V_{hollow} is added in between, also marked by blue arrow in **Figure 6.1.4 (c)**. Finally, adding O species around V cations completes the structure. The obtained structure results in an arrangement of fourfold-coordinated and threefold-coordinated vanadium cations.

The upper layer comprises a hexagonal lattice of isolated ad-species that sit in between the

 V_{top} group in the lower plane. Many reports regarding vanadium oxide assigned these bright protrusions to vanadyl (V=O) groups. Examples are, among others, the bright feature located at the corner atoms of zigzag V₆O₁₁ structure on Pd(111)^[104]; the bright blobs showed in ($\sqrt{7} \times \sqrt{7}$) R19.1° V₃O₉ structure on Rh(111)^[106]; the bright features on the 'oblique' oxide phase on Rh(111)^[106] that is similar to zigzag structure on Pd(111); the bright center of rectangular unit cell of ($5 \times 3\sqrt{3}$)V₁₃O₂₁ unit cell (O₄V=O unit)^[107]; and the reconstructed ($\sqrt{3} \times \sqrt{3}$) R30° V₂O₃ terminated with vanadyl group (the height of V=O unit is 1.61 Å)^[108]. From all the examples mentioned above, the bright protrusions observed in STM images may be reasonably assigned to V=O groups. Another fact is that the bright protrusions formed in the top layer can be removed by high bias scanning. Such behavior was also shown for vanadyl groups in previous research (see introduction section 1.5). Therefore, the nature of these bright maxima is likely upright standing vanadyl (V=O) units.

In principle, there are two basic units assembled in the model built in Figure 6.1.4 (c). One unit without vanadyl group has an overall stoichiometry of V_6O_{12} (six threefold-coordinated V ions) while the other one consists a vanadyl unit forming a structure of $V_3O_{12}V=O$ (three fourfoldcoordinated V ions and one vanadyl species). The high O content of the overall oxide layer might be due to the large reactivity of Ru with respect to oxygen. Noticeably, six $V_3O_{12}V=O$ forming a hexagon and all together make a honeycomb network for the upper layer, with one V_6O_{12} unit, comprising three threefold, two fourfold and one vanadyl vanadium, in each hexagon center. Such model only applies to the surface structure obtained after 0.3 ML vanadium deposition and oxidation. However, confirmation of this structural model is difficult due to the limited information from literature. Various vanadium oxide structures can be formed by different preparation methods, oxide coverage, and the supporting substrate. The results can be either referred to vanadium oxide grown on Pd(111) due to the similar lattice constant of the substrate (Pd: 2.75 Å; Ru: 2.71 Å) and similar electronegativity, or to a Rh(111) substrate due to its comparable oxygen affinity and chemical reactivity. At the first glance, the structure might related to $(4 \times 4) V_5 O_{14}$ thin film grown on $Pd(111)^{[105][130]}$. Here large oxide pores with twelve cations exist, with each unit consisting of one V cation in tetrahedral coordination plus four O ions. However, those islands have ~ 2.0 Å height and big corrugation of ~ 1.3 Å, which is comparable to the Ru(0001) case (~ 3.0 Å). The atomically resolved STM image of the oxide film exhibits an additional structure inside the oxide pore, which was not found for the V5O14 oxide film. This might be caused by the rapid development of $O(2 \times 2)$ superstructure formed on Ru(0001) during vanadium oxide preparation. Another related candidate shares similar height of ~ 3.0 Å with hexagonal VO₂ layer, but this layer is less stable and will grow on top of a close packed $V_2O_3(2 \times 2)$ to stabilize the whole structure, increasing the overall height to ~ 5.0 Å^[104], which is incompatible with the obtained results.

Oxide phase of $(\sqrt{7} \times \sqrt{7})$ R19.1° and a $(\sqrt{13} \times \sqrt{13})$ R13.8° found on Rh(111)^[106] have also been taken into consideration. The $\sqrt{7}$ -structure has a kagome structure while the $\sqrt{13}$ has a structure without sharing atoms either along the edge or the corner. Moreover, the pore size does not fit the present findings. Therefore, these two structures may be excluded. Another possibility, which appears if the coverage of vanadium on Rh(111) slightly increases, is the formation of vanadyl species on top of the 'oblique' oxide phase (two times lattice constant of Rh in $<1\overline{21}>$ direction) - similar to zigzag stripe oxide phase V₆O₁₄ on Pd(111)^{[124][320]} but in a more disordered way. Both

structures (the 'oblique' phase on Rh(111) and V_6O_{14} on Pd(111)) develop bright features on top. The theoretical model of V_6O_{14} structure shows it has much denser packing and the Pd(111) substrate is fully covered^[124]. Although this structure is not fitting the characteristic structure of vanadium oxide on Ru(0001) due to the smaller height of ~1.8 Å and morphology, it is a hint that vanadium oxide is possibly formed in a way that only allow the ad-species (V=O) to sit on every second stripes instead of distributing uniformly). Moreover, the order of the zigzag surface layer (check Figure 1.5.3) can be destroyed by tip scanning the same region repeatedly, which results in a progressive removal of the bright protrusions^[104] – this is a very similar behaviour as found for the present systems.

In summary, the vanadium oxide grown on Ru(0001) forms a new structure, which was never reported before. A model is proposed based on atomically resolved STM images that consists of many elements I found plausible from literature. The structure comprises two planes: (i) the lower layer formed by combination of six- and three-membered V-O rings (O also bond to Ru(0001) to rationalize the four O per V), denoted by V_6O_{12} and V_3O_{12} , respectively; (ii) the top layer (bright features) is assigned to V=O groups sitting on top of V_3O_{12} , and forming $V_3O_{12}V=O$. All the V ions in the model do not exceed the highest 5+ state, and meet the requirements on the bond length constraints. However, the structural model needs additional confirmation by vibrational spectroscopy (this technique was used for distinguishing different V compounds) as well as DFT calculations in the future.

6.1.2. Electronic structure of vanadium oxide islands

To understand the electronic properties of vanadium oxide grown on Ru(0001), a few STS measurements were performed. The dI/dV and FER (dz/dV) curves are shown in **Figure 6.1.5**. The constant height dI/dV spectra (feedback control off) were obtained from -1.5 V to +1.5 V. The ultrathin vanadium oxide does not exhibit the characteristic low-temperature band gap like bulk V₂O₃^{[321][322]}. As can be seen from **Figure 6.1.5** (**a**), similar features can be found using different setpoint (lower curve performed with ± 1.5 V while the upper curve used ± 0.5 V). Two maxima located at + 0.1 V and - 0.4 V could be found. Higher density of filled states is presumably of V 3d band [^{108]}. In the form of bulk V₂O₃ (octahedral coordination), the crystal field split the V 3d into e_g and t_{2g} manifolds near the Fermi level E_F. The upper e_g level is empty and lower t_{2g} states are partially filled and hybridizing with the O_{2p} orbitals^{[323][324]}. Indeed, the band splitting characteristic is directly connected to the local geometry. For instance, a reversed energetic ordering of the orbitals could be found if vanadium possesses a tetrahedral coordination (compare to octahedral coordination)

The FER spectroscopy of the obtained vanadium oxide on Ru(0001) is displayed in **Figure 6.1.5 (b)**. All spectra have been obtained with constant current mode. Using the spectra obtained from Ru(0001) substrate as a reference (black curve), one can observe a peak centered at around + 5.7 V, which is a bit higher than the literature value of $\sim + 5.5$ V^[326]. The higher work function I obtained may be due to the oxygen ad-layer on top or the Au tip condition. The top V=O layer

displayed two maxima positioned at + 3.25 V and + 4.25 V (dark blue curve), while the layer below shares similar electronic features but the position of the latter peak slightly shifts to higher bias to + 4.3 V (orange curve). This state represents the first field emission resonances in the tip-sample junction which gives an estimation of the work function (+ 4.25/4.3 V, lower than for the Ru substrate). Further resonances beyond 5.0 V are not detectable since the surface undergoes irreversible changes (removal of the top V=O species) at higher bias. The lower state, on the other hand, corresponds to the high-lying antibonding state of the V-O system at + 3.25 V.



Figure 6.1.5. Spectroscopy of vanadium oxide islands, lock-in parameters: frequency = 1145 Hz, amplitude = 14 mV. (a) dI/dV spectroscopy of a vanadia island taken at different setpoints: + 0.5 V (blue curve) and + 1.5 V bias (orange curve). (b) constant current FER spectra of the bottom oxide film, V=O ad-species, and the O-covered Ru(0001) surface (Adopted from Figure 3 from [327]).

To explore the electronic features of the vanadium oxide layer (structure(i)) and top V=O species (structure(ii)), dI/dV mapping of these structures was performed. A full set electronic mapping (-2.0 V to +2.0 V with 0.5 V steps) is shown in **Figures 6.1.6 (a - h)**. The strongest contrast of these two structures is at +0.5 V bias, which, on the other hand, indicates different electronic feature of these two layers, especially at high positive and low negative bias. The transition phase has higher density of states at high positive bias compared to the other two structures. The nature of this oxide phase and its growing mechanism is still unclear at the moment.

In summary, the set of dI/dV mapping has shown a different electronic structure between the bottom vanadia islands and top V=O ad-species, especially at high negative bias and low positive bias. The strongest contrast appears at +0.5 V, where a small conducting state near this bias (the strongest signal is at + 0.1 V) could be observed in the dI/dV curve. The transition phase also shows contrast with respect to the other two structures at high positive bias. The setpoint bias will not switch the conductance spectra (with disabled feedback loop from - 2.0 V to + 2.0 V) on the vanadia islands. The high bias spectroscopy under feedback control indicates a similar electronic feature between vanadia island and V=O unit (two peaks at + 3.25 and + 4.25/4.3 V).



Figure 6.1.6. dI/dV mappings of vanadium oxide at different bias. I = 0.66 nA, scanning speed = 200 Å/s; lock-in parameters: frequency = 1200 Hz, time constant = 3 ms. (a) + 2.0 V; (b) + 1.5 V; (c) + 1.0 V; (d) + 0.5 V; (e) - 0.5 V; (f) -1.0 V; (g) -1.5 V; (h) - 2.0 V. (a) - (h): $10 \times 10 \text{ nm}^2$.

6.1.3. Thermal stability of vanadium oxide structures

The surface morphology of vanadium oxide is not only determined by film coverage, but is also strongly influenced by the post vacuum annealing. One example is the O-rich $V_2O_3(0001)$ grown on Rh(111), which can be reverted back to V=O terminated $V_2O_3(0001)$ by vacuum annealing above 923 K^[108]. Another example are the planar hexagonal clusters of vanadium oxide, formed under strong oxidation condition, which can diffuse on the Rh(111) terrace if the temperature reaches 383 K^[107]. In general, the thermal stability of the surface morphology (resistance to heating) reflects the structural features in some aspects.

Therefore, a stepwise annealing from 773 K to 973 K of vanadium oxide with steps of 100 K

was performed. The LEED patterns of the samples are shown in **Figure 6.1.7**. The vanadium oxide was prepared by the optimized approach at 673 K, as shown in **Figure 6.1.7** (a), with clear (2×2) and weak (4×4) pattern. A zoom into one of the main Ru (1×1) spots is displayed for better view and further comparison. For well-ordered vanadium oxide with the characteristic two-layer structures as describe above, all the reflexes are sharp and intense. A more diffused pattern was observed after additional 10 min vacuum annealing at 773 K. Now, all the diffracted beams are elongated (could be caused by either distorted surface structure or some artefact), and the intensity of (2×2) significantly drops, as presented in **Figure 6.1.7** (b). After 10 min annealing at 873 K, as shown in **Figure 6.1.7** (c), a clear (2×2) reflex pattern appeared again, while the (4×4) spots become invisible. Noticeably, additional satellite beams around main (1×1) spots start appearing, this multiple scattering indicates some surface reconstruction like Moiré superstructure. **Figure 6.1.7** (d) shows the LEED result after 10 minutes of UHV annealing at 973 K, a more intense (2×2) diffraction pattern with similar satellite spots as for the sample annealed to 873 K.



Figure 6.1.7. LEED pattern (100 eV) of different vanadium oxide on Ru(0001). (a) Vanadium oxide prepared using optimized method at 673 K. Post annealing at (b) 773 K for 10 min, (c) 873 K for 10 min and (d) 973 K for 10 min.

The corresponding large-scale STM images of these post annealed systems are presented in Figure 6.1.8. The ordered surface structure of vanadium oxide prepared by the optimized method is shown in Figure 6.1.8 (a). After vacuum annealing at 773 K for 10 minutes, the surface structure remains the same (two layers structure) in most of the region, as displayed in Figure 6.1.8 (b). The small vanadium oxide islands start merging to bigger islands, and preferentially nucleates at the lower step edge. The lower oxide coverage and clearer substrate (some O desorbed from Ru substrate) might be the cause of the weaker (2×2) LEED pattern shown in Figure 6.1.7 (b). Additionally, some new phases (marked by the white arrows) started growing and nucleating inside those big islands. This new phase dominates the surface structure when the annealing temperature reaches 873 K, as shown in the Figure 6.1.8 (c). Noticeably, the new phase also consists of two layers. While the bottom flat structure has similar height as the low-temperature phase, i.e. approx. \sim 3.1 Å, the top layer, with big bright particles, are within 1.6 - 1.8 Å. After annealing at 973 K, the coverage of islands is significantly reduced, as shown in Figure 6.1.8 (d). The new structure has a poorly ordered arrangement, which is considered as the remnants after heating away the oxide film. Such structure contributes to the multiple scattering spots near (1×1) in the LEED pattern as shown in Figures 6.1.7 (c) and (d), the remaining (2×2) spots here should correspond to the remaining O on Ru(0001), while the new structure might also contribute to its intensity (the highest O2 thermal desorption peak is above 1000 K)^[225].



Figure 6.1.8. Large scale STM images of annealed vanadium oxide on Ru(0001). (a) Vanadium oxide prepared using optimized method at 673 K (I = 0.3 nA, V = + 1.5 V). Post annealing at (b) 773 K for 10 min (I = 0.048 nA, V = + 2.0 V. Inset: I = 0.51 nA, V = + 0.5 V, $30 \times 30 \text{ nm}^2$), (c) 873 K for 10 min (I = 0.071 nA, V = + 1.5 V) and (d) 973 K for 10min (I = 0.86 nA, V = + 1.5 V). (a - d): 200 × 200 nm².

More detailed structures of the annealed samples are resolved by STM. Various structures including three different regions can be observed after 873 K annealing, as shown in the **Figures 6.1.9 (a)** and (e). Region I occupies a very low coverage on the surface. It consists of triangular-shaped islands surrounded by a smaller network at first glance. Interestingly, such structure can be resolved by using very high negative bias (-2.0 V), as shown in **Figure 6.1.9 (b)**. The measured periodicity of the network is approx. 6.4 Å, which is about 18% enlargement with respect to the (2×2) structure. On the other hand, at positive bias (+ 1.5 V), shown in **Figure 6.1.9 (c)**, only the network near the bright particles can be resolved, indicating different surface characteristics of the network. Rarely, the region III (labelled in **Figure 6.1.9 (d)**) is observed on the surface due to its small coverage. The zoom-in STM image of region III is shown in the top side of **Figure 6.1.9 (f)**. It is most likely the transition phase of (4×4) network of vanadium oxide, with ordered structure, while the top V=O group has desorbed from the surface due to the high temperature annealing. For better comparison, the same size STM image of the oxide before annealing is placed on the bottom in **(f)**. As indicated by the blue arrows, the spacing between two dark holes is around 10.9 Å for

both cases. Notably, the structure after thermal treatment (top image) is quite homogenous compare to the one before annealing, which relates to the release of V=O. Thus, the new structure shared some similarities to the (4×4) V₅O₁₄ structure on Pd(111) (check Figure 1.5.3). Indeed, details of the structure need more confirmation from experiments.



Figure 6.1.9. Various vanadium oxide phases after annealing at 873 K: (a) Typical surface morphology of region I. (I = 0.12 nA, V = + 1.4 V, 50 × 50 nm²), and the zoom-in image of region I (b) (I = 0.66 nA, V = - 2.0 V, 10 × 10 nm²) and (c) (I = 0.66 nA, V = + 1.5 V, 10 × 10 nm²). (d) Typical morphology of region II and III (I = 0.44 nA, V = + 2.0 V, 50 × 50 nm²). (e) Zoom-in image of region II (I = 1.1 nA, V = + 1.0 V, 10 × 10 nm²). (f) Top: zoom-in image of region III (I = 1.1 nA, V = + 1.5 V, 10 × 10 nm²); bottom: vanadium oxide before thermal treatment (I = 0.51 nA, V = + 0.5 V, 10 × 10 nm²).

Most of the surface is occupied by region II (labelled in **Figure 6.1.9 (d)**), and the corresponding zoom-in image is shown in **Figure 6.1.9 (e)**. Three characteristic big bright particles differ in their apparent height and are labelled as H(high), M(medium) and L(low). Due to the big corrugation, the measured height of low particle is within 1.0 Å, for the medium particle is in between 2.0 Å and 2.5 Å, while the highest particles range from 2.7 Å to 3.2 Å. The heights of those low particles are apparently out of the range of the usual height of vanadium oxide layer (depends on the oxide phase, usually in the range of $2 \sim 5$ Å, as discussed in section 1.5). Therefore, a reasonable assumption could be that high vacuum annealing leads to the partial metallization of the vanadium, and probably alloying with the Ru(0001).

In summary, the prepared vanadium oxide is stable for temperatures below 773 K. Above 773 K, various transition phases start appearing. After annealing at 873 K, the surface exhibit three different regions, where a homogenous transition (4×4) phase without V=O on top could be observed (the LEED did not show (4×4) spots due to the very low coverage). When the annealing temperature reaches 973 K, the loss of oxygen results in the significant coverage decrease, and some of the remaining oxide layer has a very low height – indicating partial metallization of

vanadium.

6.2. STM tip-induced desorption of vanadyl species

High-bias scanning can lead to the removal of vanadyl units from the vanadium oxide surface. To understand the mechanism, detailed electron-stimulated desorption (ESD) experiments were performed on the samples. All experiments of STM tip-induced ESD were conducted in the constant current mode. After recording the image, the tip was directed to place on top of the V=O group, then a voltage ramp was started to the desired value in a short time and the bias was kept for a certain amount of time and the height spectroscopy data (z(t)) were recorded. After the experiment, the surface was scanned again to check if a successful removing event was achieved. Different parameters were applied in the STM tip-induced ESD experiments, to detect the relation between removing efficiency dependence on the bias and tunneling current. Based on the obtained data, the bond structure between the V=O species and the bottom vanadia film and desorption mechanism are reasonably interpreted.

6.2.1. Removing top vanadyl units by STM probing

The vanadyl species in the top layer were found to be removable during high-bias scanning. Typical STM images before and after successful removal event are shown in **Figure 6.2.1 (a)** and **(b)**. Different bias is applied for the zoom-in surface images of the region pointed out by the red square, ranging from + 2.0 to + 4.0 V with 0.5 V steps, as displayed in the **Figure 6.2.1 (a₁ - a₅)**.



Figure 6.2.1. STM images of desorption of vanadyl species from vanadium oxide film grown on Ru(0001): (a) Before removal of V=O groups, (I = 0.2 nA, V = + 1.0 V, 20 × 40 nm); (b) After removal of V=O groups (It = 0.66 nA, V = + 1.5 V, 20 × 40 nm). Different bias applied for scanning on the region marked by red frame in (a) at I = 0.66 nA and: (a₁) V = + 2.0 V; (a₂) V = + 2.5 V; (a₃) V = + 3.0 V; (a₄) V = + 3.5 V; (a₅) V = + 4.0 V; (a₆) at the region indicated by the green frame. I = 0.66 nA, V = + 4.0 V. (a₁) - (a₆): 10 × 10 nm².

The surface barely changed before + 3.0 V, but got slightly modified at a bias of + 3.5 V, while significant removal of the V=O groups happened at bias of +4.0 V. Zooming out the modified region and scan the morphology of the entire island at low bias again, reveals that most of the top features disappeared. This unexpected removing behavior was further confirmed by another scan of the region, as marked by the green square at + 4.0 V (see **Figure 6.2.1 (a**₆). The exposed bottom oxide layer is identical to the one described in section 6.2.1, with a distinct atomic structure with 5.4 Å periodicity along certain orientations and the development of a quasi-(2 \times 2) network.

Determine of the nature of removed species by analyzing the images before and after the manipulation (shown in **Figure 6.2.2 (a)** and **(b)**) is not trivial. Based on the model proposed before, it is ambiguous to tell only the V=O units are removed, leaves structure shown on the model displayed in **Figure 6.2.2 (b)**, or a complete tetrahedral O₃V=O pyramid with the remaining structure model being shown in **Figure 6.2.2 (c)**. On the basis of the data, the removed species were attributed to a capping V=O unit. As mentioned before, V=O species could be removed by repeatedly scanning the surface. The phenomenon was observed previously for the zigzag structure of vanadium oxide grown on Pd(111)^[104]. The STM images show a slightly higher topographic height of V₃O₁₂ structure that used to be capped with V=O unit as compared to its neighboring sixring V₆O₁₂ structure. This might be due to different local density of states by various oxidation states of vanadium cations. It also indicates that not the entire VO₄ pyramid but only the V=O adspecies bound to the top layer gets removed during desorption. Removal of the V=O alone is also more energetically favorable as the surrounding V ions are kept in their saturated chemical states and no dangling bond states are generated in the surface.



Figure 6.2.2. STM images of vanadium oxide structure (a) before high biased 4.0 V annealing (I = 0.51 nA, V= + 0.3 V, 5 × 4 nm) and (b) after high-biased 4.0 V scanning (I = 0.66 nA, V= + 0.5 V, 5 × 4 nm). Possible models after top protrusion removal: (c) removal of V=O units. (c) removal of O₃-V=O pyramids.

To have detailed analysis of the process with atomic precision and high reliability, subsequent experiments were performed using tip-induced ESD in the STM. By recording more than 500 individual spectra and categorizing them, a clear conclusion was drawn on the desorption mechanism. Each single experiment, as shown in the example in **Figure 6.2.3**, has been carried out

according to the following, optimized procedure: (i) Stabilize the scanning position of the tip using a bias of + 2.0 V (-2.0 V for negative polarity), pause and locate the tip on top of the bright feature that shall be desorbed from the surface. (ii) Set the time spectroscopy z(t) under constant current mode, a complete cycle is set to be 60 s. Ramp the bias from + 2.0 V to the desired final value (e.g. to + 3.7 V) within 3 s, and keep it at this bias for the rest 57 s. (iii) Record the z(t) spectroscopy, and re-scan the same region (+ 2.0 V) after acquiring the height spectra. (iv) Check if a successful desorption event was made at + 3.7 V. To reduce the influence from an ill-defined environment, the selected V=O unit must be perfectly in the middle of the island and have three other V=O neighbors. This implies that once a vanadyl unit desorbed from the surface, the neighboring three vanadyl units cannot be used for the measurement any more.



Figure 6.2.3. STM tip-induced ESD experiments: (a) STM image of a vanadium oxide island before applying + 3.7 V, 1 and 2 indicated two selected vanadyl units for removing (I = 0.3 nA, V = + 1.5 V, $17 \times 17 \text{ nm}^2$). (b) Height spectroscopy z(t) of the two desorption events after applying +3.7 V of the marked V=O units in (a). STM image after applying +3.7 V at 0.3 nA: (c) one V=O group (vanadyl unit 1) is desorbed (I = 0.3 nA, V = + 2.0 V, $17 \times 17 \text{ nm}^2$); (d) two V=O groups (vanadyl unit 2 and its neighbor) is removed (I = 0.3 nA, V = + 2.0 V, $17 \times 17 \text{ nm}^2$) (Edited from Figure 4 from [327]).

The recorded height (tip-sample distance) versus time spectra z(t) reveal an initial height drop in the first 3 s, indicating an increase of the tip-sample distance by ramping up the bias. Very often, the spectroscopy either shows a flat (with small fluctuation) line or a height jump. The flat line indicates no removal event, while the 'height jump' directly relates to the decrease of tip-sample distance due to desorption of one V=O unit. As shown in **Figure 6.2.3 (b)**, the height jump is around 1.5 Å, corresponding to the height of a V=O unit. Since the tip is very stable during the ESD measurements (only crashing a few times during the whole set of experiments), the desorbed V=O groups are most likely transferred to the vacuum instead of to the tip. Moreover, no partial removal was ever found, but rarely, the desorbed V=O unit was redeposited to the surface and could then be located either at the original or a neighboring position.

Noticeably, various shapes could be found in the z(t) spectra in the rest of the 57 s. Apart from a height jump, sometimes a single height drop could also be observed. More complicate cases included an initial height jump and then a drop, or a few little height jumps, etc. Moreover, sometimes one height drop can also result in either removing nothing from the surface or removing two V=O groups. This could be due to a delayed response, which did not happen within the 57s of the spectroscopy. Although these extra examples are not the majority cases during ESD experiments,

they make the desorption patterns hard to follow. Therefore, it was always required to check the surface morphology after a 'successful event (height variation)' observed from the z(t) curve, to ensure the obtained results.

In summary, an instant removing of the vanadyl species can happen using high-bias scanning (above 3.5 V). The nature of the removed species is believed to be an V=O unit, based on three reasons: (i) slightly higher remaining structure as compared to a neighboring six-ring; (ii) energetically favored for the remaining bottom V ions; (iii) the height change of around 1.5 Å which is close to the height of V=O dimer. The vanadyl groups desorbed by ESD are most probable transferred to vacuum instead of accumulating at the tip. The observation of height jumps in z(t) spectra are often related to successful desorption events.

6.2.2. Controlled V=O desorption via electron tunneling

To gain more insight into the mechanism of oxide-vanadyl bounding using ESD analysis, a few series of desorption experiments were performed by varying the bias voltage (both positive and negative) and tunneling current. The range presented for bias and tunneling current is determined based on large statistics. For example, the range of tunneling current is in between 0.03 to 1 nA, the minimum value is determined to be the one or two value before the starting point of successful removal events (which means at 0.03 nA, the possibility of successful removal event is almost 0, but at the next value 0.06 nA, there is a small possibility of V=O desorption), while the maximum value is determined by the point when almost every ESD experiment can lead to a successful removal of V=O (which means at 1.0 nA, the possibility of successful removal event is almost 100%). Based on this principle, the range of bias is in between 3.0 to 4.0 V for positive bias, -2.5 to -3.1 V for negative bias.

In principle, two values are of interest from each obtained spectroscopy: (i) the removal efficiency, which is defined as the percentage of successful removal events of V=O units per stimulation trials. Noticeably, for one ESD experiment, two adjacent ad-species might be desorbed at the same time, especially at higher bias/tunneling current, which is counted as two for removal number in the ESD results analysis, which means that obtained removal efficiency for this particular case is 200%. Therefore, the averaged value in the end could exceed 100%. (ii) the normalized desorption rate, which is defined as the removal frequency normalized by the number of impinging electrons (1 nA = 6.2×10^9 electrons in 1 s). Hereby, the frequency is determined as the inverse value of initial jump time. For example, from the top spectra in **Figure 6.2.3 (b)**, the first jump appears at 15 s, consider the initial 3 s is for ramping up, the accumulated time for one successful event is 12 s. Therefore, for the case at + 3.7 V and 0.3 nA, the desorption rate is calculated to be $(1/12)/(0.3 \times 6.2 \times 10^9) = 4.5 \times 10^{-11}$ electron⁻¹s⁻¹.

Figures 6.2.4 (a) and **(b)** depicted the removal efficiency of V=O group(s) with respect to bias (both polarities) and current. At the positive bias, successful removal of one vanadyl unit is detected above + 3.3 V using current at 0.3 nA, and above + 3.6 V with applied current of 0.06 nA. The

efficiency increases as the bias increases in both current examples. At 0.3 nA, two V=O units desorption could be observed above + 3.7 V for positive bias and - 2.9 V for negative bias, as shown in the inset of **Figure 6.2.4 (b)**. At 0.06 nA, the two removal cases start appearing at +3.8 V (not shown in the figure). The one and two V=O group(s) removal efficiency as function of current is shown in the inset of **Figure 6.2.4 (a)** by the red and black dashed line, respectively. In general, both cases behave similarly after reaching threshold current value. Such results are not out of expectation, since for either bond breaking or vibrational excitation mechanism, the number of electrons (tunneling current) and electron energy (bias) should determine STM tip-induced desorption.



Figure 6.2.4. V=O unit removal efficiency summary of the ESD experiments. (a) One V=O group removal efficiency as function of positive bias, from + 3.0 to + 4.0 V, at two different current (0.3 nA and 0.06 nA); (b) One V=O unit removal efficiency as function of negative bias, from - 2.4 to - 3.1 V. The inset in (a) indicates one V=O unit removal efficiency (red) and two V=O units removal efficiency (black). The inset in (b) indicates two V=O groups removal efficiency as function of bias in both polarities, starting from + 3.7 V for positive bias and - 2.9 V for the negative case.

To better explore the mechanism of the desorption of V=O units from the vanadium oxide layer, the summary of the full data analysis is compiled in **Figure 6.2.5**. The outcome of the desorption rate as function of bias and current indicates a similar trend as the removal efficiency. **Figure 6.2.5 (a)** and **(b)** shows vanadyl desorption rate increases steeply after reaching the critical bias in both polarities, the exponential-like curve is quite similar to the well-known model of

truncated harmonic oscillator^[328], which is applied to explain the system of hydrogen desorption from Si substrate^[143]. This might be used to explain the studied system. Simply speaking, the desorption rate is highly connected to the vibrational heating, which depends on the balance of the vibrational excitation process (proportional to the electron energy and tunneling current) and relaxation process (determined by vibrational energy coupled to phonons). In particular, the vibrational temperature generated during this process influences the desorption rate exponentially.



Figure 6.2.5. ESD experiments summary on vanadyl desorption from vanadium oxide surface: (a) Normalized desorption rate as function of negative bias at 0.3 nA. (b) Normalized desorption rate as function of positive bias at tunneling currents of 0.3 nA and 0.06 nA. (c) Desorption rate as a function of tunneling current for electrons at bias of + 3.7 V. (d) Current-dependence of the desorption rate as function of tunneling current for + 3.7, + 3.5 and -2.7 V, shown in a double logarithmic scale. The straight lines are linear fits according to Rate ~ I^{α} (Adopted from Figure 5 in [327]).

Moreover, the desorption rate as function of tunneling current (bias at + 3.7 V) is displayed in **Figure 6.2.5 (c)**. In particular, the current dependence is shown in **Figure 6.2.5 (d)** for both polarities (bias at + 3.7 V, + 3.5 V, and -2.7 V) in double logarithmic scale. The measured slope in (d) determines the number of the required electrons (α) for V=O removal, according to the approximation: rate ~ I^{α} . At positive bias, α is calculated to be 2.1 ± 0.2 (+ 3.7 V), 2.2 ± 0.2 (+ 3.5 V). At negative bias, α is determined to be 3.1 ± 0.3 (- 2.7 V). The obtained values of the slope immediately rule out the one-electron mechanism for desorption, indicating a nonlinear many-electron vibrational heating mechanism. From the broad tunneling current range (0.03 nA to 1 nA) and the high bias employed in the measurements, any effects from mechanical interactions between adsorbates and tip can be safely ignored.

The results indicate that vanadyl removal mechanism involves a many-electron (hole) process,

that includes tunneling into antibonding (positive bias) or out of bonding states (negative bias). Similar results were obtained for hydrogen desorption on Si(001) substrate. At positive bias, a desorption event can happen beyond the threshold energy of + 6.0 V when electrons tunnel into the Si-H σ^* antibonding orbital ^[143]. At negative bias, the critical value is - 5.3 V for tunneling out of filled 5 σ hole resonance state of Si(001), which leads to H stimulation and desorption^[146]. Such desorption usually requires 5 to 7 electrons depending on the bias^[146]. However, for the case hydrogen desorption from TiO₂(110)^[151], the situation is slightly different. Already one or two electron(s) at low bias (below + 1.6 V) can provide enough vibrational energy due to inelastic electron tunneling into surface hydroxyls (O-H stretch vibration). The desorption mechanism is governed by single electron processes when higher bias is used. This unusual behavior of TiO₂ that is a wide bandgap insulator, might be due to less efficient de-excitation and therefore, longer lifetime of the vibrational modes.

The relevant orbitals that contribute to the V=O desorption from vanadium oxide are either the O_{2p} character below – 2.5 V or the V_{3d} crystal-field states at high positive bias, respectively^[322]. The vanadyl-terminated V₂O₃(0001) was studied by DFT calculation. The electronic structure is dominated by the e_g and t_{2g} manifold, split from the V_{3d} states^[322]. The electronic states that are detected at around + 3.25 V (see **Figure 6.1.5 (b)**, and match the t_{2g} orbitals (see Figure 4.(b) in Ref. [322]) are directly related to the onset of V=O desorption. The electronic states with e_g character, on the other hand, are located at a lower energy level and can be excluded from the ESD of vanadyl units. In the process, the electrons/holes excite the antibonding/bonding states once the onset bias is reached. The tunneling electrons then transfer inelastic energy to the ad-species and trigger a vibrational excitation that cannot decays before next electron arrives^[329]. The manyelectron ladder climbing mechanism is therefore possible. Once the populated energy transferred from a series of inelastic electrons is sufficient, the adsorbates can be desorbed from the substrate.

In the present case, an α of 2~3 has been determined for positive and negative polarity, implying the inelastic energy transfer from two/three electrons is required to desorb a vanadyl unit. Compared to a similar thin vanadium oxide film grown on Rh(111), the vanadyl group show two vibrational peaks at 65 meV and 130 meV, with the latter one originating from the V=O bond stretching^[106]. The former one at 65 mV is related to the oxygen vibration against the metal which is not contributing to V=O desorption. The vibrations from the V=O stretching mode may now stimulate ladder climbing within the binding potential. It is worth mentioning here that relatively low electron energies can be sufficient to desorb a massive V=O group, indicating relatively low external vibrations of the vanadyl groups. The DFT calculations of V=O terminated V₂O₃(0001) ^{[323][330][331]} indicated relatively low energy for V=O desorption per surface unit cell (0.2~0.4 eV), depending on the O chemical potential. Connecting to the main vibration mode at 130 meV, this corresponds to 2~3 inelastic energy transfers to stimulate V=O unit desorption. Noticeably, the number shown here is only a rough estimation, and further studies, e.g. on the vibrational modes and the V=O interaction strengths, are needed for a more precise conclusion.

In summary, the desorption rate and removal efficiency of V=O units from vanadium oxide grown on Ru(0001) has been explored by means of STM tip-induced ESD experiments. The results

have shown a strongly bias- and current- dependent desorption probability. The desorption of the vanadyl units started at + 3.3 V at positive bias and at - 2.7 V at negative polarity. Even two V=O units could be removed in a single ESD experiment using higher bias voltage or current. The fitted slope of the desorption rates as function of tunneling current in a double logarithmic scale gave the value of 2~3, indicating that two/three electrons are required to desorb a V=O unit. The process involves the resonant population of antibonding/bonding states in the oxide and many- electron ladder climbing of V=O vibrational states within its binding potential. The underlying vibrational mode has hereby been identified to the V=O stretch vibration at 130 meV.

6.3. Summary and discussion

In this chapter, vanadium oxide film were on Ru(0001) via different growth methods. The best ordered oxide islands could be formed by introducing oxygen at 5×10^{-7} mbar onto a preheated Ru(0001) substrate held at 573 K, followed by further oxidation and final vacuum annealing. The obtained structure was not reported in the literature before. A model was proposed based on the atomically resolved STM images and similar construction principles described in literature. The structure model consists of two layers where the lower layer is formed by six-membered rings (V₆O₁₂) surrounded by six three-membered rings (V₃O₁₂). On each three-membered ring, a V=O unit sits on top and forms the complete unit of V₃O₁₂V=O. Such model appeared plausible since it meets both the common V oxidation state and the bond length constraints.

To study the thermal stability of the oxide surface, the film was annealed for 10 min in vacuum at 773 K, 873 K, and 973 K. The vanadium oxide kept the same structure up to 773 K, while new phases started appearing above this temperature. Those new oxide phases can be prepared at higher temperature (800-1000 K). Detailed analysis of their atomic structure was, however, beyond the scope of the work.

It is found that scanning at high bias caused instant removal of the vanadyl units from the oxide surface. Similar V=O removal experiments were performed on vanadium oxide films grown on Pd(111) by repeated scanning^[104]. STM tip-induced ESD experiments were performed in this work to understand the process. For this purpose, the tip was stabilized on top of a V=O unit and the bias was ramped to a desired desorption parameter. The stability of the V=O unit below the tip was then monitored in height spectroscopy as function of time. Based on more than 500, highly reproducible ESD measurements, it was observed that inelastic electron tunneling into the vanadyl groups triggered their desorption from the surface. Successful events were obtained above + 3.3 V at positive bias and below -2.7 V at negative bias (tunneling current at 0.3 nA). Moreover, the onset bias was found to shift to higher values if the current was smaller. The removal efficiency and desorption rate were rising with respect to bias voltage once reaching the threshold value.

The obtained slope from desorption probabilities as a function of tunneling current depicted in double-logarithmic plots, indicated that $2\sim3$ electrons are required in the V=O desorption process. The onset of V=O desorption at + 3.25 V found in the high bias spectroscopy hereby relates to

electron transfer into the t_{2g} orbitals split from V_{3d} crystal-field states. A suitable explanation for this many-electron ESD scheme is ladder climbing of vibrational states within the binding potential of the ad-species. Noticeably, the number of the required electrons was determined to 2~3, whereby the decisive vibrational excitation of the system was identified as the V=O stretch mode. From previous reports, it was known that the removal of vanadyls by bombarding bulk V₂O₃(0001) with high energy electrons leads to the formation of a highly reactive V-terminated substrate^{[317][318][332]}. In vanadium oxides on Ru(0001), the ESD scheme provided here makes it possible to convert from vanadyl-terminated oxide to a reactive vanadium site in a controllable manner, making vanadium oxide grown on Ru(0001) a very promising model for single site reaction schemes in the future.

7. Summary and outlook

Ultrathin metal oxide films exhibit unique properties which are not observed in their respective bulk forms, which is related to their low dimensionality and the interaction with the underlying substrate. This thesis has gone through structural, electronic and catalytic studies of iron and vanadium oxides grown on single-crystal supports: Ru(0001) (FeO_x and VO_x) and Ag(111) (FeO_x). The preparation conditions significantly influence the surface structure and film composition, thus determining oxide's properties. Characterization of the films using STM, STS, XPS and LEED aimed at resolving their structure and properties constitutes the core of this work.

Upon early studies, Pt(111) has been successfully adopted as a metallic substrate for iron oxide growth in various phases and it is proven to be an ideal model for CO oxidation catalytic studies^{[18][27]}. Ru(0001), as another substrate used for growing iron oxides, is also considered as a suitable support for model studies, particularly for CO oxidation, due to its affinity to both O₂ and $CO^{[47]}$. The temperature variance (RT to 500 K) during iron deposition has ignorable effect on the surface morphology and oxide composition on Ru(0001). FeO can grow at the terrace, at the step edge, as well as across step edges of Ru(0001). Underoxidation of iron may result in the coexistence of single- and double-layer FeO islands, where the latter case is dominating. It is found that the height of the first FeO layer grown on Ru is around 2.66 Å, while the second FeO layer is about 2.25 Å, making the overall height to be ~4.95 Å. Depending on the thickness and in-plane crystallographic direction, the measured atomic and Moiré periodicities are different. The first FeO layer results in a coincidence of a Ru–(8×7.33) cell (with lattice vectors of 21.7 Å (2.71×8) and 19.9 Å (2.71×7.33)) and FeO–(6.5×6) cell (with lattice vectors of 21.6 Å (3.32×6.5) and 19.9 Å (3.31×6). The second FeO layer adapts to the first FeO layer to a coincidence structure of a Ru– (8×7) cell and FeO–(7×6) cell.

The oxygen-rich iron oxide is prepared by using moderate pressure of atomic oxygen (a strong oxidizing agent). The structural transformations of FeO islands on Ru(0001) upon exposure to O_{at} at RT and 700 K were studied. Up to 550 K, the surface features new oxide phase similar to the RTcase. After RT-Oat treatment, the surface is fully covered with bright protrusions which significantly increase the surface roughness. The higher contribution of Fe³⁺ states and appearance of WBO species indicate the formation of FeO_x and RuO_x (1 < x < 2) phases. Vacuum annealing at 600 K can partially reduce the roughness of the surface, as well as the Fe³⁺: Fe²⁺ ratio and the amount of WBOs. Further annealing at 800 and 1000 K converts the oxide film back to the initial FeO phase. Therefore, the RT-Oat treated sample can be reduced back to FeO by thermal treatments above 800 K. For the sample after the 700 K-O_{at} treatment, the surface morphology is more organized, featuring few types of islands (which can be distinguished by their heights). The lowest flat islands have a height of 4.8 Å, with a triangular superstructure of approx. 36 Å periodicity and the atomic periodicity of about 3.5 Å. Such structure is most likely a Fe₂O₃-like structure. The other islands with bigger heights exhibit quite rough surface. Similarly, the fraction of both Fe³⁺ and WBOs component increases after such strong oxidation treatment. Vacuum annealing at 800 K would lead to even more rough surface structure with mixed phases. The Fe₂O₃-like structure becomes more distorted. Further annealing at 1000 K results in a completely disordered surface. Higher fraction of CO and H₂O components was found from XPS studies, and the appearance of metallic iron Fe⁰ suggesting strong reduction. Based on these findings, it may be concluded that the 700 K-O_{at} treatment of FeO/Ru(0001) results in an irreversible transformation to a Fe₂O₃-like structure, which is thermally stable up to 800 K.

The catalytic studies on the CO oxidation were performed both on FeO/Ru(0001) and FeO_x/Ru(0001) systems. In general, CO can be treated as both reductant and oxidant towards iron oxide on Ru(0001), which depends on the oxide phase. Pristine FeO (especially with some oxygen vacancies at the surface) was found to react with CO even at RT, as evidenced by the additional spots forming on the LEED pattern, the shoulder peak appearing at 707.3 eV in the XPS Fe 2p spectra, as well as the formation of O adatoms loops and perhaps C clusters seen with STM. When the sample is reoxidized, a more oxidized sample (with additional extended bright O-loops) can be obtained. Repeating the CO exposure leads to small reduction of the oxide. For strongly oxidized FeO_x samples, CO reaction starts at 600 K and leads to the formation of a less oxidized sample. The STM images obtained for CO600K-treated sample present a new, less ordered superstructure formed at the edges of iron oxide islands, with a periodicity of $20.8 \sim 23.8$ Å (similar to FeO), a large corrugation of ~ 2.0 Å and a height of $5.8 \sim 6.5$ Å, these parameters suggest this structure might be FeO with one O adlayers on top. The XPS results shows that the FeO_x may oxidize CO mainly through WBOs (requires thermal activation) and thus, CO treatment at RT has very limited effect on the FeO_X film. Indeed, as the first study on the low-temperature CO reaction on iron oxides on Ru(0001), the preliminary work implies some quite interesting catalytic properties of this model system, which is worth more work, such as temperature programmed desorption (TPD) for drawing a more clear conclusion in the future.

Another interesting substrate for iron oxides growth is Ag(111). The main advantages of using Ag(111) is the small lattice mismatch (5%) to FeO(111) and the little possibility of forming silver oxides at moderate oxidation conditions (used for growing FeO), which is supposed to reduce the complexity of the surface structure. The contradictory results obtained by different research groups on the structure of this system motivates the present work. Ultrathin iron oxide was prepared on Ag(111) by Fe evaporation at RT or elevated temperature (\sim 550 K) followed by oxidation in an O₂ pressure of 1×10^{-6} mbar for $15 \sim 30$ min at 700 K. Various iron oxide structures were observed. For RT-FeO/Ag(111) sample, mainly ill-defined islands (with various heights, corresponding to multilayer iron oxide) and reconstructed structures with large Moiré periodicity of 45 Å (mostly formed at the substrate step edges), were observed. The lattice constant of FeO is expanded to 3.2 Å, in line with the unit Moiré cell – (14×14) FeO on $(9\sqrt{3} \times 9\sqrt{3})$ Ag, with 30° rotation. Such structure was not reported so far. The HT-FeO/Ag(111) sample, on the other hand, showed a few more new structures. The elevated temperature helped with the structural order of multilayer iron oxide films, which can be further resolved with atomic periodicity of ~ 6 Å, corresponding to the Fe₃O₄ phase. The Moiré-reconstructed FeO islands found for the RT-case also grow at the surface. Some embedded islands on Ag surface shows similar expansion of FeO lattice (~ 3.2 Å), however, without Moiré superstructure and with line defects running along surface crystallographic directions. The Moiré-free islands are usually anchored to multilayer crystallites. The reconstruction-free islands have a height of 2.4 \sim 2.5 Å and exhibit a lattice constant of 2.94 \pm 0.08 Å. Even though the measured values are very close to that of Ag(111) substrate, the experimental facts of two sublattices seen on atomically-resolved STM images, as well as the different work function and conducting states (compared to Ag(111)) measured with STS, indicate that the reconstruction-free islands are iron oxide. The DFT calculation results obtained by our collaborators show that such reconstruction-free oxide film has a 'free-standing' character of the second layer, making it a very promising system for future model catalytic studies.

Vanadium oxide is also considered as a good model system for catalytic and electronic studies. The vanadium oxide on Ru(0001) was prepared for the first time within this work. The best ordered oxide islands can be formed by depositing vanadium in an oxygen pressure of 5×10^{-7} mbar onto a preheated Ru(0001) substrate held at 573 K. A final flash to 773 K can improve the surface cleanness and structural order. Based on the atomically-resolved STM images, a model is proposed for such structure. It consists of two layers, whereby the lower layer is formed by six-membered V-O rings (V_6O_{12}) surrounded by six three-membered V-O rings $(V_3O_{12}, O \text{ also bond to } Ru)$. On each $V_{3}O_{12}$ units, a vanadyl (V=O) unit sits on top, resulting in $V_{3}O_{12}V=O$ building blocks. While scanning the surface of vanadium oxide on Ru(0001) with STM, it was found that the periodicallyarrange surface protrusions, assigned to V=O (vanadyl) groups, can be removed permanently at a bias voltages above + 4.0 V. This behavior was investigated in detail by performing electronstimulated desorption (ESD) experiments. Successful events were obtained above + 3.3 V and below - 2.7 V at positive and negative polarities, respectively. The removing efficiency and desorption rate increased with the bias above the threshold value. Rarely, two V=O groups can be removed within a single ESD experiment. A non-linear behavior in a current-dependence plot indicated that $2 \sim 3$ electrons are involved in the desorption process. The explanation for such behavior is ladder climbing of vibrational states within the binding potential of the V=O groups. In principle, the ESD scheme provided here make it possible to desorb individual vanadyl groups, turning inert vanadyl-terminated sites to a reactive vanadium surface in a controllable manner. This makes vanadium oxide on Ru(0001) a very promising model system for single site reactions in the future.

In general, the work I present in this thesis includes different oxide/metal systems: FeO and FeO_x/Ru(0001), FeO/Ag(111), as well as VO_x/Ru(0001). The relation of preparation conditions and surface structure was closely explored, especially for the system of FeO/Ag(111) and VO_x/Ru(0001). The structural parameters of the ordered surface structure for all the system were carefully determined through large amount of statistics, and structure models were proposed for every system. Additionally, electronic properties were investigated for both FeO/Ag(111) and VO_x/Ru(0001), while the catalytic activity towards CO oxidation was investigated for FeO and FeO_x/Ru(0001) systems. Indeed, there is still large remaining field to explore for the future work, for example, to develop preparation method to obtain more homogenous structure of FeO/Ag(111); to study the reactivity and its relation to its structure of FeO_x/Ru(0001), perhaps using TPD; to investigate a STM-tip induced photolithography on VO_x/Ru(0001), etc.

List of abbreviations

DFT	Density functional theory
DOS	Density of states
ESD	Electron stimulated desorption
fcc	Face-centered cubic
FERs	Field emission resonances
FOV	Field of view
hcp	Hexagonal close-packed
HT	High temperature
IR-PLD	Infrared pulsed laser desorption
LDOS	Local density of states
LEED	Low energy electron diffraction
LEEM	Low energy electron microscopy
LT	Low temperature
ML	Monolayer
PDOS	Partial density of states
PEEM	Photoemission electron microscopy
PSD	Phase sensitive detector
QMS	Quadrupole mass spectrometer
RFA	Retarding field analyzer
RGA	Residual gas analysis
RHEED	Reflection high-energy electron diffraction
RT	Room temperature
SMSI	Strong metal-support interaction
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
ТМО	Transition metal oxides
TPD	Temperature programmed desorption
TPR	Temperature programmed reaction
UHV	Ultra-high vacuum
VCO	Voltage-controlled oscillator
WBO	Weakly bonded oxygen
XPS	X-ray photoelectron spectroscopy

List of publications (PhD studies period)

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