Crystallography and Electronic Structure of Model Metal Oxide Catalysts

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of the University College London

Department of Chemistry
University College London

2019
I, Michael James Allan, confirm that the work presented in this thesis is my own.
Where information has been derived from other sources, I confirm that this has
been indicated in the thesis.

..............................
Michael J. Allan
To my parents, for all you have done for me...
“All our dreams can come true if we have the courage to pursue them”

- Walt Disney
Abstract

This thesis embodies work studying multiple hydrogen producing metal oxide catalysts as both single crystals alongside ultra-thin films.

The first catalyst study investigates the water splitting properties of titanium dioxide by scanning tunnelling microscopy. By exploring the excess electron distribution around hydroxyls upon water splitting at an oxygen vacancy, mechanistic details from the process, along with electronic properties of the surface have been resolved.

The second catalyst explored is cerium dioxide ultra-thin films and studying both their oxidised and reduced states. As ceria is involved in the water-gas shift reaction, an important reaction which oxidises carbon monoxide with water to produce hydrogen and carbon dioxide, the understanding of its surface and any reconstructions is of great significance. This is studied by scanning tunnelling microscopy to understand the differences of the films, and high-resolution electron energy loss spectroscopy (HREELS) to give insight into the bonding environments that give rise to reconstructions.
The third catalyst studied is ceria-zirconia mixed metal oxide. The addition of zirconia to ceria improves its performance in the water-gas shift reaction. By studying the redox behaviour of the catalyst in the form of an inverse model catalyst by LEED, XPEEM, XAS and XPS, the synergy understanding between both metals has been furthered.
Impact Statement

The work in this thesis focuses on three catalysts used within the hydrogen production industry.

Many catalysts’ properties come from defects on the surface, such as vacancies or additional entities like hydroxyls or nanoparticles. Since these defects influence the functionality of these materials, their characterisation is of upmost importance. By studying the fundamentals of model catalysts used in clean energy, it helps shape the direction of future research, both academically and industrially. This is particularly true of both the automobile and hydrogen production industries, where the current research in catalysts align with the model systems studied in this work.

Titanium dioxide has received a lot of attention for its photocatalytic application in water splitting. This method, as well as electrolysis, are the preferred method to cleanly produce H₂ gas. Upon water dissociation, the hydroxyls have excess electrons associated with them. The nature of their distribution is not yet fully understood. By studying the distribution of these associated electrons, we can infer
the mechanistic details of the water splitting process. This is of relevance to both industrial and academic communities.

Ceria is a key catalyst utilised in the water-gas shift reaction. Currently, steam methane reforming is the cheapest common method of producing hydrogen. However, this H₂ cannot be used in fuel cells, such as the polymer membrane fuel cell, as the process generates syngas (H₂ + CO). The CO in the mixture poison the electrodes and render them inactive. The water-gas shift reaction allows for the conversion of CO into CO₂, while producing more H₂:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2.
\]

The presented work studies both the oxidised and reduced surfaces of ceria, in order to help understand how the surface structure changes. This can provide information on the potential impact on its catalytic activity.

The addition of zirconium to ceria increases the catalytic performance observed in industrial applications. Ceria-zirconia mixed oxide is a key component for the three-way catalyst in the automobile industry. The work presented in this thesis investigated the synergy of the mixed metal oxide, along with the morphology of the catalyst, within the industrial working conditions.
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Redox Behaviour of a Ceria-Zirconia Inverse Model Catalyst


Variation of SMSI with the Au:Pd Ratio of Bimetallic Nanoparticles on TiO$_2$(110)

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*In Preparation:*

Probing the Distribution of Bridging Hydroxyl Bound Excess Electrons on Rutile TiO$_2$(110)

M. Allan, C. Yim, M. Wolf, C. L. Pang and G. Thornton
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BGS</td>
<td>Band Gap State</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device (Camera)</td>
</tr>
<tr>
<td>CEM</td>
<td>Channel Electron Multiplier</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>FAT</td>
<td>Fixed Analyser Transmission</td>
</tr>
<tr>
<td>FEL</td>
<td>Fast Entry Loadlock</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HREELS</td>
<td>High Resolution Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>IMFP</td>
<td>Inelastic Mean Free Path</td>
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<tr>
<td>KPFM</td>
<td>Kelvin Probe Force Microscopy</td>
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<tr>
<td>LDOS</td>
<td>Local Density of States</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>LO</td>
<td>Longitudinal Optical (Phonon)</td>
</tr>
<tr>
<td>LT-STM</td>
<td>Low Temperature Scanning Tunnelling Microscope</td>
</tr>
<tr>
<td>MLE</td>
<td>Monolayer Equivalent</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near-Edge X-ray Absorption Fine Structure</td>
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<tr>
<td>OFHC</td>
<td>Oxygen Free High Conductivity</td>
</tr>
<tr>
<td>OSC</td>
<td>Oxygen Storage Capacity</td>
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<tr>
<td>PEEM</td>
<td>Photoemission Electron Microscopy</td>
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<tr>
<td>PVD</td>
<td>Physical Vapour Deposition</td>
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<tr>
<td>RAIRS</td>
<td>Reflection Absorption Infra-Red Spectroscopy</td>
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<tr>
<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>---------</td>
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<tr>
<td>RFA</td>
<td>Retarding Field Analyser</td>
</tr>
<tr>
<td>SO</td>
<td>Surface Optical (Phonon)</td>
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<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cells</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
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<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>TLE</td>
<td>Trilayer Equivalent</td>
</tr>
<tr>
<td>TO</td>
<td>Transverse Optical (Phonon)</td>
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<tr>
<td>TSP</td>
<td>Titanium Sublimation Pump</td>
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<tr>
<td>UHV</td>
<td>Ultra-high Vacuum</td>
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<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
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<tr>
<td>UV-PEEM</td>
<td>Ultraviolet Photoelectron Emission Microscopy</td>
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<tr>
<td>WGS</td>
<td>Water-Gas Shift</td>
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<tr>
<td>WKB</td>
<td>Wentzel-Kramers-Brillouin</td>
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<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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<td>XPEEM</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
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Chapter 1

INTRODUCTION


1.1 SURFACE SCIENCE

Surface science plays an important role in understanding surface reactivity and catalysis. Nanoscience has come a long way from Irving Langmuir’s studies in understanding surface reactivity\textsuperscript{1,2}, with Binnig and Rohrer’s discovery of the scanning tunnelling microscope (STM)\textsuperscript{3,4} to Gerhard Ertl’s work on chemical processes on solid surfaces\textsuperscript{5}. All of the above won Nobel prizes for their work, which recognises the significance of understanding surfaces.

When we consider surface structure, it is easy to only think about geometric structure. But equally tied to a surface’s ability to interact with atoms and molecules is its electronic structure. Having an atomic-level understanding of a surface’s geometric and electronic structure opens up the possibility to modify and improve a material’s performance in the application of interest. As a result, nanoscience studies are widespread in research areas involving catalysts, sensors, electronics, and pollution, just to name a few.

As mentioned, the invention of STM by Binnig and Rohrer furthered nanoscience by allowing real-space imaging down to a single atom scale. This was the beginning of a new field called scanning probe microscopy (SPM), which also includes atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM)\textsuperscript{6–9}. One of the most famous examples on the ability of STM is the ‘IBM’ image constructed by Eigler et al.\textsuperscript{10} (Figure 1.1). The ability to manipulate atoms on a surface demonstrates the impact SPM techniques can have when imaging surface structures, adsorbates and point defects.
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Figure 1.1: A sequence of STM images taken during the construction of a patterned array of xenon atoms on a nickel (110) surface. The atomic structure of the nickel surface is not resolved. The (1\overline{1}0) direction runs vertically. (a) The surface of the nickel sample after xenon is dosed. (b)–(f) Various snapshots of the construction as IBM is built from xenon atoms. Each letter is 50 Å. Grey scale is assigned according to the slope of the surface. The full images are reproduced with permission from reference 10.

1.2 Metal-Oxides

One of the most diverse areas of study in surface science involves metal oxides. They have properties that range from those of metals to insulators and semiconductors, giving them both technological and scientific importance. There have been extensive studies of metals by surface science techniques, which often occur under ultra-high vacuum (UHV) conditions. However, when we look at the real-world
applications of metals, it is the surface that exhibits the properties that are significant in their implementation. When exposed to ambient conditions, the surface often exists as its oxide counterpart. This is one of the reasons for the growth of studies focusing on metal oxides when trying to understand the surface science of metals.

1.2.1 THIN FILMS

The main barrier to studying metal oxides by surface science techniques arises from the wide band gap that many possess. This makes them insulators or poor semiconductors. Since most surface science techniques are electron-based, such as STM, charging of the surfaces proves a problem. The easiest way to eliminate this problem is to reduce the sample, and this is the most commonly implemented method when studying titanium dioxide. By reducing the sample through annealing, the sample is made semi-conductive, which enables surface science techniques to probe the surface. This can be visually observed since insulating TiO$_2$ is transparent, and as it undergoes reduction, it turns into darker shades of blue depending on the reduction of the sample. Another method is to dope the samples to make them semi-conductive. Unfortunately, these methods prove ineffective when the band gap is larger.

For large band gap metal-oxides, a solution is to grow ultra-thin layers (<5 nm) on conducting substrates. Metal-oxide catalysts are normally prepared as a small amount of highly dispersed metal upon a metal-oxide support. By growing thin films of the oxide upon a conducting substrate, these catalysts are known as ‘inverse model catalysts’ due to the reversed roles of the metal and metal-oxide (Figure 1.2). As
most catalytic activity happens at the interface, this solution allows the use of electron-based characterising techniques to probe model metal-metal-oxide interfaces.

![Conventional and Inverse Catalysts](image)

**Figure 1.2:** Illustration showing a conventional metal/oxide catalyst compared to an inverse oxide/metal catalyst.

### 1.3 Titanium Dioxide

Titanium dioxide, also known as titania, is one of the most studied metal oxides, particularly since Fujishima and Honda discovered its photocatalytic ability to split water\(^\text{16}\). It has far reaching applications, from heterogeneous catalysis, gas sensors, pigments, and use in solar cells as a photocatalyst, to name a few\(^\text{17-23}\). There have also been many studies that have looked into its properties and applications in the hope to discover other ways it could help improve technology across multiple platforms. Reviews by Diebold\(^\text{13}\) and Pang et al.\(^\text{12,24}\) provide a comprehensive insight into the applications, reactions and structure of the surfaces of titania.

\(\text{TiO}_2\) has multiple polymorphs which occur naturally as well as some which can be produced synthetically\(^\text{25}\). The three most abundant natural polymorphs are rutile, anatase and brookite. Of these three, only rutile and anatase have shown promising
activity in applications, thus making them the more studied polymorphs.\textsuperscript{13} Titania in its fully oxidised, stoichiometric arrangement is a wide band gap insulator (\(\sim 3\) eV)\textsuperscript{26}. This leads to problems in the absorption of sunlight due to poor frequency overlap, with TiO\textsubscript{2} exhibiting a low quantum yield. This can be overcome by the addition of dye molecules to improve efficiency\textsuperscript{27}. Other methods to activate TiO\textsubscript{2} include doping or the addition of noble metals to bridge the wide band gap\textsuperscript{28}. In this work, as discussed previously, TiO\textsubscript{2} can be made semi-conductive by annealing, which leads to a band gap state (BGS) that appears in photoemission at approximately 1 eV below the Fermi level\textsuperscript{29,30}. This has been linked to the formation of oxygen vacancies along with interstitial Ti species.

As rutile is the most abundant and readily available polymorph, it is the focus of most surface science studies of TiO\textsubscript{2}. Ab-initio and density functional theory (DFT) calculations studying periodic TiO\textsubscript{2} slabs of the (001), (100), (110) and (011) faces found that the (110) face of rutile has the lowest surface energy indicating the most stable face\textsuperscript{31,32}. Rutile will be the polymorph studied in this work, focusing on the (110) face.
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Figure 1.3: (a) The tetragonal bulk unit cell of rutile with the dimensions $a = b = 4.587$ Å and $c = 2.953$ Å. The titanium cations are octahedrally coordinated with six neighbouring oxygens, whilst the oxygen anions are coordinated to three titanium cations. (b) The stacking of the octahedra in rutile demonstrating the three-fold sharing of oxygen atoms. Titanium cations and oxygen anions are represented in red and blue respectively.

1.4 Cerium Dioxide

Cerium dioxide, CeO$_2$, also known as ceria, is a widely studied metal oxide due to its multiple applications related to its proven catalytic properties. Within industrial applications, it can be found in solid oxide fuel cells (SOFC)\textsuperscript{33,34} and automobile three-way catalytic converters\textsuperscript{35}, along with processes such as steam reforming\textsuperscript{36,37} and redox reactions including preferential CO oxidation (PROX)\textsuperscript{38}. One of its more important applications is its use as an active catalyst in the low-temperature water-gas shift (WGS) reaction\textsuperscript{39,40}. Hydrogen is a potential clean fuel source along with the more established clean energy sources like solar and wind. Currently 95% of hydrogen is produced by reforming fossil fuels, wood and biomass\textsuperscript{41}. However, hydrogen created from these sources contains 1-10% CO, which has a detrimental effect on Pt electrodes\textsuperscript{42,43}. By adding gold nanoparticles, ceria can catalyse the conversion of CO to CO$_2$, making the impure hydrogen fuel source suitable for alternative fuel systems. Ceria’s application as a catalyst heavily relies on two fundamental properties. The first
property is its ability to readily undergo oxidation and reduction between variable charge states (Ce$^{3+}$ and Ce$^{4+}$)\textsuperscript{44,45}. The second property is that ceria exhibits a high mobility of oxygen. This enables efficient oxygen storage and release, also known as oxygen storage capacity (OSC), during catalysis\textsuperscript{46,47}.

Ceria in its fully oxidised state has the fluorite crystal structure, as shown in Figure 1.4. Each Ce cation is bound to eight oxygen neighbours, whilst the oxygen anions are tetrahedrally bound to four cerium ions\textsuperscript{44}. As ceria is reduced towards Ce$_2$O$_3$, the fluorite structure is retained in a strained structure with oxygen vacancies spread throughout the lattice. Ceria’s stability has been studied by DFT and ab-initio calculations, and it was observed that the (111) face is the most stable of the low index (111), (110) and (100) faces\textsuperscript{48,49}. Bulk ceria has a large band gap, approximately 6 eV. However, the presence of empty 4f states associated with Ce$^{4+}$ is seen to give rise to a narrower band gap of $\sim$ 3.2 eV\textsuperscript{50,51}. In this work, thin films of ceria will be grown on Pt(111) in order to allow the use of e$^-$-based surface characterisation techniques.

![Unit cell of CeO2 illustrating the fluorite structure. The ceria cations can be seen bonding to eight nearest oxygen anions, with the oxygen bonding tetrahedrally to four cerium cations. The cerium cations are shown in red and oxygen anions are shown in blue.](image)

Figure 1.4: Unit cell of CeO2 illustrating the fluorite structure. The ceria cations can be seen bonding to eight nearest oxygen anions, with the oxygen bonding tetrahedrally to four cerium cations. The cerium cations are shown in red and oxygen anions are shown in blue.
1.4.1 Ceria-Zirconia Mixed Metal Oxide

As mentioned previously, ceria’s catalytic properties are derived from the high oxygen mobility within its lattice, along with its facile ability to change between two oxidation states. It has been observed that the addition of zirconium to ceria has favourable benefits to these desired properties. By incorporating zirconium, a mixed metal oxide ceria-zirconia, Ce$_{1-x}$Zr$_x$O$_2$, is produced with the fluorite structure retained. However, zirconium ions are smaller than cerium ions, which leads to a distorted structure. It has been calculated that there is an increase in oxygen mobility at lower temperatures, along with a lower barrier to the redox process between Ce$^{3+}$ and Ce$^{4+}$ oxidative states. This interesting synergy between ceria and zirconia has made it one of the most studied mixed metal oxides, as a deeper understanding of the interactions between mixed metal cations can lead to technological innovation in many areas. Examples of this include its role as an active catalyst in automobile three-way catalysis and the WGS reaction, as well as acting as a model catalyst for future systems. Most current studies have grown Ce$_{1-x}$Zr$_x$O$_2$ as nanoparticles by coprecipitation or sol-gel. In this work, ceria-zirconia mixed films were grown by depositing zirconium, followed by cerium, to form a thin film on Rh(111). This allowed surface science techniques to probe the impact of adding zirconium.
1.5 Thesis Structure

The main topic of this thesis is the investigation of key model metal oxide catalysts used in a variety of clean energy applications. By studying the crystallography and electronic structure of the surfaces, enables us to better understand the processes that can occur, which in turn can inform the development of improved catalytic processes.

This thesis consists of seven chapters.

Chapter 2 gives an insight into the theoretical considerations of a number of experimental techniques used in the work presented here. An overview of the three main techniques used: STM, HREELS and XPEEM, is provided, as it is vital to understand these techniques when analysing the results obtained from experiments. Furthermore, a number of auxiliary techniques utilised during sample preparation and characterisation are described.

Chapter 3 details the experimental instrumentation used during data acquisition in this work. This includes instrumentation to perform STM, HREELS, LEED and AES, as well as the set up at the nanoscience beamline (IO6) at Diamond Light Source used to collect XPEEM, XAS and μ-XPS data.

Chapter 4 investigates the temperature dependence of the distribution of the bridging hydroxyl (OHb) bound excess electrons on rutile TiO₂(110). In addition, the charge trapping potential of the hydroxyls is probed in comparison to oxygen vacancies.
Chapter 1: Introduction

Chapter 5 investigates a newly discovered reconstruction of CeO$_2$(111) grown on platinum(111). We aim to determine how it differs structurally from the (1 x 1) surface, alongside gaining an insight into the stability of the reconstruction.

Chapter 6 investigates the redox behaviour modification following the addition of zirconia to ceria nanostructures supported on Rh(111). We look for any synergy between the metal oxides to shed light on the mechanism in which the catalytic properties are enhanced through the addition of zirconia to ceria.

Chapter 7 summarises the work presented in this thesis alongside the key conclusions for each experimental chapter and a suggestion for future work.
1.6 REFERENCES

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Chapter 2

THEORETICAL CONSIDERATIONS
2.1 **Scanning Probe Microscopy**

Scanning probe microscopy (SPM) has become an invaluable tool for the study of surface science since the first of a series of techniques, scanning tunnelling microscopy (STM), was invented in the early 1980’s by Binnig and Rohrer. This was such a revolutionary step that it led to the Nobel Prize in Physics being awarded to Binning and Rohrer in 1986. Following on from this, further techniques, such as atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) were established, thus opening up this field to become a major branch of nanotechnology and nanometrology.

2.1.1 **Scanning Tunnelling Microscopy**

STM works upon the basis of quantum tunnelling, which enables us to probe both the electronic and geometric properties of a surface, along with other phenomena such as film growth and molecular manipulation. Figure 2.1 shows a simplistic schematic of the setup required for STM. Here it can be seen that an atomically sharp tip is rastered across a conducting or semi-conducting surface, typically within a few Å, by a piezoelectric scanner. By applying a small bias across the tip-sample junction, a resulting tunnelling current can be measured as a function of the tip-surface separation.
Figure 2.1: Simplified illustration showing a basic schematic of the experimental setup of a STM.

Figure 2.2: Illustration of the 1D wavefunction of an electron tunnelling through a potential barrier of height, $V_B$. 
If we only consider classical mechanics, there is a potential barrier which an electron cannot cross at a tip-surface separation of a few Å. This is unless the electron possesses a kinetic energy greater than the barrier height. If we consider a quantum mechanical perspective, as shown in Figure 2.2, the wavefunction of an electron does not immediately decay to zero. Instead, it exhibits exponential decay. This leads to the probability that an electron can overlap with the electronic states of the wavefunction on the opposing side of the barrier, if the separation distance is small enough. This allows the electron to have the potential to undergo ‘tunnelling’ through the barrier.

Figure 2.3 is a representation of the band structure of a metallic sample and tip which have non-identical work functions. Here, three stages of STM are shown. The first stage is when the sample and tip are separated by an infinite distance and the vacuum levels align (Figure 2.3a). As the sample and tip are brought together to a distance, \( d \), where electrical contact has occurred (Figure 2.3b), the Fermi levels, \( E_F \), are observed to align. For tunnelling to occur, an external bias has to be applied. When a small positive bias is applied to the sample (Figure 2.3c), this allows the occupied states of the tip to align with the unoccupied states of the sample. At this point, tunnelling electrons have a finite probability of traversing the potential barrier from the tip to the sample. When a small negative bias is applied to the sample (Figure 2.3d), the opposite occurs.
We can consider quantum tunnelling as a one-dimensional rectangular barrier that interacts with an electron in the z direction. By solving the Schrödinger equation for this system, the wave function of the electron, \( \psi \), within the barrier can be given by:

\[
\psi \propto e^{-\kappa z},
\]

where \( \kappa = \frac{\sqrt{2m(V_B-E)}}{\hbar} \). (2.1) (2.2)

\( \kappa \) is the decay constant, which is a function of the mass of the electron (m), the barrier height (\( V_B \)), and the energy of the state, E. As can be seen in Figure 2.3, the barrier height is not constant across the separation. However, by employing a small bias assumption, the approximation holds true by using an average value. With the barrier height representing the vacuum level in the simplest case, \( V_B - E_F \) is equal to the workfunction of the sample at the Fermi level, \( E_F^8 \). At low temperatures and low potential bias, the tunnelling current, \( I_t \), is seen to exponentially decay proportionally to the barrier width, \( d_t \):
2.1.1.1 

**TERSOFF AND HAMANN**

Earlier theory detailing STM failed to describe the experimental spatial resolution. To address this, Tersoff and Hamann began to model the tip as a locally spherical potential, where the minimum represents the point of nearest approach to the surface. Using first-order perturbation theory\(^{17}\), they postulated that the tunnelling current, I, can be described as:

\[
I = \left(\frac{2\pi e}{h}\right) \sum_{\mu\nu} f(E_\mu) \left[1 - f(E_\nu + eV)\right] \times |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu),
\]

(2.4)

where \(f(E)\) represents the Fermi function, \(V\) is the applied bias voltage, \(M_{\mu\nu}\) is the tunnelling matrix element between wavefunctions of the tip (\(\psi_\mu\)) and the surface (\(\psi_\nu\)) and \(E_\mu\) and \(E_\nu\) are the energy of the states \(\psi_\mu\) and \(\psi_\nu\), respectively, in the absence of tunnelling. By applying low temperature and small voltage limits, this reduces to:
\[ I = \left( \frac{2\pi}{\hbar} \right) e^2 V \sum_{\mu, \nu} |M_{\mu\nu}|^2 \delta(E_\nu - E_F) \delta(E_\mu - E_F), \]  

(2.5)

where \( E_F \) is the Fermi level. In order to calculate the tunnelling current in equation 2.5, it requires \( M_{\mu\nu} \) to be solved. Bardeen determined that the matrix operator can be expressed as:

\[ M_{\mu\nu} = \frac{\hbar^2}{2m} \int dS \cdot \left( \psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^* \right). \]  

(2.6)

Tersoff and Hamann imposed a further limit by considering the tip as a point probe. This imagines a tip that achieves maximum resolution whilst not interfering with the surface. This results in a matrix element proportional to the amplitude of \( \psi_\nu \) at the position \( r_0 \) of the probe, which reduces equation 2.6 to:

\[ I \propto \sum_\nu |\psi_\nu(r_0)|^2 \delta(E_\nu - E_F). \]  

(2.7)

This proposed that the tunnelling current, \( I \), is proportional to the surface local density of states (LDOS) at \( E_F \). The result of this is that an STM image can be considered as a contour map of the LDOS of the sample’s surface. Whilst this model is simplistic in its approach to modelling the tip, the resulting prediction is reasonably accurate to what Hamann and Tersoff found by modelling more realistic s-wave tips.\(^{10}\)
2.1.1.2 CHEN

Tersoff and Hamann predicted maximum lateral resolution of approximately 6 Å using the s-wave modelling. However, experiments conducted in 1989 established that structures with spacing as low as 2 Å could be resolved\(^1\). In response to this, Chen proposed an explanation to help explain this increased resolution by appreciating that s-waves fail to accurately describe the tip. This is due to most tips being composed of either tungsten, platinum or iridium, all of which are d-band metals. Tungsten tips were investigated in further detail where it was observed that at the Fermi level, the density of states (DOS) have an 85% contribution from d-states. Cluster calculations confirmed d-states have a strong affinity to form highly localised \(d_{z^2}\) dangling bonds on the apex atom, which contribute a large role in tunnelling.

Chen also introduced what is known as the reciprocity principle. This established that scanning a s-wave sample with a \(d_{z^2}\) tip is equivalent to scanning a \(d_{z^2}\) sample with a s-wave tip (Figure 2.4).

Figure 2.4: An illustration of the reciprocity principle as described by Chen. This shows how a \(d_{z^2}\) tip scanning an s-wave sample state is identical to a s-wave tip scanning a \(d_{z^2}\) sample state during STM operation\(^1\).
2.1.1.3 LANG

As surfaces are not always perfect and clean, Lang investigated the effect of adsorbates disturbing the LDOS distribution on the surface. This was approached by considering two planar metallic electrodes. The first electrode has a Na atom, which represents the tip. The second acts as the surface with 3 different adatoms (Na, S and He). Using Bardeen’s formalism, Lang calculated the state density, showing that the Na 3s and S 3p resonances lead to an increase in the LDOS at the Fermi level. However, He is seen to cause a reduction by polarising the metal states away from the Fermi level. This resultant effect on the LDOS results has an impact during interpretation of STM images; the adsorbates leading to an increase in the LDOS (Na, S) appear as protrusions whilst those leading to a decrease (He) appear as depressions. This is further illustrated in Figure 2.5. These observations give rise to the implication that the analysis of STM images is often non-trivial, as features are not determined solely by the topography. For accurate interpretation, it is important to compare experimental results with theoretical calculations.
2.1.1.4 WKB APPROXIMATION

Tersoff-Hamann theory initially made four assumptions when describing the tunnelling current. One of these was the low voltage limit. This is the assumption that the bias voltage is less than $\approx 10$ mV. Whilst this theory made gains in understanding STM, bias voltages in the range of $1 - 3$ V are needed to study oxides. Under these conditions, it can be seen that the tunnelling current cannot be described by just the states at the Fermi level, but is dependent on a range of states lying close to the Fermi level. For this to be evaluated, the semi-classical Wentzel-Kramers-Brillouin (WKB) approximation, shown in equation 2.8, is a useful model for such considerations\cite{6}. The electron tunnelling probability is calculated between two planar electrodes at 0 K, with the result being the integral over the energy range where both filled and empty states are available for tunnelling. This has the form:
\[ I = \int_{0}^{eV} \rho_s(r, E) \rho_t(r, \pm eV, \mp E) T(E, eV, r) \, dE, \quad (2.8) \]

where \( \rho_s(r, E) \) and \( \rho_t(r, E) \) are the density of states of the sample and tip, respectively, at location, \( r \), and energy, \( E \), measured with respect to their individual Fermi levels. The upper and lower portions of the \( \pm / \mp \) signs correspond to positive (\( eV > 0 \)) and negative (\( eV < 0 \)) sample bias respectively. For both conditions, the tunnelling transmission probability, \( T \), is given by:

\[ T(r, E, V) = \exp \left( -\frac{2z\sqrt{2m}}{\hbar} \sqrt{\frac{\phi_s + \phi_t}{2} + \frac{eV}{2} - E} \right), \quad (2.9) \]

where \( z \) is the tip-sample separation and \( \phi_s \) and \( \phi_t \) are the work functions of the sample and tip respectively.

The integral in equation 2.8 sums over all filled-empty state pairs with the defined voltage bias. However, upon examination of equation 2.9, we see that the transmission probability has a maximum when \( E = 0 \) for a positively biased sample. Conversely, for a negatively biased sample, a maximum is observed when \( E = eV \). This gives the result that the tunnelling probability is largest for the electronic states closest to the Fermi level of the negatively biased electrode (emitter).
2.2 **HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY**

Electron Energy Loss Spectroscopy (EELS) has over the years developed into a useful tool for studying the electronic structure of gas phase samples and thin films\textsuperscript{19}. Within the surface science field, the technique has been employed to measure surface vibrational spectra using a variant called high-resolution electron energy loss spectroscopy (HREELS)\textsuperscript{20}. It can be used to probe vibrational modes of surfaces, both clean and with adsorbates, under UHV conditions\textsuperscript{21–23}. HREELS provides similar data to that of reflection absorption infra-red spectroscopy (RAIRS). However, HREELS has the advantage that it can observe both dipole and non-dipole excitations compared to just dipole excitations for RAIRS.

The initial use of low-energy electron scattering to study the vibrational structure of adsorbed gases (N\textsubscript{2}, H\textsubscript{2}, CO, and H\textsubscript{2}O) on W(100) was carried out by Propst and Piper\textsuperscript{24}. Here, using the vibrational excitations, information on the nature of an adsorbate could be determined. After exposure to H\textsubscript{2}, energy loss lines at 135 meV and \~69 meV were observed with no loss observed near 550 meV. The expected loss at 550 meV is what would be expected if molecular hydrogen was adsorbed on the surface. The losses at 135 meV and 69 meV can be assigned to stretching vibrations of a hydrogen atom parallel and perpendicular to the tungsten surface, implying that hydrogen dissociation occurs upon adsorption. HREELS was also used to study surface optical (SO) phonons of clean semiconductors, including ZnO\textsuperscript{25} and Si (111)\textsuperscript{26}. The results are consistent with dipole scattering being the dominant mechanism\textsuperscript{27}. 
During operation, a well-defined monochromatic beam of electrons with a known energy, $E_i$, is directed towards a surface at a specific angle of incidence. Upon striking the surface, the majority of electrons reflect off the sample elastically at an angle equal to the incident angle. However, a minority of electrons scatter inelastically, exciting the samples vibrational modes, $\hbar \omega^{28}$. The energy of electrons, $E_s$, after losing energy by interacting with surface excitations is given by:

$$E_s = E_i - \hbar \omega.$$  \hspace{1cm} (2.10)

By using low energy electrons ($3 - 20$ eV), the sample penetration depth is kept minimal, which results in a highly surface sensitive probe. An additional benefit to using electrons with low energies is that there is generally insignificant beam damage.

\subsection*{2.2.1 Electron Scattering}

The process of inelastic scattering is complex and is seen to be based on the wave-particle duality principle. Whilst describing the coupling in simple terms can lead to a limited and over simplified picture, it nonetheless provides a useful solution to distinguish between three limiting cases. These are dipole, impact and resonance scattering$^{28}$. 
2.2.1.1 DIPOLE SCATTERING

Dipole scattering corresponds to the incoming electron interacting via its accompanying electric field with the dipole field of the elementary excitations of the solid. These depend on the nature of the vibrating particle, such as adsorbed molecules, ions or conduction/valence electrons, resulting in excitations including adsorbate vibrations, phonons, excitons or plasmons to name a few. Due to the slow decaying nature of the electric field near the surface of the solid, the dipole interaction begins when the electron is still far from the surface (up to 100 Å) and extends over a long period of time (of the order 10\(^{-14}\) s). The extent of the interaction has the effect that the microscopic structure of the potential induced by the elemental excitation in question does not need to be considered. The result of this is that a model of a hard wall potential reflecting the electron perpendicular to the surface is sufficient. This simplified picture can be seen in Figure 2.6. If we consider an electron impacting the surface, and travelling without changing the charge distribution, the potential the electron sees can be given by:

\[
\phi(x) = \phi_0 e^{-k_{||} x_{||}} e^{ik_{||} x_{||}}, \quad (2.11)
\]

where \(\phi_0\) is the potential of the surface independent of any incident electron, depending only upon charge-density fluctuations created by elementary excitations. \(x_{||}\) is the projection of the incoming electron onto the plane parallel to the surface and \(z\) is the perpendicular distance from the sample. \(k_{||}\) is a two-dimensional wave vector of the excited mode parallel to the surface and can be given by:
\[ k_{||} = k_i - k_s, \]  \hspace{1cm} (2.12)

where \( k_i \) and \( k_s \) are the wave vectors of the incident and scattered electron, respectively. Upon examining equation 2.11, the potential felt by an incoming electron increases exponentially as it approaches the sample. The consequence of this is that for long range interactions to occur the parallel excited mode \((k_{||})\) has to be small, and often negligible compared to \( k_i \) and \( k_s \). This leads to dipole scattering being limited to the specular direction. This allows the investigation of weaker non-dipole scattering since collecting data at an off-specular angle reduces the dipole scattering intensities.

Figure 2.6: Diagram illustrating the scattering geometry of an electron (initial wave vector, \( k_i \), and final wave vector, \( k_s \)) occurring from a surface excitation (wave vector, \( k_{||} \)). \( \theta_i \) and \( \theta_s \) are the angle of incidence and scattering, respectively, with \( \Delta \theta \) representing the deviation of \( k_s \) from scattering geometry.
Dipole scattering is also subject to the dipole selection rule which is shown schematically in Figure 2.7, assuming a simple diatomic molecule adsorbed on a surface\textsuperscript{19}. When the diatomic molecule is orientated vertically, an oscillating dipole moment is created by the molecule’s stretching frequency. This oscillation results in an image dipole within the sample along the same axis\textsuperscript{30}. Therefore, any incoming electrons encounters a dipole potential with up to twice the magnitude of the adsorbate’s dipole moment. The result is that this dipole is able to be seen far from the surface by incoming electrons. Image dipoles are also created by vibrational modes parallel to the surface. Depending on the dielectric constant of the surface these can be cancelled out, particularly in metals. However, due to a smaller relative permittivity in semi-conductors and insulators\textsuperscript{31,32}, the image dipole does not match the magnitude of the real dipole\textsuperscript{33}. This allows parallel vibrations to be seen in semiconducting oxides resulting in the orientation of the adsorbate not being determined accurately using HREELS alone.

![Figure 2.7: Diagram illustrating induced image charge resulting by a surface dipole perpendicular and parallel to the surface plane.](image)
2.2.1.2 IMPACT SCATTERING

In impact scattering, we consider the electron to be interacting as a particle. As the electron is fired towards the surface, it exhibits short-range interactions (~1 Å) upon colliding with and bouncing off the surface. During this process, large exchanges of momentum occur, resulting in impact scattered electrons having a broader angular distribution compared to dipole scattered electrons. The image dipole seen in dipole scattering exists a few Å from the surface. Due to the short-range nature of the impact resonance, the electron does not observe this dipole. This allows impact scattered electrons to probe dipole forbidden excitations that normally are not possible in techniques such as RAIRS. An experimental issue here is that an increase in the incident electron energy results in a total cross-section increase. However, it should be noted that the energy resolution is also dependent on the incident energy. Therefore, a compromise is needed to balance resolution and intensity of impact scattering.\textsuperscript{27}

To formulate impact scattering requires an explicit description of multiple scattering alongside a detailed structure of the sample potential. Due to the complexities, no classical or semi-classical methodologies have been possible, and a quantum mechanical approach is necessary. One such approach is by Tong et al.\textsuperscript{34–36} or for further information, the reader is directed to Chapter 7 of “Electron Spectroscopy for Surface Analysis” (H. Froitzheim) or Chapter 3 of “Electron Energy Loss Spectroscopy and Surface Vibrations” (Ibach and Mills) for further information\textsuperscript{19,37}.
2.2.1.3 **NEGATIVE ION RESONANCE SCATTERING**

If we treat an electron as a wave in dipole scattering and a particle in impact scattering, for negative ion resonance scattering we treat the electron in its most basic definition, a negatively charged subatomic particle. For this process, the electron interacts with surface adsorbed molecules becoming a quasi-bound electronic state. The typical lifetime of these states is around $10^{-10} - 10^{-15}$ s, after which the trapped electron is remitted. For further information, a detailed review is given by Palmer et al.\(^{38}\).

### 2.2.2 INTRINSIC ELECTRON ENERGY LOSSES

So far, we have discussed electron scattering events due to vibrational or electronic excitations caused by adsorbed species. Alongside adsorbates, the surface of the crystal also produces losses which have to be considered when analysing spectra. Here, we will discuss the three most common, phonons, plasmons and inter/intra band excitations\(^{39-41}\).

#### 2.2.2.1 PHONON EXCITATIONS

##### 2.2.2.1.1 BULK PHONON EXCITATIONS

A phonon is an elastic wave that propagates through a quantized lattice vibration of a crystalline solid. Within a three-dimensional crystal, the wave vector, $k$, contains $3N$ normal modes, where $N$ is the number of atoms in the basis\(^{42}\). 3 of these modes are caused when all the ions in a primitive cell move in-phase cooperatively.
out of their equilibrium positions. These 3 modes are known as the acoustic modes. Acoustic phonons exhibit a linear decay between the wave vector, \( k \), and frequency when at the long wavelength limit. This leaves \( 3(N-1) \) modes, which are known as optical phonon modes. Here the ions move out of phase and are analogous to molecular vibrations. Optical phonons do not exhibit the same \( k \) dependency at long wavelength limits as acoustic phonons. In addition to phonons being split into acoustic and optical, they can each be split further into longitudinal and transverse modes. Optical and acoustic phonon modes are classed as bulk modes as they propagate across an infinite lattice.

To observe the dependencies upon \( k \) of both bulk phonon modes, a phonon dispersion curve can be plotted which shows the phonon frequency dependence on the wave vector (Figure 2.8). Figure 2.8a shows part of the phonon dispersion curve for ceria\(^{43}\), whilst Figure 2.8b shows a generalised phonon dispersion curve for a \( N = 2 \) system\(^{44}\). As ceria has a \( N \) value of greater than 2, the curves are more complicated. However, the same principles apply. It can be seen that the dispersion curves for the acoustic mode are highly dependent on \( k \) and as the wave vector approaches 0, the phonon frequency decays to 0. The optical modes in contrast show less dependence on \( k \) and are flatter, showing the reduced effect the \( k \)-dependent factors have on these modes.
2.2.2.1.2 SURFACE OPTICAL PHONON EXCITATIONS

The first studies of ZnO in 1970 saw a peak at 68.8 meV\(^2\). This lay between the bulk longitudinal optical (LO) and transverse optical (TO) phonons. This was assigned to a surface optical (SO) phonon mode as predicted by Fuchs and Kliewer\(^{45,46}\). SO phonon modes differ from the bulk TO and LO modes due to the crystal’s periodicity at the surface terminating abruptly in one direction. This causes a change in the electrostatic potential.

The dielectric function, \(\varepsilon(\omega)\), of a crystal has both real and imaginary components given by:

\[
\varepsilon(\omega) = \text{Re}[\varepsilon(\omega)] + \text{Im}[\varepsilon(\omega)],
\]

(2.13)

Figure 2.8: Phonon dispersion curves for (a) Ceria, adapted from Buckeridge et al\(^{43}\). (b) a generalised 2N system\(^{44}\). Optical and acoustic phonon losses are shown in blue and red, respectively.
where $\text{Re}[\varepsilon(\omega)]$ and $\text{Im}[\varepsilon(\omega)]$ represent the real and imaginary components respectively. Figure 2.9 shows a generalised dielectric current for a one optical phonon system\(^{42}\). The probability of a loss occurring for LO and TO phonons occur at a maximum when:

$$\text{Re}[\varepsilon(\omega)] = 0,$$

with TO phonon losses occurring on the negative gradient and LO losses on the positive gradient. Between these two modes, the real component of the dielectric function is negative. The loss probability of SO phonon modes has been found to be maximum when:

$$\text{Re}[\varepsilon(\omega)] = -1.$$

As can be seen in Figure 2.9, there are two points where this condition is met. However, as the loss probability is dependent on $1/\text{Im}[\varepsilon(\omega)]$ as seen in equation 2.16\(^{42}\):

$$P(\omega, k) = \frac{4e^2k}{\pi^2\hbar^2[k^2+(\frac{\omega}{v})^2]^2}\text{Im}\left\{\frac{-1}{[\varepsilon(\omega)+1]}\right\},$$

where $v$ is the velocity of the incoming electrons incident to the surface, the first point occurs when $\text{Im}[\varepsilon(\omega)]$ is maximum so does not give rise to a SO phonon mode. By comparing the frequencies, we see that the SO lies in-between the TO and LO phonon frequencies. This agrees with Fuchs and Kliewer’s predictions and Ibach’s ZnO measurements\(^{25,45,46}\). SO phonon modes tend to appear in the loss region of $0 – 200$ meV. Therefore, a high energy resolution (~10 meV) is required to observe these phonon modes otherwise they may be hidden beneath the elastic peak.
Figure 2.9: Diagram showing the real \( \text{Re}[\varepsilon(\omega)] \) and imaginary \( \text{Im}[\varepsilon(\omega)] \) components of the dielectric function for a generalised solid with one optical mode.

In addition to loss peaks being present, energy gain peaks, analogous to anti-Stokes peaks in Raman spectroscopy, are also present\(^{19,47} \) and observed in HREELS spectra. The relation between the gain and loss peaks is given by:

\[
\frac{I_{\text{gain}}}{I_{\text{loss}}} = e^{-\frac{\hbar \omega_{SO}}{k_B T}}.
\]  

(2.17)

### 2.2.2.2 Plasmon Excitations

Another common excitation involves plasmons, which can be defined as the collective oscillation of the electron density in conductive mediums. The electric field of an incoming electron is able to couple to the oscillating electron density and subsequently excite the plasmon, resulting in a loss event. Due to the need for a sufficiently high concentration of free or quasi-free charge carriers, plasmons are more common in metallic samples but can be generated in some semi-conductors.
To approximate a plasmon’s dielectric function, we can use the Drude dielectric function for a free electron gas, given by\(^{48,49}\):

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2},
\]

(2.18)

where \(\varepsilon_\infty\) is the high frequency dielectric function, and \(\omega_p\) is the unscreened plasmon frequency given by:

\[
\omega_p^2 = \frac{n e^2}{\mu \varepsilon_0},
\]

(2.19)

where \(\varepsilon_0\) is the permittivity of free space, \(n\) is the number of oscillators, \(\mu\) is the effective mass and \(e\) is the dynamic charge of the oscillators\(^47\). By equating the solutions seen for phonon excitations, that is \(\text{Re}[\varepsilon(\omega)] = 0\) at the maximum probability for bulk plasmon and \(\text{Re}[\varepsilon(\omega)] = -1\) for maximum probability of a surface plasmon, it can be seen that the bulk, \(\omega_B\), and the surface, \(\omega_S\), plasmon frequencies are given by\(^{42}\):

\[
\omega_B^2 = \frac{\omega_p^2}{\varepsilon_\infty},
\]

(2.20)

and

\[
\omega_S^2 = \frac{\omega_p^2}{\varepsilon_\infty + 1}.
\]

(2.21)

This gives us a relationship between the bulk and surface plasmons given by:

\[
\frac{\omega_S}{\omega_B} = \left[ \frac{\varepsilon_\infty}{\varepsilon_\infty + 1} \right]^{1/2}.
\]

(2.22)
This expression shows that surface plasmons have frequencies just below their bulk counterparts.

### 2.2.2.3 Inter/Intra-band Transitions

Another excitation that can be observed in HREELS measurements is inter and intra-band transitions. These can occur from such transitions as between the conduction and valence bands of semi-conductors and can contribute significantly in the appropriate energy loss range$^{19}$.

### 2.3 Auger Electron Spectroscopy

Auger Electron Spectroscopy (AES) is a spectroscopic technique which is used to determine the elemental composition of a given surface. It is widely applied due to its sensitivity, along with the relative ease of application and implementation within vacuum chambers. Auger electrons were first talked about by Lise Meitner in 1922 whilst studying beta radiation$^{50}$. However, it was Pierre Auger who independently discovered the process who was accredited the discovery$^{51}$.

The working principle of the process is outlined in Figure 2.10$^{52}$. Here, we see an incident electron (1) causing the emission of a core electron (2). The result of this is that an electron hole in a core level is produced. Photons and ion bombardment can also be used as the initial energy source; however, electrons are the most commonly employed. The vacancy is filled by autoionization (3), where a transition of an electron from a lower binding energy results in the vacancy being filled. A consequence of this is a resultant quantum of energy, $\Delta E$, is released equal to the difference in binding
energies between the initial core electron and the autoionization electron. This can be removed by two processes. The first process is X-ray Fluorescence, where the energy is removed radiatively as a photon. The second process is the Auger effect, where the energy is transferred to a third electron, known as the Auger electron (4). The Auger electron is excited above the vacuum level, where its kinetic energy, $E_{\text{Kin}}$, is given by equation 2.23:

$$E_{\text{Kin}} = E_k - E_{L_1} - E_{L_{2,3}} - \phi,$$  \hspace{1cm} (2.23)

where $E_k$, $E_{L_1}$ and $E_{L_{2,3}}$ represent the binding energies of the three electrons in their initial states as described in Figure 2.10 and $\phi$ denotes the workfunction of the detector. The kinetic energy of the Auger electron is seen to be independent of the energy of the source initially used, the incident electron in this case, depending solely on the binding energies of the probed atom. This gives rise to the elemental specific quantity of AES. The energy of the electrons employed in AES results in a high degree of surface sensitivity due to the relatively short attenuation lengths (Figure 2.11)\textsuperscript{29}. For AES, the spectra are recorded as the total number of electrons with a given kinetic energy, $N(E)$, against said kinetic energy. This results in the Auger peaks being superimposed upon a large background which arises from secondary electrons occurring via alternative energy loss mechanisms. To overcome this shortfall, a lock-in amplifier is used in order to differentiate the signal, resulting in a $dN(E)/dE$ spectra which is more clearly defined.
Figure 2.10: Illustration of the working principles of the Auger Effect. (1) An incident electron impacts a core level occupied state. (2) A core level electron is ejected from the sample leaving a core level hole. (3) An electron from a lower binding energy relaxes and occupies the unoccupied state. (4) Energy available from the relaxation is transferred to a third electron causing it to be emitted above the vacuum level as an Auger electron.

Figure 2.11: Electron inelastic mean free path (IMFP) as a function of the initial electron kinetic energy. Individual points are experimental data points, with the theoretical model curve also displayed\textsuperscript{19}.
2.4 Low Energy Electron Diffraction

Low energy electron diffraction (LEED) is a widely used technique since its demonstration by Davisson & Germer\textsuperscript{53} and Thompson & Reid\textsuperscript{54} in the early 20\textsuperscript{th} century. This resulted in Davisson and Thompson jointly receiving the Nobel prize in physics in 1937. It is employed in order to probe surface structures and ordering on both single crystals and thin film samples\textsuperscript{55–57}. Due to its ease of implementation, in particular its ability to share optics with Auger electron spectroscopy, it is often used as a complementary surface characterization technique alongside STM, AFM, XPS and AES.

During LEED operation, a monochromatic beam of low energy electrons, typically 20-200 eV, is directed towards the sample\textsuperscript{58}. Observing the energy range typically utilised in LEED, we can see that LEED is highly surface sensitive, see Figure 2.11, with the electron’s mean free path penetrating just a few atomic layers into the surface (< 10 Å). Upon impact, the electrons can either be elastically scattered back towards the screen at discrete angles or undergo inelastic scattering. Due to these impacts, the sample is grounded to avoid any build-up of excess charge. The diffracted beams pass through a series of grids on the way to the screen, which act as a filter in order to remove any inelastically scattered electrons with a lower energy. Finally, the elastically scattered electrons impact the phosphor screen, held at high positive voltage to accelerate electrons towards it, causing light to be emitted at the point of impact. The spatial distribution exposes the principal symmetry of the sample’s surface from the resulting pattern of discrete spots. Due to the energies employed in LEED, the electrons used will have a de Broglie wavelength comparable to that of the...
interatomic spacing found in many common crystalline materials. From the wave-particle duality of electrons, the de Broglie wavelength of the electron beam, $\lambda_e$, is related to its mass, $m$, and velocity, $v$, and can be calculated using\(^{59}\):

$$\lambda = \frac{h}{mv}.$$ (2.24)

As the particles are electrons in this case, we can calculate the effective wavelength in terms of electron charge, $e$, and the acceleration voltage, $V$. By considering that the kinetic energy of the electron, $E$, is given by:

$$E = \frac{1}{2}mv^2 = eV,$$ (2.25)

we can rewrite $\lambda_e$ as

$$\lambda_e = \frac{h}{\sqrt{2meV}} = \left(\frac{150}{eV}\right)^{\frac{1}{2}},$$ (2.26)

where $m$ is the effective mass of an electron and $\lambda_e$ is measured in Ångstroms. By inputting the energies used (20 - 200 eV), we get a wavelength range of 2.74 – 0.87 Å. This makes them an excellent probe for surface structures.

By considering diffraction for a one-dimensional periodic array (Figure 2.12), it can be seen that the path difference, $\Delta s$, is given by:

$$\Delta s = a(\sin \theta_s - \sin \theta_i),$$ (2.27)

where $a$ is the lattice constant and $\theta_i$ and $\theta_s$ are the incident and scattered electron angles (with respect to the surface normal), respectively. If we consider the case
where the incident electron beam is parallel to the surface normal, equation 2.27 simplifies to:

\[ \Delta s = a \sin \theta_s. \]  
(2.28)

The constructive interference rules of Bragg’s law state that the strongest constructive interference occurs when:

\[ \Delta s = n \cdot \lambda, \]  
(2.29)

where \( \lambda \) is the de Broglie wavelength of the incident electrons. By combining equations 2.28 and 2.29, we get:

\[ \sin \theta_s = \frac{n\lambda}{a}, \]  
(2.30)

where \( n \) can take any integer. Here we can see that when we take a fixed wavelength, we get a series of well-defined values for \( \sin \theta_s \) corresponding to the allowed integer values of \( n \). This relation is what yields the diffraction pattern recorded in LEED\textsuperscript{29}.

Figure 2.12: Diffraction from a 1D array of atoms with a separation distance, \( a \), by a non-perpendicular incident electron beam. \( \theta_i \) and \( \theta_s \) are the angles of incident and diffracted beams respectively. Red lines denote the path difference, \( \Delta s \), between the parallel beams.
2.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect. Whilst first discovered in 1887 by Heinrich Hertz, it was Wilhelm Hallwachs and Philipp Lenard who performed the first initial studies before Einstein explained the phenomenon in 1905. This was credited by the Nobel Prize award in 1921.

XPS is a surface sensitive technique which is used to acquire information of a sample’s chemical composition and electronic structure. XPS works on the principle that deep core level electrons have binding energies that correspond to the X-ray photon energy region. These core level electrons do not participate in bonding. Therefore, to a first approximation, the electrons when emitted are characteristic of their parent atom independent on the environment of the atom. However, they are seen to be dependent on the oxidation state. When a crystal is exposed to a monochromatic beam with a photon energy greater than the binding energy (\(h\nu > E_B + \phi\)), the core level electrons will be ionised. The most commonly used photon energies used are 1253.6 eV (Mg Ka) and 1486.6 eV (Al Ka). When the Fermi levels of the sample and analyser are equilibrated, the kinetic energy of the emitted electron, \(E_K\), is dependent on the binding energy, \(E_B\), the photon energy used to excite, \(h\nu\), and the analyser work function, \(\phi_A\), given by equation 2.31:

\[
E_K = h\nu - E_B - \phi_A .
\]  

(2.31)

XPS is a surface sensitive technique due to the emitted electrons being in the kinetic energy range shown in Figure 2.11. To increase the surface sensitivity, we can
change the angle of the sample, with respect to the analyser. By subjecting it to a grazing angle, the distance the electrons have to travel through the sample to reach the analyser increases, thereby increasing the surface sensitivity.

2.6 PHOTOELECTRON EMISSION MICROSCOPY

The earliest form of photoelectron emission microscopy can be dated back to the 1930s. In 1932, Ernst Brüche studied the surface of a heated, planar electron-emitting cathode and demonstrated it could be imaged by the use of an electrostatic two aperture lens system\(^62,63\). The following year, he developed this discovery further by the addition of a magnetic lens, which he used to show that accelerated high-energy electrons produced by irradiation with UV light could also be used for imaging\(^64\). This showed the potential to image surfaces using photoelectrons. PEEM kept developing, with the first commercial PEEM being built in 1968\(^65\). However, like other surface science techniques of that time, it suffered from surface contamination due to operating in moderate vacuum pressures. With the advent of UHV chambers and tuneable synchrotron radiation in the 1980’s, PEEM became a powerful tool, able to study artificial nanostructures, surfaces and thin films\(^66\).

Recent studies have shown PEEM is a useful tool for measuring and characterising nanostructured materials, thin films, surfaces and interfaces\(^67–69\).

2.6.1 X-RAY ABSORPTION SPECTROSCOPY

X-ray absorption spectroscopy (XAS) is a spectroscopic technique that measures the X-ray absorbance of a material as a function of photon energy. When XAS is
applied to surface studies, it is often referred to as near-edge X-ray absorption fine structure (NEXAFS)\textsuperscript{70}.

During measurements, tuneable monochromatic soft X-rays are used to irradiate the sample resulting in a photoelectron and a core hole when a photoabsorption event occurs. There are multiple ways of recording XAS, namely fluorescence and electron yield modes. Fluorescence yield is acquired by measuring the emission of a fluorescent photon when an electron fills the core hole radiatively. Alternatively, the secondary electron yield is acquired as a measure of the surface X-ray absorption coefficient. The process employed in this work is secondary electron yield due to the process being more surface sensitive. X-rays have a deeper penetration depth than electrons. For fluorescence yield, this depth is equally measured in the resulting spectra due to measuring emitted X-rays which can be emitted from further into the bulk. For electron yield, as mentioned with XPS, the measured electrons possess low kinetic energy, resulting in only electrons from the first few atomic layers leaving the sample.

\subsection*{2.6.2 Secondary-Electron XPEEM}

X-ray absorption spectra are collected in XPEEM by acquiring ‘stacks’ of images as a function of photon energy. As the photon energy is scanned, below the absorption edges of an element, there is no absorbance and therefore no emission of Auger electrons. Here we would observe a background where any contrast results from different secondary electron yields, dominated by variations in the work function\textsuperscript{71}. As the photon energy is tuned to the absorption threshold of an element, any areas
containing the element would appear brighter due to secondary electrons emitted due to absorbance. This provides a method to chemically map the surface by highlighting elemental composition in areas by comparing images on an absorbance threshold to those pre-edge. This method of imaging is known as secondary-electron XPEEM. By integrating over all intensity of each image and plotting against photon energy, we would acquire an absorbance spectrum analogous to conventional XAS. The option of only integrating over selected regions of an image allows for absorbance spectra of nanostructures to be investigated.

### 2.6.3 µ-XPS

µ-XPS operates on the same principle as XPS as described in Section 2.5. A fixed photon energy is used to probe the surface where the emitted electrons pass through a band pass filter analyser. However, instead of just detecting the electrons, the last two lenses are used to project the dispersive plane from the energy analyser onto the detector. This is displayed as a horizontal line, where the coordinate along the line represents the binding energy along the measured spectra and the intensity represents counts. By taking a line profile, a spectrum of intensity vs. binding energy can be collected, which is analogous to XPS except the energy range is set by the dispersive plane.

The advantages of µ-XPS compared to XPS is the fast acquisition time with a comparable signal-to-noise ratio. By using a field limiting aperture, the sampling area can be as small as 2 µm. Being able to select a small area to sample coupled with fast
acquisition time (~1 s per image) allows the measurement of time-resolved observations, such as crystal growth and redox reactions on a surface\textsuperscript{72}. 

2.7 REFERENCES


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Chapter 3

INSTRUMENTATION
3.1 Ultra-High Vacuum

Ultra-high vacuum (UHV) is needed for most surface science techniques, where surface cleanliness is of upmost importance. This is to minimise interactions between the surface and any gas molecules within its surrounding environment. If there is an abundance of molecules available, the surface of interest would become contaminated before any measurements could be taken. Performing experiments in UHV, defined as pressures lower than $10^{-9}$ mbar, maximises the timeframe the surface is clear of contaminants.

Contamination of the surface can be studied by considering the flux incident upon the surface, $Z_W$, as given by the Hertz-Knudsen equation:\(^1\):

$$Z_W = \frac{p}{\sqrt{2\pi m k_B T}},$$

(3.1)

where $p$ is the pressure of the system, $m$ is the mass of the incident atom/molecule, $k_B$ is the Boltzmann constant, and $T$ is the temperature. By calculating $Z_W$, an estimate for the timeframe a sample remains relatively free of contamination can be obtained.

By assuming a temperature of 300 K in a background pressure of $10^{-10}$ mbar, a flux incident rate of $2.87 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ is the impingement rate. Considering that there is an atomic density of typically $10^{15}$ cm$^{-2}$ on most surfaces, a sample of 1 cm$^2$ would be covered by a monolayer of gas molecules in less than 10 hours. This is with the assumption of a unity sticking probability. Using this equation, we can see that at a pressure of $1 \times 10^{-6}$ torr (approximately equivalent to mbar but used historically for
Chapter 3: Instrumentation

definition), a coverage of 1 monolayer would be achieved in 1 s. This allows the Langmuir to be used as a measurement of exposure which is defined as:

\[
1 \text{ L} \equiv 1 \times 10^{-6} \text{ torr} \times 1 \text{ s} = 1 \times 10^{-6} \text{ torr s}.
\]

This leads to a useful guide that 1 L exposure gives rise to \( \sim \) 1 monolayer coverage given the earlier assumptions of a unity sticking probability which is independent of coverage\(^1\).

3.1.1 Attaining UHV

As discussed, the need for UHV for surface science experiments is critical. The materials used for chamber construction need to be carefully selected in order to reach UHV pressures\(^1,2\). Vacuum chambers are generally built out of stainless steel with glass viewports and ceramic feedthroughs. All of these materials exhibit minimal outgassing, which makes them suitable bulk materials for UHV chamber construction. For seals to be made between interchangeable flanges, malleable metal gaskets are used between flange connections. The most commonly used metal for gaskets is oxygen free high conductivity (OFHC) copper, but other metals such as aluminium or gold/silver plated copper gaskets are also used. Each flange has a sharp knife edge which cuts into the gasket when the connection is tightened, thus creating an impermeable seal.

To evacuate the chamber, a series of vacuum pumps are employed. Firstly, positive displacement pumps, such as rotary vane or scroll pumps, are used. These have two functions: the first is to bring the pressure down to the \( 10^{-2} \sim 10^{-3} \) mbar region from atmosphere; the second is to act as a backing pump for a turbo-molecular
pump which lowers the pressure further to $\sim 10^{-7}$ mbar. The equipment needs to be baked up to 140 °C between 24 and 96 hours, depending on the chamber design, to achieve pressures in the UHV region. This removes adsorbates from the chamber walls, such as water and light hydrocarbons, that have a low outgassing rate at room temperature. After the bake-out is complete, only trace amounts of H$_2$, H$_2$O and CO remain. To maintain UHV, continual use of a turbo-molecular pump is required. In cases where experiments are sensitive to vibrations, such as STM, ion-getter pumps can be employed. Supplementary to the above, titanium sublimation pumps (TSP) are fired at regular intervals. These periodically coat a predetermined region of a chamber with fresh titanium, which is reactive and traps any residual gases, causing the pressure to lower further.

3.2 SAMPLE PREPARATION

3.2.1 SAMPLE MOUNTING AND MANIPULATION

Samples were mounted using various means to suit the requirements of each individual experiment. For TiO$_2$(110), samples were mounted on Omicron sample plates using tantalum clips that have been spot-welded to the plate (Figure 3.1a). Due to higher annealing temperatures required for Pt crystals, molybdenum fixtures were used to secure the sample (Figure 3.1b). This is the preferred method, as spot-welded connections can be weakened upon prolonged annealing at high temperatures, which could potentially cause noise in STM and increase the risk of sample drops.
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Figure 3.1: Diagram showing the mounting methods used in this work. (a) TiO$_2$ crystal secured on a standard Omicron sample plate using spot-welded Ta clips (b) Pt crystal secured on a standard Omicron plate using Mo screws and fixtures. (c) Rh crystal secured on a modified Omicron plate using a Mo cap compatible with Elmitec cartridges.

For the experiments performed at Diamond Light Source, the sample was mounted on a modified Omicron sample plate by a molybdenum cap (Figure 3.1c). All samples were inserted into the UHV chambers via magnetic transfer arms within a fast entry loadlock (FEL). Each preparation chamber contained a manipulator, equipped for sample cleaning, that allowed movement in XYZ coordinates alongside 360° rotation.

3.2.2 SAMPLE CLEANING

Sample cleanliness is paramount for obtaining reliable and reproducible results when probing surfaces. A clean surface needs to be prepared at the start of each experiment, and the UHV is used to maintain sample cleanliness, along with occasional refreshing in between. The most widely used method for sample cleaning, and of which is incorporated in this thesis, is to implement successive cycles of inert ion bombardment in conjunction with sample annealing.$^3$
3.2.2.1 Argon Ion Bombardment

Inert ion bombardment, also known as sputtering, is used to remove any contaminants from a sample’s surface. In this process, the inert gas, argon being the most commonly used, is ionised by a hot tungsten filament contained within the ion sputter gun. The resulting plasma is accelerated by using a series of electrostatic lenses towards the sample until its kinetic energy reaches 1 – 1.5 kV. This kinetic energy is transferred from the incoming Ar\(^+\) ions onto atoms and adsorbates on the surface, causing them to be ejected into vacuum.

3.2.2.2 Sample Annealing

The sputtering process roughens the sample surface as it can remove a few atomic layers. The amount of roughening is dependent on the kinetic energy of the Ar\(^+\) ion beam, the incident angle, and the surface’s exposure time. To reduce roughening, the sample is held at high positive bias and heated by electron bombardment (e-beam heating) up to \(~1500\) K (See Table 3.1), which causes the crystal lattice to re-order. The temperature is monitored using an infrared pyrometer alongside a type K (chromel-alumel) thermocouple.
During the experiments, multiple metals need to be deposited under UHV conditions to grow the samples of interest. This was achieved using physical vapour deposition (PVD), which involves heating the metal of interest until sublimation occurs. Both ceria thin films and the mixed ceria-zirconia thin films are formed using this method.

For the ceria thin films, a homemade electron-beam evaporator (Figure 3.2a) was employed to deposit the cerium. Here, Ce metal foil (99.9%, Alfa Aesar) is contained within a molybdenum crucible. By passing current through a thoriated tungsten filament, thermionic emission occurs. The emission of electrons causes e-beam heating, as the crucible is held at a high positive bias with respect to the earthed filaments. This results in the crucible being heated up to ~1500 K, which is enough to evaporate Ce.
When growing thin films of ceria-zirconia mixed oxide, both metals were deposited using a commercial Omicron EFM-3 e-beam evaporator (Figure 3.2b). The evaporation principle is the same as that of the homebuilt evaporator previously described. However, it is further equipped with water cooling to prevent any heat build-up in neighbouring components of the crucible, along with a flux monitor that allows fine control of the evaporation rate.

Figure 3.2: Schematics of the evaporators used for physical vapour deposition of cerium and zirconium to grow ultra-thin films. (a) Homebuilt electron-beam evaporator. (b) Omicron EFM-3.
3.3 STM

Figure 3.3: Representations of the two common methods of STM data acquisition. (a) Constant current mode. (b) Constant height mode.

To enable the acquisition of STM images, the tip is mounted on a piezoelectric drive. This allows for coarse movement in the z-axis (tip-sample separation), as well as fine motion on the sub-Å scale in both the z-axis along with the x and y axes. This controls the approach and scanning motion when taking measurements using a raster scan.

There are two modes which STM can be operated\(^4\). The first and most common is constant current mode (Figure 3.3a). Here, the tip-sample separation is adjusted by a feedback loop\(^5\) (Figure 3.4) that controls the z-piezo to keep the tunnelling current constant. The variation in the tip-sample separation, a result of the z-piezo position, is measured at each point to build up an image.
Figure 3.4: Block diagram of the feedback regulation operated in constant current mode\textsuperscript{6}.

The second, less commonly used mode which STM can be operated with, is constant height (Figure 3.3b). Here, the tip is rastered across the surface at a constant height, and the variation in the tunnelling current is recorded at each point. The benefit of using this method is that the images can be obtained faster than using the constant current method, as it is not reliant on a feedback response time when measuring data points. However, this mode is only suitable for atomically flat surfaces, as too much variation in the surface topography would result in the tip crashing into the sample.

One of the key considerations for STM is the reduction of any vibrational noise in order to obtain stable measurements. Vibrational dampening is attained by the use of an eddy current dampening system that holds the STM stage (Figure 3.5). During operation, the stage is lowered from its locked stationary position used for sample and tip transfers, so that it becomes suspended by vertical springs. Copper fins are positioned around the stage at equal spacing and offset from the fixed magnets that align the stage to the horizontal plane to minimise slope. Along with the vibrational isolation of the STM stage, the whole chamber is on active vibrational dampeners to
further minimise noise, providing very low noise level during STM operation. Any remaining high-frequency noise observed in the STM images was removed post acquisition by filtering via a low-pass fast fourier transform (FFT) filter in Gwyddion (Ver. 2.53).

The experiments in this work were carried out on a low temperature Omicron scanning tunnelling microscope (LT-STM) along with a variable temperature Omicron scanning tunnelling microscopy (VT-STM) as described below.

Figure 3.5: Schematic diagram of the eddy dampening system employed on the Omicron LT-STM used.
3.3.1 LT-STM

The LT-STM described here is a commercial Omicron GmbH LT-STM system. This was used to carry out STM measurements performed between 7 K and 78 K. The LT-STM (Figure 3.6) is comprised of two stainless steel chambers. The first chamber is used for sample preparation. The second chamber, separated by a gate valve, is used for STM measurements. This setup preserves the vacuum within the STM analysis chamber to avoid unwanted contamination, thus maximising the time in-between sample re-preparation.

Within the STM analysis chamber, the STM stage is equipped with a high precision sample heater and a bath cryostat. The bath cryostat is separated into an inner and outer bath. The inner cryostat can be filled with either LN₂ or LHe to cool the sample to 78 or 7 K respectively. The outer cryostat is filled with LN₂ to provide thermal shielding to the inner bath and help preserve temperatures. The high precision sample heater can be operated to heat, or when using a liquid cryogen, counter-heat the sample. This allows for a range of sample temperatures to be achieved for STM measurements rather than those fixed by the cryogen of choice. As well as the STM, a rotating carousel that stores six samples/tips is also located within the analysis chamber. This enables tips and samples to be quickly exchanged within the clean environment. The pressure of the chamber is monitored by an ion gauge to ensure no leaks develop and that the cleanliness is not compromised.

Within the sample preparation chamber, the sample is housed in a manipulator, which allows transport between both chambers. The manipulator comprises of an in-built electron bombardment heater, which is used to anneal the
sample as described earlier in Section 3.2.2. The preparation chamber is also equipped with an ion sputter gun, gas inlets for high purity argon and oxygen gases, an ion gauge used for monitoring pressure as described for the analysis chamber, low energy electron diffraction (LEED) optics, a quadrupole mass spectrometer/residual gas analyser (RGA), and an electron beam metal evaporator. This is supplemented by a dual anode Al/Mg X-ray gun (VSW Atomtech Ltd) and a concentric hemispherical analyser for X-ray photoelectron spectroscopy (XPS) measurements.

Attached to the sample preparation chamber is a smaller auxiliary chamber, separated by another gate valve, which is used as a fast entry load-lock (FEL). The FEL consists of a magnetic arm for sample transfers and an access window. A rotary backed turbomolecular pump is used to evacuate the FEL, which allows for samples and tips to be inserted into the preparation chamber without compromising the pressure.
Figure 3.6: Schematic representation of the Omicron LT-STM used in this work.
3.3.2 VT-STM

The VT-STM described here is a commercial Omicron GmbH VT-STM system. This was used to carry out STM measurements performed at room temperature. As with the LT-STM, the VT-STM (Figure 3.7) is comprised of two stainless steel chambers, one dedicated to sample preparation and the other for analysis.

Within the STM analysis chamber, the STM stage is equipped with a sample heater and LN$_2$ cooling tube. This allows for a range of sample temperatures between 25 and 1500 K to be measured. As well as the STM, the analysis chamber is also equipped with Auger electron spectroscopy (AES)/LEED optics, a rotating carousel allowing storage of six samples/tips, an ion gauge, a quadrupole mass spectrometer and a manipulator capable of electron bombardment heating.

Equally, the sample preparation chamber houses a sample manipulator that contains annealing capabilities. The use of a transfer arm is incorporated on the VT-STM to facilitate transfers between both chambers. The preparation chamber is also equipped with an ion sputter gun, gas inlets for high purity argon and oxygen gases, an ion gauge, a quadrupole mass spectrometer alongside an electron beam metal evaporator. As with the LT-STM, a small auxiliary chamber, attached to the sample preparation chamber, acts as a FEL that allows transfers in and out of vacuum.
Figure 3.7: Schematic representation of the Omicron VT-STM used in this work.
3.3.3 Tip Fabrication

When imaging surfaces on an atomic scale, an atomically sharp tip is needed. There are multiple ways of producing atomically sharp tips, which include dipping in electrochemical solution\textsuperscript{6,7} or focused ion beam (FIB) milling\textsuperscript{8}. Here, tips were produced using a suspended electrochemical etching method (Figure 3.8).

During etching, the tungsten wire (0.25 - 0.4 mm diameter) is held so that it is suspended through a hole in a metallic plate, ensuring no contact is made. Here, the wire acts as an anode and the metallic plate is the cathode. An electrolyte (2 M NaOH) is pipetted on the hole to form a meniscus and creates a bridge between the metallic plate and the tungsten wire. Any additional electrolyte is removed to encourage a thin layer, with care being taken to keep the meniscus bridge intact. As a voltage is applied to the circuit (1.7 - 2 V), the tungsten is etched away at the point of contact with the electrolyte. To maintain a constant current, the electrolyte is replenished when required. As the wire reaches a critical thickness, the weight of the wire below causes a clean break. This leads to two high quality tips. It must be noted that extra care has to be taken with the tip that drops, as any contact may damage the sharp apex.
3.4 LEED and AES

Omicron rear view SPECTALEED optics (Figure 3.9) were employed during Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES) measurements. LEED was used to check long range order of the surfaces, along with monitoring growth of thin films and any adsorbates forming ordered overlayers. The optics consist of a four-grid system as well as an electron gun and a fluorescent screen. The electron gun generates a monochromatic beam of low energy electrons. The electrons impact the surface of the sample, where they are backscattered towards the fluorescent screen. The sample is earthed to avoid any charge effects influencing the scattering. Before the backscattered electrons reach the screen, they pass through four grids. The first and last grids are earthed and creates a field-free region. The inner two (retarding) grids are held at a negative potential, just below the beam energy. This forms a filter that only allows elastically scattered electrons to pass and filters out...
lower energy electrons caused by inelastic scattering. The elastically scattered
electrons are reaccelerated towards the screen, which is held at a high positive bias
(\(\sim 6-7 \text{ kV}\)). As the electrons impact the fluorescent screen, it gives rise to the diffraction
pattern, observed as bright spots against a dark background that can be recorded
using a camera.

The same optics were used to perform AES measurements in retarding field
analyser (RFA) mode. AES was primarily employed to check any sample contamination
along with monitoring metal deposition and thin-film growth. As with the LEED
operation, the outer and inner grids are earthed to create a field-free region.
However, where a variable beam energy was used in LEED, a constant beam energy
(\(\sim 1.5 – 3 \text{ kV}\)) is utilised in AES. A modulating voltage is applied to the inner two grids
to act as a band pass filter, which scans the energy range desired. The screen acts a
current collector during the scan, and the measurement is recorded as a function of
the filter voltage. A lock-in amplifier is used to provide phase-sensitive detection and
produces Auger spectra in derivative mode.
Figure 3.9: Schematic illustrating the Omicron SPECTALEED optics operated in both (a) LEED and (b) AES in RFA mode.
3.5 HREELS

The high-resolution electron energy loss spectroscopy (HREELS) experiments were performed using a commercial VSW EELS instrument (Figure 3.10). The HREELS system is split into two levels; an upper level primarily used for sample preparation and a lower level where the monochromator and electron analyser are positioned. The system is pumped using a rotary-backed turbomolecular pump alongside a titanium sublimation pump. After baking, the base pressure was in the region of $3 \times 10^{-10}$ mbar. Two ion gauges, one located near the turbomolecular pump and another in the preparation chamber, were used to monitor the pressure. Sample insertion was achieved by the use of a fast-entry loadlock (FEL) as described in Section 3.3.1.

Due to the low energy nature of the electrons used, they are susceptible to stray magnetic fields. This can cause interference to the trajectory of the electrons, which has a detrimental impact on the resolution and the signal-to-noise ratio within the spectrometer. To prevent any stray magnetic fields, the chamber is lined with mu-metal shielding. The lower level of the chamber, where the HREELS measurements are collected, is protected by an additional layer to minimise interference. As well as mu-metal shielding, only non-magnetic materials were used in the construction of the sample manipulator.
Figure 3.10: Schematic of the commercial VSW HREELS housed in the two-level chamber used. (a) Overview of the chamber highlighting layout of the additional instrumentation for sample preparation. (b) Side view of the chamber highlighting the mu-metal shielding.
3.5.1 **Upper Level**

As mentioned, the upper level is primarily employed for sample preparation and characterisation. The sample is housed in a manipulator which enables transport between the upper and lower levels. As with the LT-STM, the sample manipulator is equipped with an in-built electron bombardment heater, which enables sample annealing as described in Section 3.2.2. The upper level is equipped with high purity argon and oxygen gas inlets, a hot cathode ion gauge, LEED/AES combined optics, a quadrupole mass spectrometer/residual gas analyser and an electron beam metal evaporator.

3.5.2 **Lower Level**

The HREELS measurements were carried out in the lower level of the chamber. The instrumentation used consists of an electron monochromator and a HA 50 hemispherical analyser.

3.5.2.1 **Electron Monochromator**

The electron monochromator (Figure 3.11) consists of an electron source (hairpin tungsten filament), a hemispherical energy resolving component and a lens system. As a current is passed through the filament, it emits a Maxwellian thermal distribution of electrons (Figure 3.12). The distribution does not start at zero due to the work function barrier that needs to be overcome. A contact potential is applied to the filament and grid with respect to the rest of the spectrometer. This allows the
ability to tune into the peak of the Maxwellian distribution to maximise the intensity of electrons leaving the monochromator. The electrons are accelerated towards the hemispherical energy resolving component by an anode, passing through two radial and angular defining slits. The first is positioned at the anode and the second at the resolver entrance, which has a width of 0.5 mm. The energy resolving hemisphere is used to select a narrow bandwidth at the centre of the Maxwellian distribution. Upon leaving the analyser, the electrons pass through an exit aperture that is the same width as the entrance aperture. The electrons are then accelerated/decelerated to the required kinetic energy and focused onto the sample through a series of lenses. The pass energy of the monochromator is continuously variable between 0.5 and 50 eV. In this work, a constant pass energy of 1.35 eV was used.

Figure 3.11: Schematic detailing the design of the monochromator and HA 50 analyser used in this work.
Figure 3.12: Illustration of a typical Maxwellian distribution, where $\phi$ is the work function barrier and $\Delta E$ is a selected narrow energy bandwidth of emitted electrons at the maximum intensity.

### 3.5.2.2 HA 50 ANALYSER

The analyser used for the HREELS experiments is a VSW HA 50 hemispherical analyser (Figure 3.12). Its design is similar to the monochromator described above; however, instead of an electron source, there is an electron detector. The analyser entrance is covered by a four-element input lens, which is designed to match the electron beam profile as it leaves the monochromator. Incoming scattered electrons from the sample are focused by the lens into the 1 mm diameter entrance aperture. Alongside focusing the beam, the lens accelerates/decelerates the electrons to a constant pass energy and determines the resolution. This is known as Fixed Analyser Transmission (FAT). To eliminate noise from higher-energy electrons, there is a slot in the outer hemisphere of the analyser that allows these electrons to pass through. The electrons that possess the selected energy pass through an exit slit of the hemisphere. The exit slit has the same diameter as the entrance aperture, thus reducing any impact
of mechanical misalignment. Lastly, the electrons reach the electron detector, in this case a channel electron multiplier (CEM). During operation, the rear of the multiplier was kept at a potential of 1.9 kV, whilst the front was kept at approximately 10% of the rear. The potential gradient across the CEM, along with its high secondary electron emissivity, leads to a cascade of electrons when an electron impacts the CEM. The gain across this cascade is of the magnitude $10^8$, which leads to a measurable current pulse for every electron impact event. A charge sensitive preamplifier converts this current pulse into a voltage pulse, which is then directed to a computer for analysis.

A pass energy of 1 eV was used for the HA 50 analyser. Coupled with the pass energy of 1.35 eV for the monochromator, these provide the instrumental resolution. The resulting energy resolution, measured by recording the full width at half maximum (FWHM) of the elastic peak, was recorded as 10-13 meV across the experiments.

### 3.6 IO6 Beamline – Diamond Light Source

The experiments portrayed in Chapter 6 of this thesis were conducted at Diamond Light Source, the UK synchrotron facility. Here, the nanoscience beamline, IO6, was utilised. IO6 offers both variable linear and circular polarised radiation. For circular polarised radiation, the energy range of 106 – 1300 eV can be generated. For linearly polarised radiation, the energy range of 80 – 2100 eV and 130 – 2100 eV can be generated for horizontal and vertical polarisation, respectively.
An overview of IO6 beamline can be seen in Figure 3.13. At the start, we see two APPLE II undulators providing access to left and right circular polarised light, along with s or p linearly polarised radiation. After the undulators, there are a series of mirrors which serve two purposes: absorbing most of the unwanted power from the insertion devices, and collimating the beam to focus it into the monochromator. Here, three gratings are used: 150, 400 and 1200 lines/mm. During data acquisition, a grating of 150 lines/mm was used when measuring with photon energies below 200 eV, and 400 lines/mm for all other measurements\textsuperscript{10}. The monochromator is optimised for mid-range energies with a resolving power of $10^4 \left( \frac{\Delta E}{E} \right)$ measured at 400 eV. The X-rays reach two toroidal mirrors after leaving the monochromator, which focuses the beam towards two alternative exit slits. One slit is for the branchline and was not utilised, whilst the other slit is for the PEEM beamline. Once the X-rays pass through the PEEM beamline exit slit, there is a Kirkpatrick-Baez refocussing mirror where the X-rays are focused onto the sample. The focus of the spot size is $3 \times 10 \ \mu \text{m}$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{img/diagram.png}
\caption{Overview of the nanoscience (IO6) beamline at Diamond Light Source\textsuperscript{9}.}
\end{figure}
3.6.1 XPEEM

The instrument used was an Elmitec LEEM III housed in the UHV chamber. The equipment presented here is commonly known as a spectroscopic photoemission and low energy electron microscope (SPELEEM). This is due to the inclusion of a high stability electron gun that allows for LEEM measurements. Alongside the SPELEEM instrument, there is also a dedicated surface preparation and analysis UHV chamber. This chamber is equipped for sample cleaning and metal vapour deposition, along with STM, AES and LEED capabilities.

A schematic diagram of the PEEM instrument is shown for the three basic operation modes; imaging, diffraction and spectroscopy (Figure 3.14). For all three modes, X-rays (or electrons generated by the electron gun if needed) are directed towards the sample through the objective lens. This causes the excitation of the sample’s surface and results in the emission of photo- and secondary electrons. These electrons pass through the objective lens and are directed to the imaging column, which consist of 4 lenses (transfer, field, intermediate and the first projector lens). The electron beam then passes into the energy analyser via two retarding lenses, which act as an energy filter. The beam is accelerated within the analyser by two accelerating lenses, before leaving through a further energy filtering exit slit. Finally, a series of two projector lenses focus the beam onto a 2D electron detector, which records the resulting PEEM image and can be viewed via a CCD camera.
Figure 3.14: Schematic of the instrument setup of the Elmitec LEEM III instrument at the nanoscience (IO6) beamline at Diamond Light Source. Three modes of operation, imaging, diffraction and spectroscopy, are shown. OL – objective lens. FLA – Field limiting aperture. TL – Transfer lens. CA – Contrast aperture. FL – Field lens. IL – Intermediate lens. P – Projection lenses. ES – Exit slit. Adapted from reference\textsuperscript{11}.

### 3.6.1.1 Imaging Mode

Imaging mode covers techniques including XPEEM, XAS, LEEM and other spectroscopic imaging. Within the techniques enveloped within imaging mode, there are two further subsections. The first are non-energy filtered techniques, which include XPEEM, XAS and LEEM. Here, a variable beam energy is employed and, to allow this, the retarding lenses within the analyser are inactive. The second mode is energy-filtered imaging microscopy. This utilises a fixed energy photon beam, which requires the retarding lenses to filter the beam, selecting only electrons of the chosen energy. The field-limiting aperture may be used depending on the needs of the experiment. The field, intermediate and first projector lenses are used to magnify the sample image produced by the objective lens. An exit slit is inserted in the analyser’s dispersive plane to select the desired energy of the electrons emitted by the sample.
During this mode, the contrast aperture is inserted in order to optimise resolution by limiting the angular acceptance.

### 3.6.1.2 Diffraction Mode

Diffraction imaging covers techniques including microprobe LEED and microprobe photoelectron diffraction. Here, the objective lens produces a diffraction pattern, which the intermediate and first projection lenses image, rather than the sample. The use of an exit slit allows the measurement of photoelectron diffraction or angle resolved photoemission. The contrast aperture is not inserted during these measurements and the field-limiting aperture’s position is used to select the probed area.

### 3.6.1.3 Spectroscopy Mode

Spectroscopy imaging covers the technique micro-XPS (µ-XPS). The imaging column acts in the same way as in imaging mode during µ-XPS measurements. However, the exit slit is not inserted. This allows the complete dispersive plane to exit the analyser. The second and third projector lenses are used to image the analyser’s dispersive plane by projecting the plane onto the detector. This appears as a line where the intensity profile, generated by taking a line profile along the sample, represents the photoemission spectrum.
3.7 References

Chapter 4

PROBING THE DISTRIBUTION OF BRIDGING HYDROXYL BOUND EXCESS ELECTRONS ON RUTILE TiO2(110)

ABSTRACT

Using scanning tunnelling microscopy (STM), we investigate the temperature dependence of the distribution of the bridging hydroxyl (OH\textsubscript{b}) bound excess electrons on rutile TiO\textsubscript{2}(110). By performing simultaneously recorded empty- and filled- state STM on single OH\textsubscript{b}s at temperatures between 7 and 78 K, we determine that the distribution of the OH\textsubscript{b}-bound excess electrons retains a symmetric, four-lobe structure around the OH\textsubscript{b} at both 7 K and 78 K. This is indicative of OH\textsubscript{b}s being much weaker charge traps than bridging O vacancies (O\textsubscript{b-vac}). Also, by sequentially removing the capping H of each OH\textsubscript{b} using tip pulses, we find that the annihilation of each OH\textsubscript{b} is accompanied by the disappearance of some lobes in the filled state STM. This confirms the direct correlation between OH\textsubscript{b} and their excess electrons.
4.1 INTRODUCTION

Titanium dioxide is one of the most studied metal-oxide systems, with applications across a range of industries and technologies. These include heterogeneous catalysis, photocatalysis, gas sensors and solar cells, to name a few\textsuperscript{1–5}. Point defects, such as oxygen vacancies and hydroxyl groups, are considered to be a principal factor in determining a material’s properties and catalytic activities\textsuperscript{6–11}. This has led to multiple studies characterising the surface of TiO\textsubscript{2} on an atomic-scale level to gain an understanding of its geometric and electronic structure\textsuperscript{12,13}.

Rutile, one of the polymorphs of TiO\textsubscript{2}, has become a model system for metal oxides. This particularly applies to the (110) surface, its most stable face\textsuperscript{14}. The rutile (110) face (Figure 4.1) is made up of alternating fivefold coordinated Ti\textsuperscript{4+} ions (Ti\textsubscript{5c}) and twofold coordinated bridging O\textsuperscript{2−} ions (O\textsubscript{b})\textsuperscript{15}. TiO\textsubscript{2} is a wide band-gap insulator (\textasciitilde 3eV), which can be made semiconductive upon reduction by multiple cycles of ion sputtering and annealing\textsuperscript{16}. This results in multiple bridging oxygen vacancy (O\textsubscript{b}-vac) point defects being created\textsuperscript{17–19}. For every O\textsubscript{b}-vac created, the surface gains two excess electrons. These can either be delocalised, spreading over multiple symmetrically equivalent sites, or localised at one position. In the case of a localised excess electron, the surrounding lattice ions shift away from their equilibria positions and aids the accommodation of the extra charge. This creates a favourable potential well, thus immobilising the charge. This self-trapped charge, along with the displaced lattice ions, are known as a small polaron\textsuperscript{20}. Small polarons are characterised as having low hopping mobility, which is observed to increase with temperature\textsuperscript{21}.
Chapter 4: Probing the Distribution of Bridging Hydroxyl Bound Excess Electrons on Rutile TiO$_2$(110)

Figure 4.1: A ball model of the rutile TiO$_2$(110)-(1x1) surface. The surface consists of alternating rows of fivefold-coordinated Ti$^{4+}$ ions (red) and twofold-coordinated bridging O$^{2-}$ ions (light blue) running along the (001) crystallographic direction. Bridging hydroxyl (purple) and oxygen vacancy point defects are also highlighted.

Employing simultaneously recorded empty- and filled- state imaging in STM on isolated O$_b$-vacs of rutile TiO$_2$(110) at temperature between 7 and 78 K, Yim et al. observed the distribution of the O$_b$-vac bound excess electrons to transform from a symmetric, four-lobe structure at 78 K into one of three asymmetric, two-lobe structures at 7 K$^{22}$ (Figure 4.2). This confirms the polaronic character of the O$_b$-vac bound excess electrons as the hopping rate is observed to decrease at lower temperatures showing a temperature dependence characterised in previous studies$^{21}$. Using photoemission techniques, the excess electrons were seen to occupy a Ti$^{3+}$ 3d derived state, located at $\sim$1 eV below the Fermi level in the band gap,$^{23,24}$ also known as a band gap state (BGS). Therefore, the reduction of TiO$_2$ can be given as:

$$O^{2-} + 2Ti^{4+} \rightarrow O_{\text{vac}} + \frac{1}{2} O_{2(\text{g})} + 2Ti^{3+}.$$  (4.1)
**Chapter 4: Probing the Distribution of Bridging Hydroxyl Bound Excess Electrons on Rutile TiO$_2$(110)**

**Figure 4.2:** 3.2 x 3.2 nm$^2$ representative STM images of isolated O$_b$-vacs on TiO$_2$(110) recorded using (a-e) positive (empty states) and (f-j) negative (filled states) sample bias at different temperatures: (a,f) 78 K, (b,g) 16 K and (c-e,h-j) 7 K. Filled state images in (f-j) were recorded in the vicinity of different isolated O$_b$-vacs. Rectangles are drawn around the O$_b$-vacs and mark the same areas between the empty- and filled- state images. Scan parameters: (a) $(V_s, I_T) = +0.9$ V, 20 pA; (b) +1 V, 20 pA; (c) +1 V, 10 pA; (d-e) +1 V, 5 pA; (f) -1.1 V, 5 pA; (g) -2 V, 1.6 pA; (h-j) -2 V, 0.3 pA. Adapted with permission from Reference$^{22}$.

H$_2$O molecules adsorb dissociatively at O$_b$-vacs at room temperature, forming a pair of bridging hydroxyls (OH$_b$) for each O$_b$-vac$^{25-29}$ (Figure 4.3). According to Kurtz et al.$^{23}$, water dissociation at O$_b$-vacs causes no change in the BGS population. As such, it is generally assumed that upon H$_2$O dissociation, the excess electrons that originally belong to O$_b$-vacs are transferred to the newly formed OH$_b$ pairs, with each pair sharing two excess electrons. After a OH$_b$ pair is formed, over time the OH$_b$ inside the pair diffuse away from each other along the [001] direction and leads to two single OH$_b$.

It was believed that after separation, each OH$_b$ shares one of the excess electrons originating from the O$_b$-vac. However, this belief was challenged by Zhang
et al.’s STM work\textsuperscript{26}, which showed that the OH\textsubscript{b} that forms at the position of the O\textsubscript{b}-vac is ten times less likely to take the first hop away from the other OH\textsubscript{b}. Such probability imbalance indicates that the splitting of H\textsubscript{2}O at O\textsubscript{b}-vac leads to two inequivalent types of OH\textsubscript{b}, with the inequivalence possibly arising from their difference in excess electron distribution. In a simplistic view, upon initial dissociation of H\textsubscript{2}O, the OH\textsubscript{b} at the O\textsubscript{b}-vac site will be surrounded by two Ti\textsuperscript{3+} ions and the OH\textsubscript{b} formed on the nearest O\textsubscript{b} will have one Ti\textsuperscript{3+} and one Ti\textsuperscript{4+} ion adjacent. However, in reality the 3d electron density is more diffused\textsuperscript{22}. Subsequent studies by Li et al. showed that the hopping rate for the hydroxyls once separated were comparable between the hydroxyls formed at the vacancy and those formed on the nearest O\textsubscript{b}\textsuperscript{30}. This suggests the inequivalence is only present during the initial dissociation.

We aim to achieve two goals in this study. First, we aim to confirm the polaronic character of the OH\textsubscript{b} bound excess electrons. Second, by sequentially removing the capping H of each isolated OH\textsubscript{b} while monitoring change(s) in the filled state STM, we aim to determine the number of excess electrons belonging to each OH\textsubscript{b}. 

Figure 4.3: Ball model illustration highlighting the process of water dissociation occurring at O\textsubscript{β}-vacs on the non-stoichiometric rutile TiO\textsubscript{2}(110) surface. (a) Stoichiometric rutile TiO\textsubscript{2}(110) surface. (b) O\textsubscript{β}-vacs created by annealing the sample. (c-d) H\textsubbox{2}O occupies the O\textsubbox{β}-vac. (e-f) H\textsubbox{2}O undergoes dissociation resulting in a pair of hydroxyls that diffuse preferentially along the [001] rows.
4.2 EXPERIMENTAL METHODS

STM experiments were performed using an Omicron GmbH low temperature scanning tunnelling microscope (LT-STM) housed in a UHV system (see Chapter 3). In order to probe the excess electrons associated with OH$_b$, we recorded filled-state (negative sample bias) and empty-state (positive sample bias) STM images. In the forward scan in the fast direction, a line of data is recorded at positive sample bias; and in the backward scan, a line of data is recorded with negative sample bias so that the two images are recorded quasi-simultaneously. This eliminates the effects of thermal or piezo drift so that the scans with opposite polarity can be easily correlated. To rule out the introduction of features from the forward scan to the backwards scan, occasionally we reversed the polarity, i.e. the forward scans were negatively biased and backward scans were positively biased. No difference was observed in the resulting images.

We used a special preparation procedure in order to obtain a sample sufficiently conductive at 7 K: (i) Fresh rutile TiO$_2$ (110) samples (Pi-Kem) were subjected to approximately ninety Ar$^+$ ion sputtering and annealing cycles up to $\sim$1000 K. (ii) Such ‘as-prepared’ samples were left in the preparation chamber with a background pressure of $2 \times 10^{-10}$ mbar at room temperature. Here, water from the residual vacuum reacts with O$_b$-vacs, forming two bridging hydroxyls (OH$_b$) for each O$_b$-vac$^{25-27}$. In this way, a TiO$_2$ (110) surface, namely h-TiO$_2$, is formed with a significant density of OH$_b$ without the presence of any O$_b$-vac$^{31}$.

Yim et al. showed that O$_b$-vac polarons that are separated from each other by at least three unit cells along the [001] direction, or one unit cell along the [110]
direction, have no interaction with each other\textsuperscript{22}. Based on their observation, we prepared individual OH\textsubscript{b}s on h-TiO\textsubscript{2} using the following methodology. First, with the use of simultaneously recorded empty- and filled- state imaging (also known as dual mode imaging) in STM, we located the OH\textsubscript{b} species on h-TiO\textsubscript{2} that are not in close proximity to any region containing charge impurities (see Appendix 1). Then, by applying tip pulses (+3 V, 1 ms at 78K; +3.5 V, 1 ms at 7 K), we removed the capping H of all other OH\textsubscript{b} species surrounding the targeted OH\textsubscript{b} species\textsuperscript{32}. This led to a small area (usually 5 x 5 nm\textsuperscript{2} in size) on the TiO\textsubscript{2}(110) surface that contains only a single OH\textsubscript{b} species. By performing dual mode imaging on the single OH\textsubscript{b}, the distribution of the excess electrons surrounding it was determined. Occasionally, we removed the capping H of the OH\textsubscript{b} species one by one with tip pulses (+3 V, 1 ms at 78K; +3.5 V, 1 ms at 7 K) and recorded STM images obtained in dual mode before and after the removal of each capping H. This provided an STM dataset showing the instant change in the excess electron distribution before and after each of the capping H removal events.
4.3 RESULTS AND DISCUSSIONS

Figure 4.4: 4 × 4 nm² (a) empty- and (b) filled- state images of TiO₂(110) with a single OH₆ (marked with dashed rectangles). The images were taken at 78 K. (c,d), as (a,b), taken after the removal of the capping H of the OH₆ with a +3 V, 1 ms tip pulse. (e,f) 1.5 × 3 nm² zoom-in images of the region around the single OH₆ recorded before (e) and after (f) the removal of its capping H. The shuttle feature associated with the OH₆ is marked with a solid oval. Scan parameters: (a,c) Vₛ = +0.9 V, Iₜ = 50 pA and (b,d) Vₛ = -1.0 V, Iₜ = 5 pA. High frequency noise was removed from the STM images via use of a low-pass fast fourier transform (FFT) filter.

Figure 4.4 shows the empty- and filled- state STM images of the TiO₂(110) surface taken before (Figure 4.4a-b) and after (Figure 4.4c-d) the removal of the capping H of a single OH₆ using a tip pulse (VSAMPLE = +3 V, duration = 1 ms). The images were recorded at 78 K. By comparing the filled state images (Figure 4.4b,d), we noticed that the shuttle feature, which is at the same position as the OH₆ in the empty state image (Figure 4.4a), disappears after the capping H removal. In addition, as shown in the magnified filled state images with enhanced contrast (Figure 4.4e-f), the lobes that
were distributed at the Ti$_{5c}$ sites, diagonally next to the OH$_b$, also vanish. Minato et al. also observed the symmetric, four-lobe structure in their STM work that was performed at 78 K$^{33}$. They reported that this structure corresponds to the distribution of the excess electrons that are associated with OH$_b$.

Figure 4.5 shows empty and filled state images recorded before and after each of the capping H removals of two single OH$_b$ with tip pulses (+3 V, 1 ms). The images were taken at 78 K. In the filled state images, we find that after the capping H of the OH$_b$ on the left is removed (Figure 4.5c), the four lobes that were originally present at the Ti$_{5c}$ sites surrounding that OH$_b$ (Figure 4.5d-e) also disappear (Figure 4.5f). The four lobes are highlighted by subtracting the filled state image after the capping H is removed from the image previous to the removal to observe the change in electron distribution associated with the hydroxyl (Figure 4.5h). However, the OH$_b$ on the right is different. Some residual intensity remains on the Ti rows after the capping H is removed (Figure 4.5e). This indicates that while the excess electron distribution of the OH$_b$ on the left (Figure 4.5d) has a symmetric, four-lobe structure (Figure 4.5h), that of the OH$_b$ on the right is asymmetric.

As mentioned, some residual charge remains on the rows where the hydroxyl on the right was located (Figure 4.5f). This is characterised as three lobes highlighted by dashed ovals. As these residual charges still remain on the surface after the hydroxyl is removed, this suggests that they are not associated with any of the OH$_b$s. This residual charge also influences the distribution of the excess electron around the hydroxyl with the distribution around the left hydroxyl appearing more symmetric than the corresponding distribution around the right hydroxyl (Figure 4.5d). This is supported by a larger-scale empty-state image taken in the same region (see Appendix
A1), which shows that the bright lobe at the lower right is situated at the periphery of a charged impurity region and appears as a bright patch in the empty-state STM. Such charged impurity regions were found to be devoid of surface point defects (O$_{b}$-vac) and unreactive to O$_{2}$\textsuperscript{34}. As such, we propose that the charged impurity regions impose a strong, long-range influence on the spatial arrangement of the excess electrons on the TiO$_{2}$ surface, including those associated with OH$_{b}$. 
Chapter 4: Probing the Distribution of Bridging Hydroxyl Bound Excess Electrons on Rutile TiO$_2$(110)

Figure 4.5: Simultaneously recorded (a) empty- and (d) filled- state images of TiO$_2$(110) containing two individual OH$_b$. The images were taken at 78 K. (b,e) as (a,d), following the removal of the capping H of the OH$_b$ on the right using a +3 V, 1 ms tip pulse; (c,f) as (b,e), following the removal of the capping H of the OH$_b$ on the left with another tip pulse. Circles mark the positions of the OH$_b$ species. Dashed ovals represent residual charged regions not associated with the hydroxyls. (g) A difference image formed by subtraction of the filled state image in (d) from that in (e). (h) Another difference image formed by subtracting the filled state image in (e) from that in (f). Scan parameters: (a-c) $V_s = +0.9$ V, $I_I = 100$ pA and (d-f) $V_s = -1.42$ V, $I_I = 4$ pA. High frequency noise was removed from the STM images via use of a low-pass FFT filter.
Yim et al. reported that the distribution of the O\_b-vac bound excess electrons of TiO\_2(110) transforms from a symmetric, four-lobe structure at 78 K into one of three asymmetric, two-lobe structures at 7 K\textsuperscript{22}. This confirmed the polaronic character of those excess electrons. This motivates our investigation on the temperature dependence of the OH\_b bound excess electron distribution. Before looking into this, we first examined how the image contrast in the filled state STM changes after all capping H are removed using tip pulses. The result is shown in Figure 4.6. After all of the capping H located at the centre of the image (marked with rectangles) are removed, the OH\_b-void region in the filled state is characterised by rows that appear significantly darker than those in the OH\_b-rich region. This confirms a direct correlation between the OH\_b and the excess electrons that appear as lobes on the Ti\textsubscript{5c} rows (Figure 4.6b). All of the lobes disappear after all the capping H are removed. On this basis, we speculate that owing to the disappearance of charge traps (OH\_b), the excess electrons that originally belong to the OH\_b either redistribute themselves to the neighbouring OH\_b-rich region or migrate into the sub-surface layer of the TiO\_2 sample.
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Figure 4.6: 10 × 10 nm$^2$ (a) Empty- and (b) filled-state image of the hydroxylated TiO$_2$(110) surface (h-TiO$_2$), taken after the capping H of all OH$_b$ in the central part of the image (marked with rectangles) were removed one-by-one using +3.5 V, 1 ms tip pulses. Scale bar: 5 nm. The images were recorded at 7 K. Scan parameters: (a) $V_S = +2$ V, $I_T = 10$ pA and (b) $V_S = -2.0$ V, $I_T = 1$ pA. High frequency noise was removed from the STM images via use of a low-pass FFT filter.

Figure 4.7 shows the empty- and filled-state STM images recorded before and after the capping H of two single OH$_b$s were sequentially removed using +3.5 V, 1 ms tip pulses. The images were also recorded at 7 K. In the filled state image (Figure 4.7d), each OH$_b$ appears to be characterised by a nearly symmetric, four-lobe structure. This is very different from the case for O$_b$-vac, whose excess electron distribution is transformed from a symmetric, four-lobe structure at 78 K into one of three asymmetric, two-lobe structures at 7 K (Figure 4.2). We relate this difference to the quenching of polaron hopping at 7 K that only happens to the O$_b$-vac bound excess electrons, but not to those associated with OH$_b$. When water dissociates at the vacancy, the associated charge of the vacancy (formally 2+) is partially compensated by the hydroxyl. As each hydroxyl (formally 1+) has a weaker attracting force, this can explain the observations. The formation of a OH$_b$ (by adding one H to a O$_b$) causes
much less structural distortion of the TiO$_2$ lattice compared to an O$_b$-vac (by losing one O$_b$). As such, OH$_b$s are likely to be much weaker as charge traps than O$_b$-vacs. Consequently, the OH$_b$ associating excess electrons are only required to overcome a small barrier to hop between the Ti sites around the defect (OH$_b$) compared to those of an O$_b$-vac.

Figure 4.7: Simultaneously recorded (a) empty- and (d) filled-state images of TiO$_2$(110), containing two individual OH$_b$s. The images were taken at 7 K. (b,e) as (a,d), with the capping H of the OH$_b$ on the left removed with a +3.5 V, 1 ms tip pulse; (c,f) as (b,e), with the capping H of the OH$_b$ on the right removed with another tip pulse. Circles mark the positions of the OH$_b$ species. (g-h) Difference images formed by subtraction of the filled-state image in (d) from that in (e) and of the filled-state image in (e) from that in (f) respectively. Scan parameters: (a-c) $V_S = +2$ V, $I_T = 30$ pA and (d-f) $V_S = -2$ V, $I_T = 1$ pA. High frequency noise was removed from the STM images via use of a low-pass FFT filter.
We then examined the change in the filled state contrast before and after each of the capping H removals. As shown in Figure 4.7, after the capping H of the OH$_b$ on the left (Figure 4.7a) is removed (Figure 4.7b), not only does the shuttle feature located at the OH$_b$ centre disappear, but lobes that are distributed at the Ti sites around the OH$_b$ (Figure 4.7d) disappear as well (Figure 4.7e). This observation also applies to the OH$_b$ on the right (Figure 4.7f). To better visualise the change in the filled state, we subtracted the filled state image taken before each capping H is removed (Figure 4.7d,e) from that after the capping H of each OH$_b$ is removed (Figure 4.7e,f). This leads to the difference images shown in Figures 4.7g-h. In the difference images (Figure 4.7g-h), each OH$_b$ is characterised by a bright feature at the centre with four lobes distributed at each of the second-nearest Ti$_{5c}$ sites around the OH$_b$. This confirms the observation of the nearly symmetric, four-lobe structure for the distribution of the OH$_b$ bound excess electrons at 7 K. The OH$_b$ on the right is seen to undergo electron redistribution as the left capping H of the OH$_b$ is removed. This is observed as an additional lobe of electron density loss along with an area exhibiting an increase in electron density (Figure 4.7g). In addition, the difference images (Figure 4.7g-h) show only reduction in the filled state contrast in close proximity to the OH$_b$, while that in the surrounding region is unaltered. This indicates that owing to the disappearance of their charge traps (OH$_b$), the OH$_b$ bound excess electrons relocate themselves to the subsurface region of TiO$_2$(110) and become invisible in the STM images.

As mentioned previously, when a H$_2$O molecule adsorbs dissociatively at an O$_b$-vac, two OH$_b$s are formed. One of the OH$_b$s is formed at the newly occupied O$_b$-vac (namely OH$_b$-v) and the other (namely OH$_b$-b) is formed by the protonation of one of
the two nearest-neighbour $O_b$ ions. Using STM to monitor hydrogen hopping along the $[001]$ rows, Zhang et al. determined the capping $H$ of $OH_b$-b to be ten times more likely to hop. This shows the inequivalence between the two different types of $OH_b$ species. One possible explanation for this is that the two excess electrons, which originally belong to the $O_b$-vac, are unequally distributed between the $OH_b$ inside the $OH_b$ pair. They can be distributed in three different ways: (i) each $OH_b$ has one excess electron, (ii) $OH_b$-v has both electrons while $OH_b$-b has none, or (iii) vice versa.

In order to gain more insight into this issue, we employed a ‘pulse and track’ approach. In this approach, we recorded empty- and filled- state images before and after the capping $H$ of each $OH_b$ is successively removed with tip pulses. In doing so, we aim to find out how the excess electron(s) are distributed around each $OH_b$.

Figure 4.8 shows a series of simultaneously recorded empty- and filled- state images, recorded at 6.6 K, taken before and after the sequential removal of each of the capping Hs with STM tip pulses (+3.5 V, 1 ms). Before imaging, the capping $H$ of most of the $OH_b$ originally present in the imaged region were removed using tip pulses. This results in only five $OH_b$s and one $OH_b$ pair remaining in the imaged region. As shown in the filled state images (Figure 4.8f-j) as well as the difference images in Figures 4.8k-n, the removal of each capping $H$ is always accompanied by changes in the image contrast in the filled state STM. For instance, after the capping $H$ of the $OH_b$ at the bottom right (Figure 4.8a) is removed (Figure 4.8b), the two lobes that were originally present at the Ti rows above that $OH_b$ in the filled state (Figure 4.8f) disappear. This is accompanied by some enhancement in the intensity of the lobes at the Ti sites above the $OH_b$ pair at the top right of the image (Figure 4.8g).
Therefore, this indicates that following the removal of that capping H, the excess electrons which originally belong to that OH$_b$ are redistributed and migrate to the bulk. The excess electrons that are associated with the OH$_b$ pair at the top right have also become redistributed but remain at the surface. The removal of other capping Hs also causes similar changes in the filled state STM, i.e. it causes migration of its associated excess electrons to the bulk and the redistribution of excess electrons that are associated with the nearby OH$_b$/OH$_b$ pair along the same O$_b$ row.
Figure 4.8: (a,f) Simultaneously recorded empty- (a) and filled- (f) state image of h-TiO$_2$(110). Beforehand, the capping H of most of the OH$_b$s originally present on the surface were removed using +3.5 V, 1 ms tip pulses, leaving five OH$_b$s and one OH$_b$ pair remaining in the imaged area. (b-e, g-j), as (a,f), following the capping H of each of the OH$_b$ species was sequentially removed using the same tip pulses. Solid circles mark the positions of the OH$_b$ species. Open circles mark those of the OH$_b$ pairs. Arrows indicate the capping H that was removed in each frame. All images were recorded at 6.6 K. (k-n) Difference images formed by subtraction of the filled state images obtained before from that after the removal of each capping H. Scan parameters: (a-e) $V_s = +2$ V, $I_t = 30$ pA and (f-j) $V_s = -2$ V, $I_t = 1$ pA. High frequency noise was removed from the STM images via use of a FFT filter.
We also investigated how the distribution of the OH\(_b\)-pair associated excess electrons varies upon the sequential removal of both of its capping Hs. The results are shown in the STM images in Figure 4.9. In the filled state (Figure 4.9d), the OH\(_b\) pair (Figure 4.9a) is characterised by three lobes. As seen in Figure 4.8, the loss associated with each hydroxyl was not the characteristic four lobes seen earlier for isolated hydroxyls and therefore it can be interpreted that neighbouring hydroxyls influence the distribution of associated excess electrons. As hydroxyls become more isolated as surrounding hydroxyls are pulsed, the lobes are seen to begin to take more identifiable forms again. After the capping H at the bottom part of the OH\(_b\) pair is removed (Figure 4.9b), the lobes became dimmer and dissipate away from the position of the OH\(_b\) pair. This indicates that after the OH\(_b\) pair is converted to a single OH\(_b\), the distribution of the OH\(_b\)-pair associating excess electrons becomes decentralised from the resultant OH\(_b\). This suggests that the OH\(_b\)s are weaker as charge traps compared to OH\(_b\) pairs. By removing the remaining capping H (Figure 4.9c), the lobes that were originally present in the filled state (Figure 4.9e) disappear (Figure 4.9f) and the intensities along the Ti rows next to the OH\(_b\) pair become more uniform. This means that after all the capping Hs are removed, the OH\(_b\)-pair associating electrons are no longer confined around a particular position at the surface. Rather, they either redistribute along the same Ti rows, or migrate into the subsurface region.
Figure 4.9: (a,d) Simultaneously recorded empty- (a) and filled- (d) state image of a TiO$_2$(110) surface containing one single OH$_b$ and one OH$_b$ pair. (b-c), as (a), after the capping Hs inside the OH$_b$ pair were sequentially removed using +2.6 V, 200 ms tip pulses. Solid circles mark the OH$_b$, open circles mark the OH$_b$ within the OH$_b$ pairs. Arrows indicate the capping H that was removed in each frame. (d-f) The corresponding filled-state images of (a-c) respectively. All images were recorded at 6.6 K. (g-h) Difference images formed by subtraction of the filled state images obtained before and after the removal of each capping H inside the OH$_b$ pair. Scan parameters: (a-c) $V_s = +2$ V, $I_t = 30$ pA and (d-f) $V_s = -2$ V, $I_t = 1$ pA. High frequency noise was removed from the STM images via use of a low-pass FFT filter.
4.4 SUMMARY

Employing simultaneously recorded empty- and filled state imaging in STM, we investigated the spatial distribution of the OH$_b$ associating excess electrons on rutile TiO$_2$(110). We found that the distribution of the OH$_b$ bound excess electrons retained a symmetric, four-lobe structure at 6.6 K, similar to that observed at 78 K. This suggests that OH$_b$s are weaker as charge traps compared O$_b$-vacs, with their associated excess electrons requiring less energy to overcome the barrier to hop between Ti sites surrounding the OH$_b$ at low temperature. Also, using voltage pulses in STM, we removed the capping H of each of the OH$_b$s in a sequential manner and monitored the changes in the image contrast in the filled-state STM. We discovered that every capping H removal is accompanied by the disappearance of some filled state contrast surrounding the removed capping H, which suggests that each OH$_b$ contains one excess electron.

Comparing the results presented here with the earlier studies by Zhang et al., we see no asymmetry in the hydroxyl pair, which would suggest this is not the reason behind the inequivalent geminate OH groups. However, Li et al. suggests that there is a rapid equivalence between geminate OH groups, which agree with our studies here.$^{30}$
4.5 REFERENCES


Chapter 5

INVESTIGATING THE (√3 x √3) RECONSTRUCTION OF CeO₂(111)

Abstract

Using high resolution electron energy loss spectroscopy (HREELS), we investigated the vibrational structure of a series of CeOₓ films grown on a Pt(111) substrate. Two thicknesses of ceria, 2 and 5 MLE, were grown by post oxidation of Pt/Ce surface alloys and investigated in both their oxidised and reduced form. The oxidised forms of both films exhibit similar vibrational fingerprints, which are in good agreement with previous bulk studies. The reduced 5 MLE CeO₂ₓ film is shown to be a mix of Ce₂O₃(0001) and CeO₂(111) with a 9/4 (√3 x √3)R30° periodicity seen in LEED associated with oxygen vacancies. Investigating the reduced 2 MLE CeO₂ₓ, we observed the (√3 x √3)R30° periodicity by LEED. This was seen to degrade during exposure to the electron beam. By comparing electron beam exposed areas to fresh areas, peaks in good agreement with a Ce-O double bond vibration were observed. This suggests a Ce-O double bond terminated surface for the reconstruction.
5.1 INTRODUCTION

Ceria is known as one of the most important catalysts used in many modern technologies. Processes where ceria demonstrates important catalytic behaviour include three-way catalysis and fluid catalytic cracking amongst others\(^1\text{"10}\). However, it is its application within the low-temperature water-gas-shift (WGS) reaction that merits the attention it has gained\(^1\text{"13}\). Here, it produces a source of hydrogen by catalysing the reaction between \(\text{H}_2\text{O}\) and \(\text{CO}\) as shown in Equation 5.1:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 .
\]

What distinguishes ceria from other catalysts presently used in the WGS reaction is its stability and ability to operate at temperatures low enough for commercialisation\(^1\text{"16}\).

Ceria has been shown to be a good catalyst support due to the ease of oxygen vacancy formation leading to an excellent oxygen storage capacity (OSC), along with its ability to readily convert between the \(\text{Ce}^{3+}\) and \(\text{Ce}^{4+}\) oxidative states\(^1\text{"18}\). These properties are interconnected as each oxygen vacancy that forms leaves electrons that localise on unoccupied f-states\(^1\text{"20}\). For every neutral oxygen atom removed, there are two \(\text{Ce}^{4+}\) that are reduced to \(\text{Ce}^{3+}\). This reduction proceeds from ceria existing as stoichiometric \(\text{CeO}_2\) with \(\text{Ce}^{4+}\) until it is completely reduced with all the cerium existing as \(\text{Ce}^{3+}\). In this complete reduced state, ceria exists as \(\text{Ce}_2\text{O}_3\) (Equation 5.2)\(^2\text{"1}\):
\[
\text{CeO}_2 \rightleftharpoons \text{CeO}_{2-x} + \frac{x}{2}\text{O}_2 \rightleftharpoons \text{Ce}_2\text{O}_3.
\] (5.2)

As defects and reconstructions of many oxides, including transition metals and rare-earth oxides, are known to be crucial to their reactive behaviour, it is imperative to understand their surface structure. Nolan et al. and Paier et al. both calculated the formation energy of oxygen vacancies on the surface compared to the bulk\textsuperscript{22,23}. In their studies, they concluded that surface vacancies are more stable than their bulk counterpart. This leads to the conclusion that surfaces are highly influential on the reactions that involve the exchange of oxygen.

Bulk CeO\(_2\) exists in the fluorite structure. The (111) surface has been seen to be the most thermodynamically stable surface of the low index faces, thus it has gained the most attention\textsuperscript{22,24}. CeO\(_2\)(111) has a trilayer structure\textsuperscript{21} (Figure 5.1), where each trilayer is defined as \(\text{O}^2^-\) - Ce\(^{4+}\) - \(\text{O}^2^-\). Whilst each plane within the trilayer is charged, the overall trilayer has no net dipole moment perpendicular to the surface due to the symmetrical configuration\textsuperscript{25}.

![Figure 5.1: Ball and stick model of CeO\(_2\), highlighting the trilayer structure. Cerium and oxygen ions are coloured blue and red respectively.](image)

\[0.31\text{nm}[111]\]

\[\text{One Trilayer}\]

[111]
Stoichiometric bulk ceria exhibits a large band-gap, which prevents many surface science techniques from being utilised\textsuperscript{26,27}. In order to probe ceria’s surface, ultra-thin films grown on a metal support have been extensively studied. Numerous metals have been used for a support including Rh(111)\textsuperscript{28–30}, Ru(0001)\textsuperscript{31–33}, Cu(111)\textsuperscript{34–36}, and Pt(111)\textsuperscript{37–39}. These studies have shown that the properties of bulk ceria which influence its activity in catalysis, such as oxygen vacancies, are also present in ceria ultra-thin films.

\subsection*{5.1.1 (\sqrt{3} \times \sqrt{3}) R30° Ceria}

Whilst studying a 2 MLE ceria thin film, Hyun-Jin et al. saw some discrepancies in the atomic spacing expected of CeO$_2$(111)-(1 x 1) thin films (Figure 5.2)\textsuperscript{40}. Figure 5.2a shows a typical 200 x 200 nm area with ceria islands grown on a Pt(111) substrate. Here, we see circular islands with larger and smaller islands intermixed. A histogram of island heights can be collated by taking representative line profiles of each island (Figure 5.2d). An average island height of 2.72 ± 0.25 nm is observed with islands between 2.6 and 2.7 nm being the most common. A zoomed in view of one of the islands is shown in Figure 5.2b-c. This allows a line profile of the oxygen-oxygen atomic distance to be taken (Figure 5.2e). By averaging over multiple bond lengths, we see an average oxygen-oxygen distance of 0.59 ± 0.03 nm.
Figure 5.2: STM images of ultra-thin CeO$_2$(111)-(\(\sqrt{3} \times \sqrt{3}\))R30° films prepared by post oxidation of Pt$_x$Ce surface alloys. The images were taken at 78 K. (a) large area filled state STM image of ceria islands grown on a Pt(111) substrate (200 x 200 nm$^2$, $V_s = -4.4$ V, 10 pA). (b) A representative filled state STM image of an atomically resolved island (25 x 25 nm$^2$, $V_s = -4.4$ V, $I_t = 10$ pA). (c) Zoomed in image of (b) of the atomically resolved reconstructed surface. (15 x 15 nm$^2$, $V_s = -4.4$ V, $I_t = 10$ pA). (d) Histogram taken of the average island heights across image (a) with a bin width of 0.1 nm. (e) Line profile indicating the inter-atomic distance between the terminating oxygen corresponding to the white line in (c). STM images are reproduced with permission from Reference 40.

In comparison, Figure 5.3a shows typical islands expected of a 2 MLE CeO$_2$(111)-(1 x 1) thin film. Here, the islands are observed to be more elongated compared to those observed in Figure 5.2a. Whilst these images were typical of the films across the platinum substrate, this is still a small sample of individual films. The island heights were collated and presented as a histogram as before (Figure 5.3d). Here, we can see an average island height of 1.08 ± 0.15 nm. An average oxygen-oxygen bond distance of 0.34 ± 0.03 nm is observed by zooming in on one of the islands (Figure 5.3b-c) and taking a line profile. This agrees with literature values for
the (1 x 1) surface\textsuperscript{21,41}. Comparisons of the two bond distances shows the first film can be denoted as a ($\sqrt{3} \times \sqrt{3}$) reconstruction of ceria.

Upon analysis of the ($\sqrt{3} \times \sqrt{3}$) reconstruction using low-energy electron diffraction (LEED) (Figure 5.4), the reconstruction is seen to be rotated with respect to the Pt(111) substrate by 30°. It is also time-dependent as it was seen to disappear and degrade upon low-energy electron bombardment. By moving the sample, the reconstruction can again be observed.

Figure 5.3: STM images of ultra-thin CeO$_2$(111)-(1 x 1) films prepared by post oxidation of Pt, Ce surface alloys. The images were taken at 78 K. (a) large area filled state STM image of ceria islands grown on a Pt(111) substrate (200 x 200 nm$^2$, $V_s = -2.5$ V, 20 pA). (b) A representative filled state STM image of an atomically resolved island (30 x 30 nm$^2$, $V_s = -4.4$ V, $I_t = 20$ pA). (c) Zoom of the atomically resolved reconstructed surface. (4 x 6 nm$^2$, $V_s = -4.4$ V, $I_t = 20$ pA). (d) Histogram taken of the average island heights across image (a) with a bin width of 0.05 nm. (e) Line profile indicating the inter-atomic distance between the terminating oxygen corresponding to the white line in (c). STM images are reproduced with permission from Reference\textsuperscript{40}. 
Figure 5.4: Low energy electron diffraction pattern of a ceria ultra-thin film grown on a Pt(111) substrate. Sharp spots from the Pt(111)-\(1 \times 1\) and CeO\(_2\)(111)-\(1.37 \times 1.37\) are highlighted by green and blue respectively. Additional spots from the CeO\(_2\)(111)-\(2.37 \times 2.37\)R\(30^\circ\) reconstruction, \((\sqrt{3} \times \sqrt{3})R30^\circ\) relative to the CeO\(_2\)(111)-\(1 \times 1\)), periodicity are highlighted by red circles. LEED image was reproduced with permission from Reference\(^{40}\).

Figure 5.5: (a) Filled state and (b) empty state images of the CeO\(_2\)(111)-\(\sqrt{3} \times \sqrt{3}\) reconstruction obtained quasi-simultaneously. The images were taken at 78 K. Scan parameters: (a) \(V_s = -4\) V, \(I_T = 30\) pA, and (b) \(V_s = +1.7\) V, \(I_T = 30\) pA. (c) Marked images highlighting the oxygen ions and oxygen vacancy locations. (d) Marked images highlighting the cerium ions and cerium vacancy locations. (e) Model of top layer oxygen ions and oxygen vacancies superimposed over the second layer cerium ions. Oxygen ions and vacancies shown as blue closed and open circles respectively. Cerium ions and vacancies are shown as red closed circles and green open circles respectively. STM images are reproduced with permission from Reference\(^{40}\).
Figure 5.5 shows filled- (Figure 5.5a) and empty- (Figure 5.5b) state images of the CeO$_2$(111)-($\sqrt{3} \times \sqrt{3}$) reconstruction. Filled state images are taken by holding the sample at a negative bias relative to the tip during scanning. As such, the bright protrusions observed are assigned as the terminating layer of oxygen, which are expected to be the dominant contributions from O 2p orbitals at the high biases used$^{18}$. Empty state images are taken by holding the sample at a positive bias relative to the tip. Here we can assume that the Ce$^{4+}$ cations provide the majority of empty states and are assigned to the bright protrusions. Marking the positions of the ions and their respective vacancies (Figure 5.5c-d) and then overlaying the oxygens over the cerium lattice allows us to see how the two topmost layers interact. We can observe that the position of defects in filled- and empty- state images almost coincide with each other, that is an oxygen vacancy occurs at the same place as a cerium vacancy.

This is not the first report of a CeO$_2$(111)-($\sqrt{3} \times \sqrt{3}$)R$30^\circ$. Olbrich et al. observed the reconstruction whilst growing thin films on top of a Si(111) substrate$^{42}$. They also observed the reconstruction to co-exist with the (1 x 1) surface termination, allowing for easy identification. Upon annealing, the reconstruction was seen to convert to the (1 x 1) surface. The ($\sqrt{3} \times \sqrt{3}$) periodicity is proposed to originate from three oxygen vacancies. Two oxygen vacancies are proposed in the surface trilayer and one in the third trilayer from the surface. One important factor is the oxygen vacancies in the first trilayer are all located in the subsurface plane of oxygen and none are seen in the terminating oxygen plane. This leads to a stoichiometry of Ce$_3$O$_5$ for their predicted model. Calculations using density functional theory performed by Murgida et al. saw
that the proposed Ce$_3$O$_5$ proposed structure is not a stable bulk phase\textsuperscript{43}. However, they predicted its stability could increase as a thin film near the surface.

Lustemberg et al. reported a $\sqrt{3}$-reconstructed CeO$_{2-x}$(111) ultra-thin film grown on Pt(111)\textsuperscript{44}. They observed that Au adsorption on the surface is governed by kinetics. The Au following a diabatic path as it undergoes diffusion towards the oxygen vacancies, which the occupancy is thermodynamically preferred. However, they did not propose a model for the reconstruction.

In this study, by growing multiple ultra-thin ceria films on a Pt(111) substrate, we aim to gain insight into the bonding structure of the newly discovered reconstruction. This will be approached by comparing both oxidised and reduced films of CeO$_{2-x}$ and probing the surface structures by high resolution electron energy loss spectroscopy (HREELS) with the use of LEED to distinguish reconstructions.

\section*{5.2 Experimental Procedure}

The HREELS experiments were carried out using a VSW HREELS system housed in a UHV chamber with a base pressure of 3 x 10$^{-10}$ mbar at room temperature (see Chapter 3). The UHV chamber was equipped with a monochromator and analyser used for HREELS analysis, along with an ion sputter gun, sample heater, quadrupole mass spectrometer, metal deposition sources and facilities for AES and LEED analysis. HREELS measurements were carried out in the specular geometry. An incident electron energy of 10 eV was used during HREELS measurements. Each spectrum was collected at 300 K, with a dwell time of 0.1 s, step size of 0.5 meV and were produced by averaging a minimum of 50 individual scans. To ensure no degradation of the film
was occurring, a single scan was collected before collecting the averaged scans to allow comparison. Spectra are normalised to the elastic peak.

A Pt(111) substrate was prepared by successive cycles of Ar⁺ sputtering (1.5 keV) and annealing at 1100 K in UHV. Sample cleanliness was confirmed by observing a well-ordered LEED pattern for Pt(111)-(1 x 1) with no impurities detected using AES. In order to facilitate the removal of carbon and embedded impurities, occasional cycles of annealing were performed at ~1000 K in 1 x 10⁻⁷ mbar O₂. The ceria ultra-thin film was prepared using a post-oxidative process by first evaporating cerium metal (Alfa Aesar, 99.9%) via physical vapour deposition onto the clean Pt(111) substrate at 300 K from an electron-bombardment type evaporator. The metal was then subsequently annealed, at 1000 K, in a partial pressure of up to 5 x 10⁻⁶ mbar O₂ for an oxidised sample and up to 1 x 10⁻⁷ mbar O₂ when studying reduced oxygen conditions for 20 mins. The sample is then allowed to cool for 10 to 20 minutes in the same partial pressure of O₂. This method yielded well-ordered films of CeO₂(111)-(1x1) in the oxidised conditions. The temperatures were monitored using a Minolta infrared pyrometer alongside a type K thermocouple.

In this work, one ceria monolayer (ML) is defined as one O–Ce–O trilayer unit with a thickness of 0.31 nm. As the Ceria film exhibits a Volmer-Weber growth, film thickness is presented in monolayer equivalent (MLE), where the coverage is estimated from the island thickness and the surface area fraction measured by STM.
Chapter 5: Investigating the ($\sqrt{3} \times \sqrt{3}$) Reconstruction of CeO$_2$(111)

5.3 RESULTS AND DISCUSSION

5.3.1 PROPOSED MODEL

Models of the (1 x 1) and the ($\sqrt{3} \times \sqrt{3}$) surfaces, constructed from the STM observations, are shown in Figures 5.6 and 5.7 respectively. Each plane of the trilayer is seen to be equivalent within the (1 x 1) surface (Figure 5.6a-c). Superimposing the top two planes of the trilayer (Figure 5.6d) shows each cerium ion is visible and offset from the terminating oxygen plane above. When we include the third plane of the trilayer (Figure 5.6e), the sub-surface oxygens are all visible when using a reduced space-filling model. This highlights the fact that each plane is offset from the remaining two planes of the trilayer.

In comparison, the three planes which build the trilayer within the ($\sqrt{3} \times \sqrt{3}$) reconstruction (Figure 5.7a-c) are each shown to be different in their complexion. The third sub-surface plane of oxygen is assumed to be the same as for the (1 x 1) surface. The cerium ion plane is observed to occupy only 2/3 of the sites with respect to the (1 x 1) surface. The topmost terminating oxygen plane is seen to occupy only 1/3 of sites in comparison to the (1 x 1) surface. Superimposing the top two planes of the trilayer (Figure 5.7d) shows that the terminating oxygen plane now resides on top of 1/2 of the cerium ions. This creates two types of Ce coordination. One coordination of Ce ions is exposed without a capping oxygen ion, with the other coordination underneath a capping oxygen. Using the assumption that the third layer is undisturbed, the stoichiometry can be calculated as:

\[
\text{O}_{1/3} + \text{Ce}_{2/3} + \text{O}_{1} \rightarrow \text{Ce}_{2/3}\text{O}_{4/3} = \text{CeO}_2. \\
(1\text{st \ Layer}) \quad (2\text{nd \ Layer}) \quad (3\text{rd \ Layer})
\]
Chapter 5: Investigating the \( (\sqrt{3} \times \sqrt{3}) \) Reconstruction of CeO\(_2\)\(\{111\}\)

Figure 5.6: Model showing the surface trilayer of the \( 1 \times 1 \) lattice. (a) The oxygen third layer of the surface trilayer. (b) The cerium mid layer of the trilayer. (c) The oxygen topmost layer of the surface trilayer. (d) The topmost oxygen layer superimposed on top of the cerium lattice. (e) The complete trilayer.

Figure 5.7: Model of the proposed reconstruction. (a) The oxygen third layer of the surface trilayer. (b) The cerium mid layer of the trilayer. (c) The oxygen topmost layer of the surface trilayer. (d) The topmost oxygen layer superimposed on top of the cerium lattice. (e) The complete trilayer.
For the CeO$_2$(111)-(\(\sqrt{3} \times \sqrt{3}\))R30° reconstruction observed on Pt(111), we can predict a change in the bonding of the surface termination due to the inequivalence between the Ce ions. The proposed model here has half of the cerium ions with a capping oxygen, instead of a shared bridging oxygen between all cerium ions. This would represent a Ce-O double bond surface termination. This explains the shift in position of the terminating oxygen from being offset to the cerium ion plane below, to capping half of the Ce ions. This has previously been observed with vanadyl terminated surfaces$^{45-47}$. The corrugated atomic height seen for vanadyl terminated surfaces in STM was observed to be \(~0.5 \text{ Å}\)^47. Vanadyl has a slightly shorter bond length compared to the Ce-O double bond as seen in inorganic compounds$^{48}$. Hyun-Jin et al. observed a corrugated atomic height of \(~0.6 \text{ Å}\)^40. Comparing the terminating vanadyl stretching frequency observed with HREELS with those observed in infrared spectroscopy with inorganic compounds shows good agreement between the two methods$^{49,50}$. Cerium coordinated to oxygen via a double bond has been observed in inorganic compounds$^{51,52}$, which we can use to predict where the oxygen double bond termination on ceria would appear in HREELS. Damon et al. and So et al. observed the Ce-O double bond vibration to occur at about 740 cm$^{-1}$, the exact position depending on the chemical environment$^{48,53}$. 
Chapter 5: Investigating the $(\sqrt{3} \times \sqrt{3})$ Reconstruction of CeO$_2$(111)

5.3.2 STM

5.3.2.1 DOSER CALIBRATION

The Ce evaporator was initially calibrated using a VT-STM (see Chapter 3) in order to reproduce the 2 MLE ceria deposition that was utilised in the earlier STM work. This was to gain an understanding of the deposition rates to extrapolate dosing conditions within the HREELS chamber for films of multiple thicknesses. This was done as the dosage quantity of cerium is not only dependent on time and heating power of the source material, but also of crucible-substrate separation, which is specific to each chamber.

5.3.2.2 CLEAN PLATINUM

Figure 5.8: STM images of the Pt(111) substrate at different stages of cleanliness. The images were taken at 300 K. (a) Empty state STM image of the Pt(111) substrate showing some residual impurities (150 x 300 nm$^2$, $V_s = +1.0$ V, $I_t = 0.1$ nA). (b) Empty state STM image of the Pt(111) substrate after additional cleaning (200 x 200 nm$^2$, $V_s = +1.2$ V, $I_t = 0.1$ nA). (c) Large scale empty state STM image of the Pt(111) substrate after additional cleaning highlighting another area of the crystal (500 x 500 nm$^2$, $V_s = +1.0$ V, $I_t = 0.1$ nA).
Figure 5.8 shows the Pt(111) substrate at varying degrees of cleanliness. The number of visible adsorbates/impurities on the surface is reduced as the substrate undergoes further sputter-anneal cleaning cycles (Figure 5.8a-b). This was continued until atomically flat (111) terraces separated by well-defined monoatomic steps of 0.23 ± 0.01 nm were formed (Figure 5.8b-c). Defects, such as screw dislocations, are visible in the clean Pt(111), which appear as an abrupt termination of a step edge as a terrace splits into multiple terraces. The step edges have been seen to act as preferential nucleation sites for ceria island to grow.

A typical low-energy electron diffraction (LEED) pattern from the clean Pt(111) substrate (Figure 5.9) shows a low background with sharp reflexes from the Pt(111)-(1 x 1) surface. This is complemented with Auger electron spectroscopy (Figure 5.10), which was used to ensure the cleanliness of the substrate. The spectrum is plotted in derivative mode using RFA detection and shows the Pt LMM peak groups.

![LEED pattern](image)

Figure 5.9: LEED diffraction pattern of the clean Pt(111) substrate acquired at 45.6 eV. Sharp spots from the Pt(111)-(1 x 1) are highlighted by green circles.
Chapter 5: Investigating the ($\sqrt{3} \times \sqrt{3}$) Reconstruction of CeO$_2$(111)

Figure 5.10: Derivative Auger electron spectrum of the clean Pt(111) substrate

5.3.2.3 Replicating Islands Heights on STM

Figure 5.11: STM images of ultra-thin CeO$_2$(111) films prepared by post oxidation of Pt$_x$Ce surface alloys. The images were taken at 300 K. (a) 300 x 300 nm STM image of a CeO$_2$(111) film grown on a Pt(111) substrate using a post-oxidation method after 3.5 minute deposition of cerium and then annealed at 1000 K in 1 x 10$^{-7}$ mbar oxygen. (b) Further annealed in oxygen 5 x 10$^{-7}$ mbar oxygen. Histograms for the island heights are shown on the right. Scan parameters: $V_s = -3.4$ V, $I_t = 0.1$ nm.
As described in the experimental section of this chapter, the ceria films were grown using post-oxidative method compared to reactive deposition methods. As each chamber’s geometry is unique and sample-doser distance varies, this has an impact on evaporation time in order to replicate results. Due to poor signal-to-noise ratio of the Pt peaks observed with AES in this work, AES cannot be used to determine the coverage of the thin films by measuring the attenuation of the substrate peak\(^{54}\).

An Omicron VT-STM (see Chapter 3) was used to image ceria islands grown across a series of deposition times to extrapolate the condition for films of multiple thicknesses. Here, the sample-doser distance within the HREELS chamber was positioned to \(\pm 0.1\) cm compared to the VT-STM, which allows comparable results. Figure 5.11 shows an ultra-thin film of CeO\(_2\)(111) grown on a Pt(111) substrate with a calculated 2 MLE thickness. The film initially grown in \(1 \times 10^{-7}\) mbar oxygen (Figure 5.11a) shows more rounded islands with a range of smaller and larger islands. Here we can see a range of heights spanning from 1.2 nm up to 4.0 nm in height, with a favourability towards lower islands. Hyun-Jin et al. observed that the reconstructed terminated islands were taller in height than the (1 x 1) terminated islands\(^{40}\). The wide span of heights observed in the STM (Figure 5.11a) suggests a mix of both reconstructed and (1 x 1) terminated surfaces. The absolute heights can vary due to how stepped the substrate surface in the analysed area is, which makes direct comparisons impractical. We see the islands become more uniform upon further annealing in \(5 \times 10^{-7}\) mbar oxygen (Figure 5.11b), and the island heights favour the lower height species showing similar trends to the earlier studies. This occurs as the islands tend towards (1 x 1) termination in more oxidising conditions.
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5.3.3 HREELS

5.3.3.1 DATA ANALYSIS

Figure 5.12: Derivative Auger electron spectrum of a CeO$_2$(111) film grown on a Pt(111) substrate.

Figure 5.13: Raw (black curve) and Fourier deconvoluted (blue curve) HREEL spectra of a 10±2 MLE ceria thin film. Primary and multiple phonon loss peaks have been marked on the spectra. Spectra were collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 70 cm$^{-1}$. 
To monitor the cleanliness of the ceria film grown within the HREELS chamber, a thick film (10±2 MLE) was grown by post oxidation of a Pt₅Ce alloy in 1 x 10⁻⁶ mbar oxygen. This is achieved by depositing cerium onto the platinum substrate, forming an alloy, which is then subsequently annealed in oxygen. This was to check for impurities from the cerium source material along with the chamber environment. Auger electron spectroscopy was employed to check the purity of the sample (Figure 5.12) and no impurities were observed. The HREEL spectrum of the 10±2 MLE CeO₂(111) film (Figure 5.13) shows significant loss features at 564, 1128 and 1684 cm⁻¹. The elastic peak is shown at 0 cm⁻¹ along with an anti-Stokes energy gain peak at -549 cm⁻¹. The loss at 564 cm⁻¹ arises from the interaction of the incident electron with the surface optical (SO) phonon mode of CeO₂(111). The remaining loss features, 1128 and 1684 cm⁻¹, are assigned to multiple scattering events, appearing as multiple integers of the primary SO phonon loss. A shoulder appears on each loss peak at a lower loss energy. For the primary SO phonon loss, this shoulder is found at 400 cm⁻¹. This has been assigned to the interface phonon agreeing with previous HREELS studies on CeO₂. The features seen in this spectrum are consistent with previous studies of ceria single crystals along with comparison to the dielectric function of CeO₂, which predicts a single surface optical phonon. Due to the dominance of phonon losses within the lower energy region, Fourier deconvolution can be employed to remove multiple phonon losses. This allows hidden vibrational features to be more easily identified. The spectrum of the ceria film before and after deconvolution is shown in Figure 5.13. As can be seen, the multiple scattering losses are removed from the spectra, leaving just the primary loss feature at 564 cm⁻¹.
One unexplained feature present in the deconvoluted spectrum is seen at 3139 cm\(^{-1}\). Here, a negative intensity loss is observed. Previous work using Fourier deconvolution have observed discrepancies within the deconvolution process due to an over/under-estimation of multiple scattering events arising from a divergence from a Poisson distribution. This has been seen in cases of deviation in the path geometry as the sample is probed off-specular, which results in imperfect tuning of the spectrometer and also from enhancements in the scattering cross-section due to temporary negative ion resonance states\(^{59-61}\). For the predicted structure of the reconstructed surface, the vibration of the double bond is expected to be located close to the primary phonon loss region. This makes Fourier deconvolution impractical for the work presented here. Another method commonly used is background subtraction\(^{62}\). This method is commonly utilised when it is necessary to remove peaks arising from environmental conditions that are reproducible across multiple spectra. As HREELS is performed in UHV, there is an even environment across each measured spectrum. Spectra of films in different oxidative conditions can be subtracted from each other by normalising the elastic peaks and evaporating equivalent amounts of cerium. This allows easy observation of any differences and identification of new loss features.
5.3.3.2 CLEAN PLATINUM

Figure 5.14: Raw HREEL spectrum taken of clean Pt(111) after multiple cleaning cycles until AES confirmed no contamination. Magnified view of the 0 – 3000 cm\(^{-1}\) region is included to highlight the loss peaks. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The FWHM of the elastic peak was measured as 150 cm\(^{-1}\).

The Pt(111) substrate was cleaned using multiple sputter and anneal cycles. The sample was heated up to 1100 K, alternating between a UHV and a partial pressure of 1 x 10\(^{-7}\) mbar oxygen environment. The sample’s cleanliness was confirmed using AES to the level presented in Section 5.3.2.1 and LEED was used to confirm good long-range order and no additional spots, which would indicate a presence of additional phases. A HREEL spectrum was collected (Figure 5.14) to confirm the cleanliness since Pt(111) should exhibit a featureless spectrum. However, a loss feature at 1113 cm\(^{-1}\) is observed to occur. This is likely due to embedded cerium being constantly pulled to the surface and alloying with the Pt after each cleaning cycle. Previous ultra-thin film growth methods which observed the CeO\(_2\)(111)-(\(\sqrt{3} \times \sqrt{3}\))R30° reconstruction used AES as an indicator for cleanliness. As the cerium levels are below the amount which can be detected in AES, the trace amount of cerium observed in HREELS can be assumed to have no negative impact on the ability to form
Chapter 5: Investigating the \((\sqrt{3} \times \sqrt{3})\) Reconstruction of CeO\(_2\)(111)

The reconstruction. Upon leaving the sample in the chamber for an hour with a partial pressure of \(1 \times 10^{-8}\) mbar carbon monoxide, equivalent to a 38 L dose of CO, two additional losses at 1827 and 2100 cm\(^{-1}\) were observed (Figure 5.15). These are consistent with previous reflection absorption infrared spectroscopy (RAIRS) studies on CO/Pt(111) and can be assigned to the CO-Pt(111) twofold bridging and CO-Pt(111) atop stretching frequencies respectively\(^{63,64}\). This confirms our calibration of the HREELS analyser and allows us to assign these peaks from any background CO remaining in the partial pressure of the vacuum chamber.

![Figure 5.15: Raw HREEL spectrum taken of clean Pt(111) after being left in a background pressure of \(1 \times 10^{-8}\) mbar CO for an hour. Magnified view of the 0–3000 cm\(^{-1}\) region is included to highlight the loss peaks. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The FWHM of the elastic peak was measured as 110 cm\(^{-1}\).](image-url)
5.3.3.3 **Ceria films – 5 MLE**

5.3.3.3.1 **(1 x 1) Surface Film**

A 5±1 MLE CeO$_2$(111)-(1 x 1) ultra-thin film was grown by post oxidation in 1 x $10^{-6}$ mbar oxygen. The formation of a well-ordered (1 x 1) film was confirmed using LEED (Figure 5.16). The LEED pattern displayed a low background and sharp reflexes associated with the Pt(111)-(1 x 1) substrate and the CeO$_2$(111)-(1.37 x 1.37) film. Whilst the CeO$_2$(111) is expected at (1.4 x 1.4) with respect to the Pt(111) substrate according to its single crystal parameters, the 1:1.37 ratio arises from the lattice mismatch between the CeO$_2$(111) film and the Pt(111) substrate$^{65}$. The HREEL spectrum of the CeO$_2$(111)-(1 x 1) film (Figure 5.17) shows significant loss features at 571, 1135 and 1655 cm$^{-1}$. The elastic peak is shown at 0 cm$^{-1}$ along with an anti-Stokes energy gain peak at -549 cm$^{-1}$. This agrees with the thicker film and shows no changes as the cerium coverage is halved. The loss at 571 cm$^{-1}$ arises from the interaction of the incident electron with the surface optical phonon mode of CeO$_2$(111). The remaining loss features, 1135 and 1655 cm$^{-1}$, are assigned to multiple scattering events as they appear at multiple integers of the SO phonon. A shoulder at a lower energy loss to the surface optical phonon, assigned to the interface phonon, is also observed$^{56}$. The second multiple scattering loss located at 1655 cm$^{-1}$ is shifted from its expected position at 1713 cm$^{-1}$. This is due to multiple combination losses occurring more frequently at higher energies, broadening the peaks.
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Figure 5.16: Low energy electron diffraction pattern of a 5±1 MLE CeO$_2$(111)-(1 x 1) ultra-thin film grown on a Pt(111) substrate acquired at 44.2 eV. Sharp spots from the Pt(111)-(1 x 1) and CeO$_2$(111)-(1.37 x 1.37) are highlighted by green and blue circles respectively.

Figure 5.17: Raw HREEL spectrum of a 5±1 MLE CeO$_2$(111)-(1 x 1) thin film. Primary and multiple phonon loss peaks have been marked on the spectrum along with the energy gain peak. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 120 cm$^{-1}$. 
5.3.3.3.2 Reduced Film

Figure 5.18: Low energy electron diffraction pattern of a 5±1 MLE ceria ultra-thin film grown in reduced oxygen conditions on a Pt(111) substrate acquired at 46.6 eV. Sharp spots from the Pt(111)-(1 x 1) are highlighted by green circles and the spots from CeO$_2$-(1.37 x 1.37) are highlighted by blue. A (9/4 (√3 x √3)R30° periodicity) is also observed, highlighted by red circles, which arises from oxygen vacancies at the surface.

Figure 5.19: Raw HREEL spectrum of a 5±1 MLE ceria thin film grown in reduced oxygen conditions. Primary phonon loss peaks have been marked on the spectrum. Magnified view of the 100 – 1200 cm$^{-1}$ region is shown to highlight the loss peaks overlaid with the results of the gaussian peak fitting. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 110 cm$^{-1}$. 

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We see a change in the LEED pattern observed when we reduce the film by annealing the film in $1 \times 10^{-7}$ mbar oxygen (Figure 5.18). The LEED pattern displays a low background and sharp reflexes associated with the Pt(111)-(1 x 1) substrate (denoted by green circles) and the CeO$_2$-$x$(1.37 x 1.37) film (denoted by blue circles) along with a $9/4 \left(\sqrt{3} \times \sqrt{3}\right)R30^\circ$ periodicity (denoted by red circles). Luches et al. observed the $9/4 \left(\sqrt{3} \times \sqrt{3}\right)R30^\circ$ periodicity alongside a (3 x 3) periodicity for Ce$^{3+}$ concentrations of 40%$^{66}$. Upon further annealing, they observed the (3 x 3) periodicity to disappear and only the $9/4 \left(\sqrt{3} \times \sqrt{3}\right)R30^\circ$ periodicity to remain. Here, the Ce$^{3+}$ concentration was between 60 and 80%. The Ce$^{3+}$ concentration, an indication of the reduction amount, is explained by different oxygen vacancy concentrations, which order giving rise to the (3 x 3) and $9/4 \left(\sqrt{3} \times \sqrt{3}\right)R30^\circ$ periodicities. One reduced ceria phase is the c-Ce$_2$O$_3$. This would result in a (4 x 4) superstructure on the surface, which is not observed. The other reduced phase is the h-Ce$_2$O$_3$(0001), which gives rise to a hexagonal diffraction pattern exhibiting a 2% contraction to the CeO$_2$(111)-(1 x 1) periodicity. This makes it very difficult to distinguish between h-Ce$_2$O$_3$(0001) and CeO$_2$(111)-(1x1) in LEED.

The HREEL spectrum of the ceria film (Figure 5.19) shows 5 loss features at 169 ($\nu_1$), 321($\nu_2$), 442($\nu_3$), 565($\nu_4$) and 758($\nu_5$) cm$^{-1}$, which are located using the Multi-peak fitting 2.0 program in Igor Pro. Here, the program was instructed to find the best fit for a series of Gaussian peaks using a chi-square minimization procedure by subtracting the clean platinum HREEL spectrum as a background. As no (4 x 4) superstructure was observed in the LEED pattern (Figure 5.18), we can rule out the presence of a c-Ce$_2$O$_3$ reconstruction. In order to confirm presence of a h-Ce$_2$O$_3$(0001)
reconstruction, a comparison to the similarly structured h-Cr$_2$O$_3$ can be made. Cr$_2$O$_3$ shows peaks at 173, 417, 634 and 714 cm$^{-1}$, along with a peak at 323 cm$^{-1}$ at higher CO coverages$^{67,68}$. The most intense peak observed in Cr$_2$O$_3$ is the 714 cm$^{-1}$ loss which was assigned as a Fuchs-Kliewer phonon along with the 417 and 634 cm$^{-1}$ losses. The 442 and 758 cm$^{-1}$ loss peaks in the reduced ceria can be assigned to their equivalent Fuchs-Kliewer phonon modes. The peak seen at 634 cm$^{-1}$ for Cr$_2$O$_3$ is weaker than the other two Fuchs-Kliewer phonon modes observed and therefore an expected peak for the ceria film maybe unresolved$^{67}$. The loss at 173 cm$^{-1}$ on Cr$_2$O$_3$ was assigned as a surface vibration phonon as it was attenuated with increasing CO coverage. The remaining loss at 323 cm$^{-1}$, which was only present with CO coverage, was assigned as either the CO vibration against the substrate or a counterpart of the surface vibration of the clean surface. Both peaks were equally present with low CO coverage. These can therefore be assigned to the loss peaks at 169 and 321 cm$^{-1}$ in h-Ce$_2$O$_3$. The remaining peak, 565 cm$^{-1}$, does not occur in the Cr$_2$O$_3$ HREEL spectrum. This can be seen to show a good vibrational energy match with the surface optical phonon of the CeO$_2$(111)-(1x1) film and can be assigned as such. This suggests that the film exhibits both areas of h-Ce$_2$O$_3$ alongside areas of CeO$_2$(111)-(1x1).
5.3.3.4 CERIA FILMS - 2 MLE

5.3.3.4.1 1 x 1 SURFACE FILM

Figure 5.20: Raw HREEL spectrum of a 2±1 MLE CeO$_2$(111)-(1 x 1) thin film grown on Pt(111). Primary and multiple phonon loss peaks have been marked on the spectrum. Magnified view of the 0 – 2400 cm$^{-1}$ region is shown to highlight the loss peaks overlaid with the results of the gaussian peak fitting. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 96 cm$^{-1}$.

A 2±1 MLE CeO$_2$(111)-(1 x 1) ultra-thin film film was grown by post oxidation in 1 x 10$^{-6}$ mbar oxygen. The formation of a well-ordered film was confirmed using LEED, which was the same as the LEED pattern for the 5 MLE CeO$_2$(111)-(1 x 1) thin film shown in Figure 5.16.

The HREEL spectrum of the CeO$_2$(111) film (Figure 5.20) shows significant loss features at 545 and 1124 cm$^{-1}$. The loss at 545 cm$^{-1}$ arises from the interaction of the incident electron with the surface optical phonon mode of CeO$_2$(111). The remaining loss feature at 1124 cm$^{-1}$ is assigned to a multiple scattering event as it appears at twice the vibration frequency of the SO phonon. This shows a slight shift to a lower energy loss compared to the thicker films. Two further losses can be determined by a
gaussian multi-peak fitting (Multi-peak fitting 2.0, Igor Pro), located at 423 ($v_1$) and 879 ($v_2$) cm$^{-1}$, using a chi-square minimization procedure. The loss at 423 cm$^{-1}$ is assigned to the incident electron interacting with the interface phonon$^{56}$, while the loss at 879 cm$^{-1}$ is a multiple scattering event of the interface phonon.

### 5.3.3.4.2 Reduced Phases

![Figure 5.21: Low energy electron diffraction pattern of a 2±1 MLE ceria ultra-thin film grown in reduced oxygen conditions on a Pt(111) substrate acquired at 43.4 eV. Sharp spots from the Pt(111)-(1 x 1) are highlighted by green circles and the spots arising from CeO$_2$-x(111)-(1 x 1) are highlighted by blue. The spots associated with the CeO$_2$(111)$-(\sqrt{3} \times \sqrt{3})$R30° reconstruction are highlighted by red circles. Spots associated with the Pt$_2$Ce alloy are marked by black circles.](image-url)
We see a change in the LEED pattern observed by reducing the (1 x 1) film by annealing the film in $1 \times 10^{-7}$ mbar oxygen (Figure 5.21). The LEED pattern displayed a low background and sharp reflexes associated with the Pt(111)-(1 x 1) substrate (denoted by green circles), the CeO$_2$-(111)-(1 x 1) film (denoted by blue circles), the reconstructed CeO$_2$(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface, relative to the CeO$_2$(111)-(1 x 1), (denoted by red circles) and a (2 x 2)R30° periodicity (denoted by black circles) typically associated with a Pt$_x$Ce alloy$^{69}$. The presence of the LEED pattern associated with the reconstruction was observed to degrade upon exposure to the electron beam making it difficult to capture.

The sample position for HREELS was aligned to the position used to capture the LEED image in Figure 5.21, with the resulting HREEL spectrum shown in Figure 5.22.

Figure 5.22: Raw HREEL spectrum of a reduced 2±1 MLE ceria thin film on Pt(111). The sample area has been calibrated to the area exposed to the electron beam during LEED measurements. Magnified view of the 250 – 2500 cm$^{-1}$ region is shown to highlight the loss peaks overlaid with the results of the gaussian peak fitting. Primary and multiple phonon loss peaks have been marked on the spectrum. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 109 cm$^{-1}$.
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The HREEL spectrum of the CeO\(_{2-x}\) film exposed to the electron beam for LEED analysis shows significant loss features at 571, 1057 and 2107 cm\(^{-1}\). The loss at 571 cm\(^{-1}\) arises from the interaction of the incident electron with the surface optical phonon mode of CeO\(_2\)(111)-(1 x 1) as seen previously for the thicker 5±1 MLE ceria thin film (Figure 5.17). The loss at 2107 cm\(^{-1}\) can be assigned to the CO-Pt(111) atop stretching frequency as seen earlier for the CO/Pt(111) HREELS spectra (Figure 5.15). The loss at 1057 cm\(^{-1}\) is lower in energy than the predicted multiple loss events for the SO phonon, along with having an intensity greater than previous multiple loss events. As it is quite broad, it is likely a combination of the multiple loss peaks for the SO phonon and the loss features associated with the Pt\(_x\)Ce, as observed earlier in Section 5.3.3.2.

The area being probed by HREELS was then moved by 1 mm to an area that was not exposed to electron bombardment during LEED analysis. The HREEL spectrum (Figure 5.23) of the new area of the CeO\(_{2-x}\) film shows loss features at 536 (\(\nu_1\)), 775 (\(\nu_2\)), 1014 (\(\nu_3\)), 1144 (\(\nu_4\)), 1247 (\(\nu_5\)) and 2081 (\(\nu_6\)) cm\(^{-1}\) located by use of a gaussian multi-peak fitting as previously described. The spectrum recorded from the surface exposed to the LEED beam can be used as a background to subtract, as any losses associated with the reconstruction will exhibit an increased intensity. The resulting spectrum highlighting the peaks associated with the reconstruction is shown in Figure 5.24.
Figure 5.23: Raw HREEL spectrum of a 2±1 MLE ceria thin film grown in reduced oxygen conditions on Pt(111). The sample area was moved to 1 mm above the area exposed to the electron beam during LEED measurements. Magnified view of the 250 – 2400 cm⁻¹ region is shown to highlight the loss peaks overlaid with the results of the gaussian peak fitting. Primary and multiple phonon loss peaks have been marked on the spectrum. The spectrum was collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 84 cm⁻¹.

Figure 5.24: Spectrum of the reduced film with a background subtraction of the area exposed to LEED.
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The spectrum highlighting losses associated with the reconstruction (Figure 5.24) shows two significant losses at 781 and 1257 cm\(^{-1}\). The loss at 781 cm\(^{-1}\) is in good agreement with the predicted vibration of the cerium-oxygen double bond\(^{48,53}\). The loss intensity of the CO-Pt(111) stretch (2087 cm\(^{-1}\)) and the CeO\(_2\)(111) SO phonon (541.2 cm\(^{-1}\)) are observed to have similar intensity with and without the reconstruction present. If the surface is terminated in double bonds, with two types of cerium ions, we can expect different surface optical phonons along with surface vibration phonons associated with the reconstruction. The additional loss feature observed at 1257 cm\(^{-1}\), along with the generally increase in intensity seen in regions of Figure 5.24, can be tentatively assigned to these expected losses associated with the reconstruction.

Figure 5.25: Raw HREEL spectra of a 2\(\pm\)1 MLE ceria thin film grown in reduced oxygen conditions on Pt(111) exposed to an electron beam of 50 eV (black curve), 75 eV (red curve) and 100 eV (blue curve) for 10 mins sequentially. Raw HREEL spectrum of the pre-exposed surface is also shown (green curve). Primary and multiple phonon loss peaks have been marked on the spectra. The spectra were collected in a specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 104 cm\(^{-1}\).
The area exhibiting the reconstruction was exposed to 50, 100 and 150 eV for a duration of 10 minutes each sequentially and a HREEL spectrum was taken after each exposure (Figure 5.25). The sample after being exposed to 50 eV does not exhibit any noticeable change compared to the pre-exposed area. Whilst, the energy is comparable to the energy used during LEED analysis, the flux is weaker in order to keep the beam in the same location for HREELS analysis. After the sample is exposed to 75 eV, we begin to see a reduction in the peak association with the Ce-O double bond ($\nu_3$). Upon exposure to 100 eV for 10 minutes, we see a large reduction in the Ce-O double bond loss peak. The peak tentatively assigned to additionally losses associated with the reconstruction ($\nu_6$) is also seen to exhibit a weaker intensity following exposure to 100 eV. This is concurrent with a rise in the peak associated with the CeO$_2$(111) surface phonon ($\nu_2$). All other peaks do not show any observable change.
5.4 SUMMARY

Using HREELS, we investigated multiple films of varying thicknesses of ceria grown on a Pt(111) substrate in both fully oxidising conditions along with reduced oxygen conditions. In this work, we have observed the conversion of the 5 MLE CeO$_2$(111) oxidised surface into the reduced Ce$_2$O$_3$(0001) surface by annealing in lower partial pressures of oxygen. A new reconstruction was grown on the 2 MLE thin film, which was observed under LEED. Upon exposure to the electron beam used during LEED, the pattern associated with reconstruction is seen to degrade. By comparing an area previously exposed to an electron beam to a fresh area of the sample, the vibration peaks associated with the reconstruction have been observed and are in the predicted area for a Ce-O double bond vibration. By exposing the sample to a higher energy electron beam, the reconstruction is observed to degrade back to the (1 x 1) termination, agreeing with earlier STM and LEED studies.
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5.5 REFERENCES


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Chapter 6

REDOX BEHAVIOUR OF A CERIA-ZIRCONIA INVERSE MODEL CATALYST

Abstract
The redox behaviour modification following the addition of zirconia to ceria nanostructures supported on Rh(111) has been investigated using a combination of Low Energy Electron Diffraction (LEED) and X-ray Photoemission Electron Microscopy (XPEEM). Soft X-ray irradiation was employed to reduce ZrO$_{2-x}$(111) supported on Rh(111) and, by introducing oxygen, the re-oxidation process of the thin film was monitored. CeO$_2$(111) was then deposited on zirconia/Rh(111) and, using XPEEM, we determined that the mixed metal oxide formed a phase-separated structure with CeO$_2$(111) nanoparticles on top of the zirconia. Upon exposure of CeO$_{2-x}$/ZrO$_{2-x}$/Rh(111) to X-ray illumination, the zirconia no longer undergoes any observable reduction while at the same time the ceria is reduced. Our results indicate a synergy between the zirconia and ceria in the phase-separated system expected in the working catalyst, with oxygen transfer between the metal oxides. This sheds light on the mechanism of the enhancement of catalytic properties seen with the addition of zirconia to ceria and highlights the oxygen storage and release ability of ceria.
6.1 INTRODUCTION

Ceria and ceria-based mixed metal oxides have been widely studied due to their use in applications including heterogeneous catalysis\(^1\), organic synthesis\(^2\), chemical sensing\(^3\) and fuel cells\(^4\). These applications stem from ceria’s readily available and easily interconvertible Ce\(^{3+}\) and Ce\(^{4+}\) oxidation states as well as its high oxygen storage capacity\(^1,5\). One important technological area in which ceria is employed is in three-way catalytic converters\(^6\). These are typically made up of three components, namely a noble metal such as rhodium or platinum, ceria or a ceria-based material and also a support, usually Al\(_2\)O\(_3\)\(^7\). The interaction between noble metals and ceria is also of relevance to understand its catalysis of CO oxidation in the water-gas shift (WGS) reaction. This has been studied previously on so-called inverse model catalysts, where ultra-thin films of ceria were prepared on the desired noble metal surface\(^8-13\).

The addition of zirconia to ceria leads to the formation of a mixed metal oxide, Ce\(_x\)Zr\(_{1-x}\)O\(_2\). This has been shown to enhance the catalytic performance of ceria by increasing the reducibility of the oxide. It results in a greater number of oxygen vacancies, the key component thought to be responsible for the catalytic activity\(^14\). Addition of zirconia also improves the resistance towards sintering, with the optimal composition for catalytic performance being Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)\(^15\). The mixed oxide has previously been studied experimentally by STM and XPS in conjunction with computational modelling\(^16-18\). As for ZrO\(_2\)(111), this has been studied extensively using STM, LEED and other surface sensitive techniques including resonant photoemission spectroscopy\(^19-24\).
Figure 6.1: Unit cell illustrating the fluorite structure of potential morphologies for Ce$_{0.5}$Zr$_{0.5}$O$_2$. a) Phase separated into Zr-rich and Ce-rich oxides. On the left is ZrO$_2$ and on the right is CeO$_2$. b) Mixed phase of the oxides showing Ce and Zr interspersed amongst the unit cell. On the left is a more disordered dispersion and on the right is more ordered with alternating planes of Ce and Zr. The cerium and zirconium cations are shown in red and yellow respectively and oxygen anions are displayed in blue.

The mixed metal oxide can exist as two potential morphologies (Figure 6.1). The first morphology is a phase-separated structure, which would be seen as areas of Ce-rich and Zr-rich oxides. Figure 6.1a shows the fluorite structure that both zirconia and ceria exhibit. The second morphology is an interspersed structure (Figure 6.1b). Here, we can see two potential occupancies. One is seen to be more disordered in the occupancy (Figure 6.1b left), whilst the other shows a more ordered structure with alternating planes of Ce and Zr (Figure 6.1b right). As Zr$^{4+}$ has a smaller ionic radius then Ce$^{4+}$, the lattice constant of a Zr-doped CeO$_2$ is contracted in comparison to pure CeO$_2$. Studies by X-ray diffraction (XRD) and density functional theory (DFT) have
shown that the lattice constant decreases from 5.4 Å for CeO$_2$ to 5.3 Å for Ce$_{0.5}$Zr$_{0.5}$O$_2$.\textsuperscript{17,25,26} Grau-Crespo et al. calculated that the phase separated structure is more likely to occur in the working conditions of the catalyst\textsuperscript{27}. They observed segregation of the Zr will occur, with Ce enrichment of the (111) surface. This was explained by the more covalent character of Zr-O bonds in comparison to Ce-O bonds. As both Ce and Zr ions appear to be linked to the enhancement of the oxygen storage capacity, the effect of the morphology on the synergy of Ce-Zr is important to be understood.

In this work we focus on the influence of zirconia on the redox behaviour of ceria. We employ micro-focused soft X-rays from a third-generation light source to probe and modify the oxidation states of the ceria-zirconia system. The reduction of ultra-thin metal oxide films by an X-ray beam is a methodology that has been extensively studied\textsuperscript{11,14,28–33}. We compare the behaviour of the individual metal oxides with that of the mixed metal oxide, making use of previous studies that have investigated the reduction and re-oxidation of ceria ultra-thin films\textsuperscript{29}.

### 6.2 Experimental

Synchrotron radiation measurements were carried out using the Elmitec LEEM III spectroscopic photoemission and low-energy electron microscope (SPLEEM) at the Nanoscience soft X-ray beamline (I06) at Diamond Light Source. Here we employed Near-edge X-ray Absorption Fine Structure (NEXAFS) alongside secondary electron XPEEM and $\mu$-X-ray Photoelectron Spectroscopy ($\mu$-XPS).
The Rh(111) single crystal (SPL) was prepared by repeated cycles of Ar+ sputtering and annealing to 1100 K in UHV and 800 K in 1 x 10^{-6} mbar O_2, followed by a final flash anneal at 1500 K in UHV. This resulted in a well-ordered surface as monitored by LEED, with no contamination seen with XPS, Auger Electron Spectroscopy (AES) or X-ray Absorption Spectroscopy (XAS). An epitaxial ZrO_{2-x}(111) film was prepared by depositing Zr (99.2%, Goodfellow) onto Rh(111) from an electron-beam evaporator (Focus EFM-3). This was carried out with the sample at 1200 K in 5 x 10^{-7} mbar O_2 and was followed by further heating for 5 mins and subsequent cooling in oxygen. Epitaxial Ce_{0.4}Zr_{0.6}O_{2-x} was prepared by first depositing Ce (99.9%, Goodfellow) followed by Zr (99.2%, Goodfellow) onto the previously grown ZrO_2(111). This was again carried out with the sample at 1200 K in 5 x 10^{-7} mbar O_2 and was followed by further heating for 5 mins and subsequent cooling in oxygen. The coverages of the oxides were determined using a calibration of the evaporator using ex-situ atomic force microscopy (see Appendix A2).

The photon energies employed for XPS were as follows: Zr 3d: 250 eV, Ce 4f (on-resonance for 4d-4f excitation): 120.8 eV. Binding energies are referenced to the Fermi level of the Rh (111) substrate. The electron kinetic energy (KE) in the SPLEEM instrument is controlled by applying a potential to bias the sample, namely the start voltage (S.V.). The kinetic energy of the emitted/scattered electrons is given by KE = S.V. - ΔΦ, where ΔΦ is the difference in workfunction between the sample and the instrument and is of the order of a few eV. µ-XPS spectra were acquired by imaging the exit slit of the analyser. This probes a 4 µm^2 area of the sample, corresponding to an energy window of approximately 12 eV and has the advantage of very fast acquisition times (~ 1 second per spectrum).
6.3 RESULTS AND DISCUSSION

6.3.1 REDOX BEHAVIOUR OF A ZIRCONIA THIN FILM

Figure 6.2: AES of ZrO$_2$,(111)/Rh(111) used to observe deposition of zirconia and to ensure no contamination was present.

Figure 6.3: X-ray absorption spectrum of zirconia at the Zr $M_3$ and $M_2$ edges to determine the photon energy to be used when investigating zirconia using XPEEM.
ZrO$_{2-x}$(111) on Rh(111) was studied initially to examine its photo-reduction and subsequent re-oxidation. AES was employed to confirm that the sample grown was free of contaminants (Figure 6.2). Alongside AES, XAS was used to confirm the presence of Zr as well as determine the photon energies to be employed when studying the film with XPEEM (Figure 6.3). Here, the Zr M$_2$ and M$_3$ edges are visible with a separation of 13.2 eV. This agrees with the expected separation of 13.7 eV for metallic Zr with the difference being accounted due to a difference in oxidation states. The M$_2$ edge was selected to probe zirconium in the XPEEM.

Figure 6.4a shows the LEED pattern obtained from a 6±1 monolayer equivalent (MLE) zirconia film on Rh(111), where one monolayer is defined by a single ZrO$_2$ trilayer unit. First order Rh(111)-(1 x 1) substrate beams are highlighted in red in the inset. The ZrO$_{2-x}$(111)-(1.33 x 1.33) beams are aligned with the substrate, highlighted with black circles in the inset corresponding to a real space unit cell 1.3x larger than the substrate. A (2.66 x 2.66) supercell is also observed, as indicated by the green spots in the inset. Here, the (1.33 x 1.33) superstructure can be considered as the ZrO$_2$(111)-(1 x 1) structure and the (2.66 x 2.66) superstructure as a (2 x 2) superstructure with respect to the ZrO$_2$(111)-(1 x 1) planes. These observations, as well as the additional beams from the ZrO$_{2-x}$(111)/Rh(111) interface, are similar to those described by Maurice et al.$^{22}$ Note that in contrast to this earlier work, we use the periodicity notation that has been employed in the more recent and extensive work on CeO$_2$(111) ultra-thin films. Figure 6.4b is a secondary electron XPEEM image obtained at the Zr M$_2$ edge. Here a uniform brightness is observed, suggesting an essentially complete and uniform coverage of ZrO$_{2-x}$(111) on Rh(111).
Figure 6.4: Structure and morphology of a 6±1 MLE ZrO$_2$,$_x$(111) ultra-thin film on Rh(111). (a) LEED pattern (88.6 eV) of ZrO$_2$,$_x$(111)/Rh(111). The beams arising from ZrO$_2$,$_x$(111)-(1.33 x 1.33) are highlighted with black circles, p(2.66 x 2.66) are highlighted in green, with substrate spots in red. (b) Secondary electron XPEEM image at the Zr M$_2$ edge (FOV = 10 μm, hν = 349.5 eV).

Figure 6.5a shows successive plots of the Zr 3d XPS region, which evidence the Zr redox behaviour as it undergoes photo-induced reduction as monitored by μ-XPS. Figure 6.5b highlights the spectra obtained at various periods of X-ray exposure. In the initial oxidised form (red spectrum), we can see the dominant peak of the Zr$^{4+}$ 3d$_{5/2}$ component (~ 182.7 eV Binding Energy (BE)). As we expose the surface to 250 eV soft X-rays for 140 s (blue spectrum), 350 s (green spectrum) and 500 s (black spectrum), we see a decrease in the Zr 3d$_{5/2}$ peak associated with Zr$^{4+}$. Concurrently we observe an increase at ~ 180 eV BE, which is indicative of a reduced species, or sub-oxide, being formed. Peak fitting of the sub-oxide region, Figure 6.5c, shows there are two components, namely sub-oxide A (Zr 3d$_{5/2}$ centred on 180.7 eV BE) and B (Zr 3d$_{5/2}$ centred on 179.2 eV BE). There is some debate over the exact assignment of these species$^{24,34}$. Nevertheless, as they increase upon photo-induced reduction and they appear at a lower binding energy than for the Zr$^{4+}$, they are assigned here simply to a
reduced oxide. The transition from Zr$^{4+}$ to lower oxidation states can be followed through the variation with photon dose of the intensity profile of Zr$^{4+}$ 3d$_{5/2}$ and that for the 3d$_{5/2}$ component of the more intense sub-oxide (A) (see Figure 6.5d). The efficient reduction observed for the zirconia at a photon energy of 250 eV is likely due to the large X-ray absorption cross-section at the M$_{3,4}$ delayed onset$^{35}$, assuming a Knotek-Feibelman type mechanism for the photon stimulated desorption of oxygen$^{36,37}$.

Figure 6.5: a) µ-XPS Zr 3d spectra (hν = 250 eV, FOV = 2 µm) of 6±1 MLE ZrO$_{2-x}$ on Rh(111) as a function of exposure to the soft X-ray beam. At 0 seconds, the beam was moved to a fresh area which is oxidised and then XPS spectra of 11 eV width centred on the Zr 3d orbitals were obtained over 520 seconds. Data have been corrected for a minor band bending shift of the Zr 3d peaks, which can be observed in the background. b) Snapshots of the XPS spectra obtained after 0, 140, 350 and 500 seconds of photon exposure. c) µ-XPS of the Zr 3d region recorded after 450 s. Deconvolution of the spectra was performed using Gaussian-Lorentzian line shapes, after subtraction of a Shirley type background with the full width at half maximum (FWHM) constrained to be equal. d) The evolution with time of the Zr (sub-oxide) and Zr$^{4+}$ 3d$_{5/2}$ peaks.
The re-oxidation of the reduced film by oxygen was investigated in order to test the reversibility of the X-ray reduction process. The resulting Zr 3d spectra are displayed in Figure 6.6, showing the effect of introducing an oxygen pressure of $1 \times 10^{-8}$ mbar and then ramping up to $1 \times 10^{-7}$ mbar. At the start of the experiment, in UHV, the spectrum has both Zr$^{4+}$ components at 182.7 eV BE and 185.1 eV BE but also contains some components associated with sub-oxides. At $2 \times 10^{-8}$ mbar, a reversal of the reduction begins with a decrease in the amount of sub-oxide species and an increase in the Zr$^{4+}$ component. By $5 \times 10^{-8}$ mbar, there is a complete reversal of the reduction with no sub-oxide components observed. Upon removal of the oxygen, immediate reduction is observed to begin again, as shown in Figure 6.6c.

Figure 6.6: a) $\mu$-XPS Zr 3d spectra ($h\nu = 250$ eV, FOV = 2 $\mu$m) of 6±1 MLE ZrO$_2$ on Rh(111) that monitor the re-oxidation of a partially reduced zirconia thin film as the pO$_2$ is increased from $1 \times 10^{-8}$ mbar to $1 \times 10^{-7}$ mbar, showing near complete re-oxidation of zirconia at 300 K. b) Selected spectra correspond to the initial reduced thin film (red spectrum), pO$_2$ at $2 \times 10^{-8}$ mbar (blue spectrum), $1 \times 10^{-7}$ mbar (green spectrum) and once oxygen has been pumped out to $1 \times 10^{-10}$ mbar (black spectrum). c) A line profile showing the change in intensity of the Zr$^{4+}$ 3d$_{5/2}$ XPS signal over the range of pO$_2$. 
6.3.2 Redox behaviour of Zirconia/Ceria mixed oxide system

Figure 6.7 shows the LEED pattern after Ce/Zr reactive deposition onto 6±1 MLE ZrO$_{2-x}$/Rh(111) followed by annealing to form the model mixed oxide inverse catalyst. Assuming that this additional coverage of oxide remains distinct, the stoichiometry is Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$. AES was again employed to ensure no contamination occurred during the deposition of cerium and zirconium (Figure 6.8). The zirconia spots are still visible, with the (1.33 x 1.33) beams overlapping the CeO$_{2-x}$(111)-(1.37 x 1.37) beams with respect to the Rh(111)-(1 x 1) substrate. The interface beams are no longer visible, which is consistent with the formation of a thicker oxide overlayer.

Figure 6.7: LEED (84.6 eV) pattern of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$/6±1 MLE ZrO$_{2-x}$/Rh(111). The spots corresponding to the zirconia are highlighted in green, ceria in blue and the substrate in red. The only apparent difference between this pattern and that in Figure 6.4 is the addition of intensity to the beams marked in blue, which lie on top of ZrO$_{2-x}$(111)-(1.33 x 1.33) beams.
Figure 6.8: AES of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$(111)/6±1 MLE ZrO$_{2-x}$/Rh(111) used to observe deposition of ceria and zirconia and to ensure no contamination was present.

In order to examine microscopically the morphology of the mixed metal oxide, secondary electron XPEEM was employed to obtain images at the Ce M$_4$ and Zr M$_2$ absorption edges (902 eV and 349.5 eV, respectively). Selected 5 µm snapshots from large-scale (FOV = 10 µm) images are shown in Figure 6.9a (Ce M$_4$) and Figure 6.9b (Zr M$_2$). In Figure 6.9a, the ceria nanoparticles are characterised as bright features against a dark background. A number of nanoparticles are highlighted to allow comparisons to other images. In Figure 6.9b a uniform brightness is observed with no discernible preference for the highlighted areas of the ceria nanoparticles. What fine structure there is can be ascribed to a spatial variation of detector efficiency. This suggests that the morphology of zirconia layer covering the substrate is largely unchanged by the decoration with ceria nanoparticles.
Figure 6.9: XPEEM identification of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ after depositing Ce/Zr on top of ZrO$_2$(111) whilst annealing in oxygen at 1200 K. 5 µm selected snapshots taken from images recorded with a 10 µm field of view and 2 V start voltage; the images were recorded at the same location at a photon energy of (a) 902 eV and (b) 349.5 eV, which correspond to the Ce M$_4$ and Zr M$_2$ edges, respectively. The outlines highlight representative ceria nanoparticles in (a) and their respective location in (b). (c) Ce M$_5$ edge X-ray absorption spectra on and off the ceria nanoparticles.

Figure 6.9c shows XAS spectra at the Ce M$_5$ edge, recorded from a sample of ceria nanoparticles along with areas away from the nanoparticles. Both the M$_4$ and M$_5$ edges were probed showing similar intensities and yield similar oxidation state information. Here we can see the preference for cerium within the nanoparticles compared to the background. By comparison of the two, and by reference to model data\textsuperscript{29} we see that cerium is more oxidised within the nanoparticles. Comparing XAS spectra taken at the Zr M$_{2,3}$ edge shows no difference between spectra taken on the ceria nanoparticles compared to off the nanoparticles. This is consistent with lack of contrast in the Figure 6.9b XPEEM image.

The XPEEM image in Figure 6.9a is consistent with a 13% area coverage of the surface. This is also the coverage obtained from ex-situ AFM measurements (see...
Appendix A2), where the height of the islands is measured to be about 11 nm. This corresponds to approximately thirty-five CeO$_2$ trilayers. This majority phase-separated structure agrees with previous studies and what has been predicted theoretically for active conditions$^{27}$.

Ex-situ HREELS was also employed to give further insight into the morphology (Figure 6.10). The HREEL spectrum of the Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ film shows significant loss features at 535 and 665 cm$^{-1}$. These were located using the Multi-peak fitting 2.0 program in Igor Pro and subtracting a background taken of the clean Rh substrate. The peak at 535 cm$^{-1}$ is in good agreement with literature values for CeO$_2$(111)$^{39}$. This arises from the interaction between the incident electron with the surface optical phonon of CeO$_2$(111). The peak at 665 cm$^{-1}$ is in good agreement with literature values of ZrO$_2$(111)$^{40}$. This arises from the interaction between the incident electron with the surface optical phonon of ZrO$_2$(111). An additional weaker broad peak appears at 1113 cm$^{-1}$ and encompasses the expected energies of the secondary multiple scattering losses associated with the primary losses. Therefore, this can be assigned as a combination of the multiple scattering events of the primary losses. The HREEL spectrum gives further evidence for a phase separated morphology as each of the loss features match the individual oxides with no additional losses present.
Figure 6.10: Raw HREEL spectrum of the Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$(111)/6±1 MLE ZrO$_{2}$(111)/Rh(111) thin film. Primary and multiple phonon loss peaks have been marked on the spectrum along with the energy gain peak. The spectrum was collected in specular geometry with an incident electron energy of 10 eV. The measured FWHM of the elastic peak was 82 cm$^{-1}$.

Figure 6.11 shows successive plots investigating the Zr redox behaviour within Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ as it undergoes photo-induced reduction, along with a comparison with pure ZrO$_{2-x}$/Rh(111). Focussing on the spectra obtained at selected lengths of X-ray exposure (Figure 6.11b), we see much less reduction than observed for zirconia. A comparison of the reduction of Zr within Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ to what was seen in ZrO$_{2}$ is shown in Figure 6.11c. A steady-state is reached much earlier for the former, after approximately 210 s, with only a 10% reduction in the Zr$^{4+}$ 3d$_{5/2}$ in Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$. This compares with 50% for ZrO$_{2}$, which only reaches a steady state after 500 s. This was repeated up to 2000 s to test for further reduction in the mixed oxide, none being observed. By comparing this to ceria reduction as probed by resonant XPS of the Ce 4f contribution to the valence band (see Figure 6.12) we see that ceria undergoes similar redox behaviour to that seen in previous studies$^{28,29}$. 
Figure 6.11: a) $\mu$-XPS Zr 3d spectra ($hv = 250$ eV, FOV = 2 $\mu$m) of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$/(111)/6±1 MLE ZrO$_{2-x}$/Rh(111) as a function of photo-reduction by exposure to the soft X-ray beam. At 0 seconds, the beam was moved to a fresh, unexposed area of the sample which is still fully-oxidised and then XPS spectra were obtained over the next 1000 seconds. Data have been corrected for minor bandbending of the Zr 3d peaks, which can be observed in the background. b) Snapshots of the XPS spectra obtained after 0, 280, 630 and 980 seconds of photon exposure. c) Time evolution of the normalised Zr 3d$_{5/2}$ intensity for both ZrO$_2$ (red) and Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ (black).

By moving to a freshly oxidised area, Figure 6.12a shows successive VB spectra at a photon energy of 120.8 eV (on resonance for Ce$^{3+}$) versus photon exposure with selected spectra shown in Figure 6.12b. The results in Figure 6.12c highlight the immediate reduction towards Ce$^{3+}$ upon removal of oxygen and the re-oxidation with the introduction of oxygen. This observation that ceria continues to undergo reduction while the reduction of zirconium appears inhibited provides some explanation for the synergy evidenced in reaction studies 41–44, with oxygen transfer...
occurring between the ceria and zirconia. Here, it was not possible to carry out a complete resonance photoemission spectroscopy experiment to determine the cerium oxidation state of the mixed oxide, but by comparison of the island O 2p/Ce 4f photoemission spectrum to previous work we identify the Ce/O stoichiometry as approximately CeO$_{1.65}$.

Figure 6.12: a) μ-XPS valence band spectra of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$(111)/6±1 MLE ZrO$_{2-x}$/Rh(111) recorded on the Ce$^{3+}$ 4f resonance investigating the effect of illumination with soft X-rays ($h\nu = 120.8$ eV, FOV = 2 μm). Upon moving to a freshly oxidised area, oxygen is removed, leading to ceria being reduced, followed by the introduction of oxygen to 1 x 10$^{-7}$ mbar where ceria begins to re-oxidise. b) Selected spectra for the initial oxidised film (red), the reduced film (green) and the re-oxidised film (black). c) Time evolution of the Ce$^{3+}$ 4f normalised intensity.
6.4 **SUMMARY**

A model mixed metal oxide of CeO$_{2-x}$(111) and ZrO$_{2-x}$(111) supported on Rh(111) has been prepared to probe the redox behaviour of the mixture. Soft X-ray irradiation was used to reduce zirconia with re-oxidation occurring upon the introduction of oxygen at 300 K. Upon the addition of ceria, the zirconia no longer undergoes an observable beam-induced reduction, indicating a synergy between the zirconia and ceria with oxygen transfer occurring between the two. Ceria within the mixed oxide was seen to undergo the same redox behaviour as seen in previous studies of ceria ultra-thin films. This provides some explanation of the effects of adding zirconia to ceria in order to enhance its catalytic role in such processes as the water gas shift reaction.
6.5 **REFERENCES**


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Chapter 7

SUMMARY
7.1 SUMMARY

The work presented in this thesis has explored both the crystallography and electronic structure of model metal oxide catalysts. By studying the catalysts’ surfaces, we aimed to better understand the processes that can occur, which in turn can inform the development of improved catalytic processes.

STM was employed to examine the spatial distribution of excess electrons on \(h\)-rutile \(\text{TiO}_2(110)\) associated with \(\text{OH}_b\). Firstly, the distribution of the excess electrons was probed at 78 K. Here, it was observed that the electrons exhibit a symmetric, four-lobe structure. The distribution was then probed at 6.6 K, where the distribution was seen to retain a similar nearly symmetric, four-lobe structure. This suggests that \(\text{OH}_b\) are likely to be weaker charge traps compared to oxygen vacancies. This suggests that there exists a smaller potential barrier to hopping between Ti sites at low temperatures around \(\text{OH}_b\). Second, we sequentially removed the capping H of a series of \(\text{OH}_b\)s and monitored any changes in the filled state STM. Using this method, we observed a change in the surrounding image contrast upon every capping H removal. This indicates that each \(\text{OH}_b\) contains one excess electron. Finally, we saw upon removal of one of the capping H within an \(\text{OH}_b\) pair that there is an additional redistribution of electrons dissipating away from the formerly \(\text{OH}_b\) pair. From this we can infer that the charge trapping potential of \(\text{OH}_b\)s is weaker than that associated with \(\text{OH}_b\) pairs.

HREELS was used to study the vibrational structure of a series of CeO\(_x\) films grown on a Pt(111) substrate. Firstly, a 5 MLE CeO\(_2\)(111) film was grown in oxidising conditions. A surface optical phonon with the same vibrational frequency as the bulk
crystal was observed. Annealing this film in reduced oxidising conditions showed a
different vibrational fingerprint, which was assigned to the $\text{Ce}_2\text{O}_3(0001)$ surface. The
LEED pattern showed a $9/4(\sqrt{3} \times \sqrt{3})$ periodicity which has been thought to arise from
oxygen vacancies. The HREEL spectrum shows no further peaks for vibrations not
associated with the $\text{Ce}_2\text{O}_3(0001)$ surface, which supports the literature suggestion that
oxygen vacancies form a superstructure on the reconstructed surface. Second, a 2
MLE thin film of $\text{CeO}_2(111)$ was grown in fully oxidising conditions. The vibrational
fingerprint matches with its thicker counterpart, however a slight shift to a lower
energy was detected. By reducing the film, we aimed to grow the newly observed
$\text{CeO}_2(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction grown on Pt(111), which is seen to degrade
under low energy electron bombardment. By calibrating the HREELS position to the
LEED position upon observing the $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity, we saw vibrational peaks
matching the predicting Ce-O double bond in areas not exposed to LEED and no peaks
where we performed LEED. To provide further evidence, we subjected an area to
further electron bombardment and measured the vibrational spectrum afterwards.
Here, we observed the reconstruction peaks to begin to degrade at 75 eV before
completely disappearing after being bombarded with electrons possessing 100 eV
energy. This was accompanied with an increase in intensity in the $(1 \times 1)$ associated
vibrational peak.

Spectroscopy measurements of a mixed metal oxide of $\text{CeO}_2-x(111)$ and $\text{ZrO}_2-x(111)$ supported on Rh(111), using synchrotron radiation, were employed to probe
the redox behaviour of the addition of zirconia to ceria. Firstly, a $\text{ZrO}_2(111)$ film was
prepared on Rh(111) and was subjected to soft X-ray irradiation to observe its
reduction. Upon introduction of oxygen at 300 K, the film is seen to re-oxidise back to
the ZrO$_2$ stoichiometry. Second, we evaporated cerium and additional zirconium before re-oxidising the film to form the mixed metal oxide. Again, we subjected the film to soft X-ray irradiation to observe the reduction. Ceria was seen to undergo the same redox behaviour as seen in previous studies of ceria thin films. However, the zirconia no longer underwent any observable beam-induced reduction. This indicates a synergy between the zirconia and the ceria with oxygen transfer occurring between the two metal oxides. This provides some explanation of the effects of adding zirconia to ceria, which is seen to enhance its catalytic role in such processes as the water gas shift reaction.

7.2 **Future Work**

This work has addressed three model metal oxide catalysts used in industrial applications, particularly in the hydrogen production sector. New insights into catalytic mechanisms and surface structures have been observed that can lead to new directions for research.

Hydroxyl bound excess electrons could be studied further using scanning tunnelling spectroscopy (STS) in order to probe any variations in the local density of states (LDOS) compared to excess electrons bound to oxygen vacancies. This could lead to further understanding of the water splitting process and the involvement of defects as catalytic sites. As seen during the studies in this work, isolated hydroxyls are observed to have four lobe symmetric distribution for the associated excess electron. This was also observed to be influenced by any residual charge which we saw influenced the shape of the distribution so that the lobe closest to the residual charge...
was less occupied. However, neighbouring hydroxyls are also seen to break this
distribution with the associated electron appearing to occupy only one or two lobes
when in close vicinity to other hydroxyls. This influence could be studied more by
comparing the influence of neighbouring hydroxyls on the same row, adjacent rows
and further afield. Upon removal of the hydroxyl by voltage pulsing, we observe the
excess electron to disappear. Three potential destinations for the excess electron can
be assumed. The first is it leaves with the hydrogen as a hydride ion. The second is the
electron remains on the surface of the titania sample and migrates along the rows
until a new stable location is found whilst the final destination is the electron migrates
to the bulk of the sample. Excited electrons have been observed to transfer to metal
atoms such as gold and platinum before undergoing recombination during
photocatalyst. By depositing gold atoms on the surface, a location consisting of a
single hydroxyl close to a gold atom can be studied. Using STS or Kelvin probe force
microscopy (KPFM), the LDOS of the gold atoms before and after the hydroxyl is
removed can be studied. This would give potential insight if the electron remains on
the sample or leaves with the hydrogen. The drawback for this method is it would
likely not differentiate between electrons remaining on the surface or migrating to the
bulk.

Further studies on the new reconstruction observed in Chapter 5 would
provide further evidence for both its growth mechanism along with its morphology.
Using additional oxygen isotopes, such as oxygen-18, during the formation of the
CeO$_2$(111) films will give further information on the morphology of the reconstruction.
Any change to the vibrations observed by growing the reconstruction in Oxygen-18
compared to oxygen-16 would provide evidence on the bonding exhibited between
ceria and oxygen. By alternating the use of oxygen-16 and oxygen-18 during initial growth and reduction and reoxidation cycles, we could gain insight into the growth mechanism to observe how the bonds are formed and broken. During catalytic applications, Au nanoparticles are often supported on the surface of ceria. It would be instructive to investigate the difference in catalytic behaviour of Au on CeO$_2$(111)-(\(\sqrt{3} \times \sqrt{3}\))R30° compared with the CeO$_2$(111)-(1 x 1) termination. This reconstruction has only been observed using a Pt(111) substrate. Rh(111) has also been extensively studied as a substrate for ceria growth and it would be insightful to see if the reconstruction can be grown on Rh(111) and how the substrate plays a role in the growth.

In Chapter 6, we observed a phase separated structure with a zirconia film lying below ceria islands. Repeating this experiment by growing a ceria film first and then growing zirconia islands on top would prove useful to see if the same observations of the synergy is consistent. This would change the semiconducting film that is in contact with the Rh support, providing insight into the role of the noble metal as well as the interaction between ceria and zirconia. It would be ideal to also to compare the redox behaviour we observed to an intermixed metal oxide film. This would allow the comparison between morphologies of the working catalyst. A key study on the intermixed catalyst would be the ability to alter the composition of the catalyst by adjusting the amount of zirconia added to cerium to observe any changes to the synergy which is would allow industrial catalysts to choose correct compositions for efficient catalysis. Pt(111) could also be used as the substrate for growth to compare to Rh(111) to see the influence of different noble metals along with depositing noble
metal atoms on top of the films to so if noble metal morphology will influence the synergy between zirconia and ceria.
A1 | Locating suitable areas for excess electron distribution imaging.

A 1: 20 × 20 nm² (a) empty- and (c) filled- state images of TiO₂(110). The images were taken at 78 K. (b,d), as (a,c), taken after removal of the capping H within a suitable area with a +3 V, 1 ms tip pulses. Scan parameters: (a,b) Vₛ = +1.4 V, Iᵣ = 50 pA, and (b,d) Vₛ = -1.4 V, Iᵣ = 10 pA. Suitable areas are denoted with black rectangles. Surface charge impurities are highlighted with black open circles. A surface adsorbate is highlighted with a white dashed rectangle.
Careful selection of an area to study the distribution of hydroxyl bound excess electrons is needed to avoid any influence from charge defects. By taking control scans of an area (A 1a,c), we can observe suitable areas to probe.

Charge defects are observed as bright spots in the filled states image (A 1c) but do not have any obvious correlating species in the empty state image (A 1a). These have been highlighted by black open circles as seen in A 1c. These defects are seen to have a greater influence along the [001] rows. Therefore, this means we need to prioritise areas that are void of any charged species along the [001] rows of suitable areas. Three suitable areas are shown in A 1c.

A surface adsorbate is highlighted by a dashed white rectangle in A 1a. These species were avoided as any tip contrast changes made the comparison of sequential images impractical. This rules out the area previously deemed suitable that lies lower in the image than the species, so as to avoid any interactions. This leaves two potential areas to study.

By centring on a suitable area, we can see any defects all around the potential area. The area as seen on the right of A 1c, was centred and the resulting area after voltage pulses were used to remove capping H’s is shown (A 1b,d). It can be seen that there are no charge defects within the area highlighted, making this a suitable candidate.
A2 | Determining Ce$_{1-x}$Zr$_x$O$_2$ composition by AFM

A 2: a) Constant frequency AFM image of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ performed ex-situ (2 x 2 µm$^2$, Δf = +169 kHz). b) Histogram of island heights measured from AFM image. c) Zoomed in region of secondary electron XPEEM image of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ after depositing Ce on top of ZrO$_2$(111) whilst annealing in oxygen at 1200 K. Image recorded with a 10 µm field of view, S.V. = 2 V. The photon energy is 349.5 eV (Zr M$_2$). d) Zoomed in region of secondary electron XPEEM image of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$ after depositing Ce on top of ZrO$_2$(111) whilst annealing in oxygen at 1200 K. Image recorded with a 10 µm field of view, S.V. = 2 V. The photon energy is 902 eV (Ce M$_4$).
An ex-situ AFM image of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$(111) is shown in Figure A 2a. As zirconia and ceria exhibit Volmer-Weber thin-film growth under the conditions the film was grown, we can calculate the island heights by taking line profiles using the dark areas with no islands as the substrate height. The dark areas with no islands were seen to be comparable in height. By comparing the island heights, we see there are multiple components present. By collating the heights into a histogram, Figure A 2b, we can see that there is the most prevalent group of islands with a height preference of ~ 8.5 nm (blue curve). These can be assigned to be zirconia islands since the Zr M$_2$ edge XPEEM exhibits a uniform coverage of Zr within its resolution (Figure A 2c). What fine structure there is in the XPEEM in Figure A 2c can be ascribed to a spatial variation of detector efficiency.

The density of the Zr islands is measured to be 56 ± 3 µm$^{-2}$. As the O-Zr-O trilayer of ZrO$_2$(111) has an in-plane lattice constant of 0.350 nm, using the average height of 8.5 nm, the islands are seen to be approximately 25 trilayers thick. From the AFM image, the fractional coverage of zirconia islands was calculated to ~ 50%, equivalent to ~ 12 trilayer equivalents (TLE).

The island height profile also suggests preferences for the formation of islands with heights centred around 15 nm (red curve) and 25 nm (green curve), with lower populations than the component centred at ~8.5 nm. The density of both these taller islands is measured at 9 (± 2) µm$^{-2}$. This is the same as seen for the bright ceria features in the XPEEM images (Figure A 2d); as such we assign the taller features in the AFM images to ceria. During sample growth, zirconium was deposited in two equal amounts. One prior to cerium deposition and one after. This would equal 6 TLE during each deposition. With an in-plane lattice constant of 0.31 nm, we can measure the
ceria islands to contain ~ 30 trilayers for the smaller islands (centred at 15 nm) and ~ 60 trilayers for the taller islands (centred at 25 nm), once the initial zirconia layer is subtracted. With 13% fractional coverage observed for the ceria islands, using the ratios of the island heights, ~ 4 trilayer equivalents of ceria was calculated.

As the first deposition was annealed separately to perform the ZrO$_2$ studies, we assume the cerium deposition and second zirconium deposition are distinct. This leaves us with 4 TLE of ceria and 6 TLE of zirconia giving us a stoichiometry of Ce$_{0.4}$Zr$_{0.6}$O$_{2-x}$.

Due to the island heights measured, we have disregarded any surface adsorbates that may have adsorbed during ex-situ AFM.