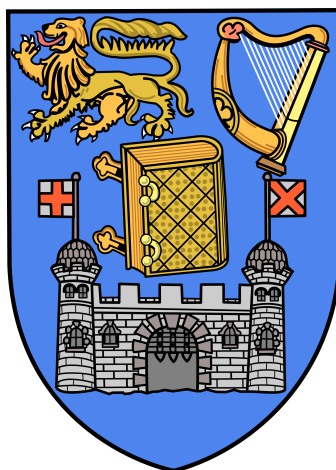

Surface Studies of Oxidised Metals: Mo, Nb and Cu



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Doctor of Philosophy

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Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and apart from the advice, assistance and joint effort acknowledged and mentioned in the text, it is entirely my own work.

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Summary

The atomic structure and evolution of ultra-thin film oxides is investigated for Mo, Nb and Cu using surface sensitive techniques such as scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). In particular, the structural and electronic properties of the oxide layer and the way in which the oxide layer governed further oxidation through its barrier to oxygen incorporation is investigated.

An O-Mo-O tri-layer oxide structure terminates ($\text{MoO}_2/\text{Mo}(110)$). Over-oxidising $\text{MoO}_2/\text{Mo}(110)$ results in an oxygen-rich $\text{MoO}_{2+x}/\text{Mo}(110)$ termination. The extra oxygen takes the form of adatoms, which reside on the row structure of $\text{MoO}_2/\text{Mo}(110)$. Applying a bias pulse between the STM tip and the surface, results in the removal of oxygen adatoms from the surface. The electric field produced between the STM tip and the surface is concluded to “push” the adatom into the surface through the terminating layer: Finite element method (FEM) simulations using an electric field support the experimental results and indicate that an electric potential of 0.45 V is required for the adatom for it to overcome the barrier. An intermediate state for the oxygen adatoms is observed, partially contained within the oxide layer. Adatom removal is only observed with positive sample bias. The oxygen adatom is removed from the surface *via* penetration through the surface oxide layer. Density functional theory (DFT) calculations indicate that the oxygen adatom opens a “channel” in the oxide layer, by relaxing a neighbouring Mo atom from its lattice position into the topmost oxygen layer. This relaxation reduces the potential barrier and allows for oxygen incorporation with relative ease compared to the unrelaxed case. The size

of region on the surface from which adatoms are removed depends on the magnitude of applied voltage pulse. The highest resolution of the pulsing mechanism is on the sub-nanometer scale.

An ultra-thin NbO layer terminates Nb(110). This oxide layer produces a surface with two terrace structures, one of which has terrace edges in the $[001]$ direction and the other exhibits terrace edges in both the Nb $[001]$ and $[\bar{1}11]$ directions. STS measurements indicate a difference in the local density of states (LDoS) between the nanocrystals which terminate the surface and the “channel” separating neighbouring nanocrystals. The two types of terrace edges Nb $[001]$ and $[\bar{1}11]$ are electronically distinct from one another. The terraces edges which runs in the Nb $[001]$ direction regularly exhibit a terrace width of one NbO nanocrystal.

Low dosage oxygen exposure at 78 K results in oxygen adatoms and small clusters randomly scattered on the surface the NbO surface. Annealing the surface resulted in oxygen clusters residing in the channels between the nanocrystals, where the LDoS is larger. The clusters are regular in size and appearance and fill the channels, resulting in a oxide row structure within the channels. These oxide clusters and the adatoms prior to annealing could not be induced to penetrate the oxide layer using the STM tip. The barrier for oxygen penetration through the NbO terminating layer is high. NbO acts as a protective layer for the underlying Nb bulk.

A variety of disordered and ordered sub-monolayer oxide structures are observed when exposing a Cu(111) single crystal to oxygen at various annealing temperatures from 78–850 K. The change in the structure of these oxides is monitored over the different preparation conditions. Many oxides co-exist at low temperatures. Increasing the annealing temperature during oxidation reduces the number of distinct oxides. A new ordered oxide structure is observed at 750 K. At 850 K the ordered oxide observed at 750 K has grown from the terrace edges by coalescing the oxide islands which exist on the terraces. The oxide structure has a hexagonal symmetry and a period of 1 nm. A second, larger, ordered oxide structure is also observed. This structure has a period of 1.6 nm and exhibits a 3-fold symmetry substructure.

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I dedicate this work to my parents

List of publications

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2. *Control of binding of C_{60} molecules to the substrate by Coulomb blockade*
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List of abbreviations

UHV	- ultra-high vacuum
STM	- scanning tunneling microscopy
DFT	- density functional theory
1D	- one-dimensional
2D	- two-dimensional
XPS	- x-ray photoelectron spectroscopy
XPD	- x-ray photoelectron diffraction
STS	- scanning tunneling spectroscopy
DoS	- density of states
LDoS	- local density of states
CCM	- constant-current mode
CHM	- constant-height mode
LEED	- low-energy electron diffraction
TSP	- titanium sublimation pump
LDA	- local density approximation
GGA	- general gradient approximation
FCC	- face-centred cubic
BCC	- body-centred cubic
HCP	- hexagonal close-packed
PAW	- projector-augmented-wave
wrt	- with respect to
FT	- Fourier Transform
FO	- Friedel Oscillation
FFT	- Fast Fourier Transform
ARPES	- Angle resolved photoelectron spectroscopy
RMSD	- Root mean square difference
SCF	- Self Consistent Field

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Chapter 1

Introduction

Metal oxides see applications in a wide range of industries, with their use in heterogeneous catalysis and electronic/optoelectronic devices being the most prevalent. Their importance in these fields, and others, can be traced to the wide range of physical and chemical properties exhibited through differences in the multitude of oxidation states and relative stoichiometries of the metal oxides. Increasing the oxidation number generally results in the chemical bonds changing from ionic to covalent, changing the properties of the metal oxide from metallic to semiconducting or insulating. Careful control of the oxygen content can therefore result in tunable electronic properties, resulting in their widespread use in nanoelectronics (metaloxidesemiconductor field-effect transistor (MOSFET))[1], photocatalysis[2] and thin film devices such as gas sensors [3]. Nanostructures such as 1-dimensional (1D) nanowires provide physical and chemical properties which may see use in future microelectronics[4, 5].

Metal oxides comprise the largest family of catalysts in heterogeneous catalysis[6]. Transition metals oxides in particular dominate the catalyst industry owing to their low cost of production, easy regeneration and gas selectivity in catalytic reactions. They are used in many organic reactions, such as oxidation, dehydration, dehydrogenation and isomerization [7]. Metal oxides are used in the petrochemical industry to upgrade light alkanes to chemicals of higher economical value such as fuels. ZnO based catalysts are

used for methanol synthesis which has a current demand of 50 million tons per year and is expected to rise by 11% annually. Furthermore, the oxidation of methanol to formaldehyde uses $\text{Fe}_2(\text{MoO}_4)_3$ catalysts[8].

The initial oxide layer which terminates a metal provides a protective barrier against further oxidation, preventing the degradation of the metals structural and electronical integrity. A famous example of this is the Statue of Liberty, New York, where the characteristic green Cu_2O terminating layer protects the underlying Cu from further oxidation. The size of the barrier determines the rate of oxidation and dictates the oxidation process as the interface between the metal and metal-oxide structures. Passive oxide layers are important in many structural applications, they are intentionally grown on aluminium alloys and stainless steel to protect the metal from corrosion. Passivation of stainless steel is achieved by exposing the metal to nitric acid, removing iron and leaving behind a chromium rich surface which then forms a protective Cr_2O_3 layer. Metal oxide surfaces, which can vary in physical and electronic properties to the bulk, are critical in these applications. Characterisation of the surface on the nano-scale is necessary in order to effectively and efficiently use metal oxides in heterogeneous catalysis reactions and modern electronics.

As such, the physical and electronic properties of Mo, Nb and Cu oxides are analysed through scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements. Furthermore, the role that these initial oxide layers play in dictating further oxidation is investigated. LEED and XPS measurements, along with computational methods such as DFT and FEM, compliment the main work. These experimental techniques are discussed in chapter 2, followed, in chapter 3, by an in-depth analysis of Mo, Nb, Cu, their oxides and the relevant work on the oxide surfaces present in the literature.

In Chapter 4, oxygen adatoms on $\text{MoO}_{2+x}/\text{Mo}(110)$ are pulsed using the STM tip, resulting in their removal from the surface. The electric field is concluded to be responsible for the removal of adatoms using both STM measurements and FEM simulations. Oxygen adatoms are concluded to penetrate the oxide layer, by overcoming the incorporation barrier via the

electrostatic potential induced by the bias applied between the STM tip and surface. Theoretical work such as DFT models of $\text{MoO}_{2+x}/\text{Mo}(110)$ provide insight into the process; the oxygen adatoms induce relaxation of a Mo atom in the O-Mo-O trilayer to the oxide layer above, opening a channel in the oxide layer which facilitates oxygen atom penetration through surface layer. An intermediate state where the adatom has not fully penetrated the surface is observed. Surface modification has been achieved using the electric field between the STM tip and the surface, resulting in nano-scale lithography. Scanning probe Nanolithography processes are used to fabricate conjugated molecular wires, optical micro-lenses and complex quantum devices[9].

In Chapter 5, the electronic and structural properties of a NbO terminated Nb(110) single crystal is investigated using STM, STS and XPS measurements. The surface is terminated by NbO nanocrystals, 2–3 nm in length. STS measurements indicate a large difference in the LDoS between these nanocrystals and the disordered region (channel) separating them. XPS measurements indicate the presence of two different oxygen chemical states on the surface. Low dosage oxidation and subsequent annealing results in regular size and shaped oxide clusters residing in the channels between NbO nanocrystals, with the nanocrystals remaining clean. The NbO termination layer thus dictates the initial oxide growth on the surface. The electronic and structural properties of the nanocrystal termination prevents oxygen diffusion through the oxide layer. Pulsing the oxygen clusters in the channels did not result in their incorporation into the oxide layer, indicating the protective nature of the NbO terminating layer. Nb is superconducting below 9.2 K whereas NbO has a superconducting critical temperature of 1.7 K. Pure Nb is highly desired for use in low temperature superconductors, an NbO terminating layer can be used to protect the Nb bulk from further oxidation.

Chapter 6 presents an oxidation study of Cu(111) for annealing temperatures ranging from 78 K to 850 K resulting in a sub monolayer oxide coverage. STM measurements exhibit a large range of distinct oxides over the course of annealing temperatures with disordered oxides at lower temperatures and ordered oxides, which coalesce at the terrace edges at high oxidation temperatures. The differences between the oxides is examined and the change

in the type and abundance of oxides present on the surface, as the preparation temperature is increased, is analysed. Two ordered oxide structures are observed following oxidation at 850 K, one of which exhibits a complex internal structure, which may be due to vacancies in the oxide structure. The observed oxides are compared to those presented in the literature and appear distinct. Cu oxides are widely used as catalysis owing to their good reaction rates and desirable selectivity.

The appendix presents a study of surface defects on Cu(111). While studying the oxidation of Cu(111), a number of defects were observed in STM images. These defects persisted beyond cleaning procedures. Their complex structure and lack of detailed documentation in the literature prompted an investigation. DFT calculations were employed in order to assist in the identification of defects. During the process of producing a model of which simulated STM images could be produced, inadequacies in the conventional convergence criteria used in DFT simulations was discovered. A new method of convergence based on the DoS of the system was produced. This method allows for accurate convergence tests with a quantitative measure of accuracy. The measure of accuracy can be extended to the simulated STM images. Finally, a comparison between simulated STM images and the experimental images is presented.

Chapter 2

Experimental Techniques & Set-up

2.1 Scanning tunneling microscopy

Microscopy began in the 15th century using magnifying glasses to amplify light in order to observe insects. Optical microscopy has a resolution limit of about $0.2\text{ }\mu\text{m}$, owing to the shortest wavelength of visible light being $0.4\text{ }\mu\text{m}$. In order to probe structures with higher resolution a light source with a smaller wavelength is required. Electron microscopes such as the scanning electron microscope (SEM) and transmission electron microscope (TEM) enabled the imaging of atomic structures for the first time, however, the STM is the most versatile and sensitive of the probes. Its invention led to the Nobel prize in physics being awarded to Gerd Binnig and Heinrich Rohrer in 1986.

Binnig and Rohrer had the ingenious idea that an extremely sharp metallic tip could image the surface of a conductive material at the atomic scale by measuring the current between the tip and surface when a potential is applied[10]. The invention of the STM was a huge step forward in surface science, exceeding previous resolution of instruments such as the SEM by a factor of 10 and for the first time allowing the visualisation of individual atoms. Using a STM, resolution down to a few picometers is possible.

[11]. STM takes advantage of the strong correlation between the tip surface distance and the resulting tunneling current in order to achieve its impressive vertical resolution. The advantage of using an STM over other surface analytical techniques is that no lenses or special light/electron sources are required, such as those used in TEM. STM presents some clear disadvantages, it is relatively slow and the size of the scan area is typically limited to a region less than $0.25\mu^2$. Other methods, such as atomic force microscopy (AFM) can scan much larger areas at a higher rate. Furthermore, STM can only scan conductive surfaces which are, in generally, atomically flat. AFM uses the force measured between the tip and surface to adjust the tip height and produce an image of the surface, so does not encounter the same issues as STM. Many set ups have a combined STM and AFM system so that each method may cover the disadvantages of the other.

2.1.1 Tunneling theory

The main principle behind the STM is quantum tunnelling. In classical mechanics, particles are considered to be point-like structures. If these classical particles encounter a potential well that exceeds their kinetic energy, they are reflected. In quantum mechanics particles are considered to be waves and are represented by a wave function $\psi(x)$ that follow Schrödinger's wave equation. These waves have a non-zero probability of appearing on the other side of the potential barrier in a process known as tunneling. A schematic of quantum tunneling is presented in Fig.(2.1). By measuring the number of electrons which tunnel through the potential barrier between the STM tip and the surface being scanned, a map of the electron density of the surface can be obtained. The number of electrons which tunnel through the barrier depends on a number of factors but when considering the STM, the most important factor is the distance between the STM tip and the surface.

The tunneling current is now derived in 1D using the 1D time independent Schrödinger wave equation:

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V\right)\psi(x) = E\psi(x) \quad (2.1)$$

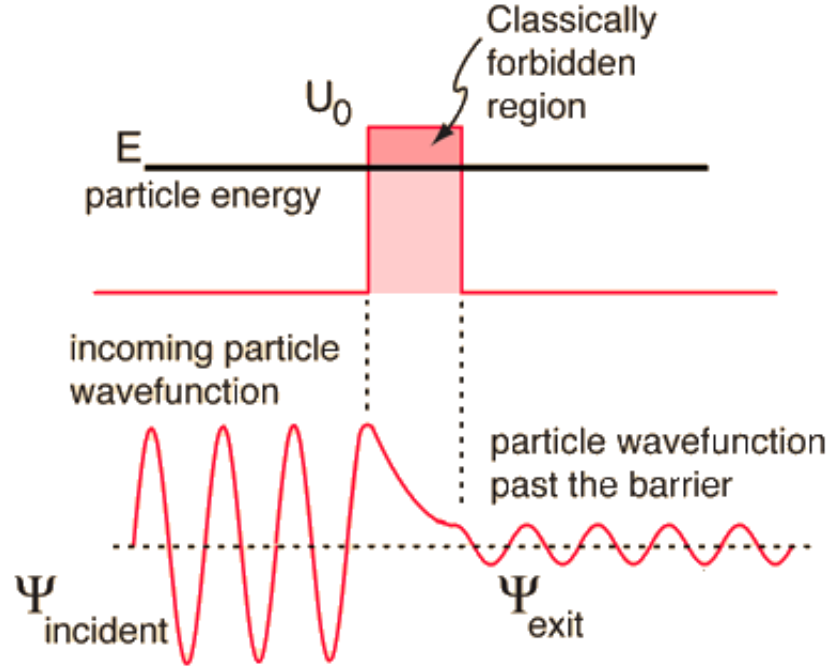


Figure 2.1: **Schematic of quantum tunneling effect.**[12] Classically, a particle with an energy less than the barrier height cannot pass through the barrier. The tunneling effect describes the ability of particles which behave as waves to penetrate a barrier. The resulting wave function of the particle is smaller in magnitude following the tunneling effect.

Solving for the 1D case, the probability for an electron to transition across the barrier is given by:

$$P = \psi(0)^2 \exp(-2\kappa d) \quad \kappa = \sqrt{\frac{2m\phi}{\hbar^2}} \quad (2.2)$$

where m is the mass of the electron, d is the width of the barrier (tip-sample separation), and ϕ is the height of the barrier (work function), which is actually some combination of the work functions of the tip and sample.

At 0 K, a bias voltage, V , must be applied between the STM tip and the surface for electrons to tunnel from the tip into unoccupied states in the sample.* Applying the bias increases the Fermi level of the tip relative to the sample (or *vice versa* depending on the bias), thus dictating the energy range for which tunnelling can occur. The potential barrier which the electrons must tunnel through depend on the tip-surface distance d . This potential arises from the change in potential from the tip to the vacuum and then to the sample. The tunneling current is proportional to the sum of the individual probabilities (Eq.(2.2)) for an electron at each energy increment to tunnel, over the energy range $E_f - eV \leq E \leq E_f$, where E_f represents the Fermi energy of the tip when the bias voltage is applied such that

$$I_t \propto \sum_{E_f - eV}^{E_f} |\psi(0)|^2 \exp(-2\kappa d) \quad \text{where} \quad \kappa = \sqrt{\frac{2m\phi_s}{\hbar^2}}. \quad (2.3)$$

The number of electrons which tunnel through the potential barrier depends on the number of available states in the DoS of the sample, up to the bias energy eV . By definition, the density of states (DoS) at some energy, E , is the sum of the square of the wave-functions between E and $E - eV$, per unit energy. The DoS, ρ is given by

$$\rho(E, x) = \frac{1}{eV} \sum_{E - eV}^E |\psi_n(x)|^2$$

where $\psi(x)$ represents the wave-function at a distance of x from the surface, taking $x = 0$ results in the wave-functions at the surface i.e. the surface states. Summing up these surface states gives the DoS at the surface, ρ_s , localised underneath the tip up to the Fermi energy.

$$\rho_s(E_f, 0) = \frac{1}{eV} \sum_{E_f - eV}^{E_f} |\psi_n(0)|^2 \quad (2.4)$$

*For the simplicity of the derivation, the tip and surface are assumed to have identical Fermi levels.

Thus an expression for the tunneling current can be obtained by combining Eq.(2.3) and Eq.(2.4).

$$I_t \propto V \rho_s(E_f, 0) \exp(-2\kappa d) \quad \kappa = \sqrt{\frac{2m\phi_s}{\hbar^2}} \quad (2.5)$$

Some important notes on this equation: (1) The tunneling current is directly proportional to the bias voltage applied across the tunneling junction. (2) The tunneling current varies exponentially with d , the tunneling gap. For a typical metallic work function of 4 eV, the tunnelling current reduces by a factor of 10 for every 0.1 nm increase in the distance, d . Over an atomic distance of say 0.3 nm, the current changes by a factor of 1000. This is the underlying reason behind the STM vertical sensitivity and allows for the high resolution imaging of atomic features.

Scanning tunneling spectroscopy

Scanning tunneling spectroscopy[13] (STS) is used to provide information on the number of surface states, filled or empty, in some localised region as a function of their energy. During a spectroscopy measurement the STM tip is positioned above some point on the sample surface and the tip surface distance is kept constant by turning the height control feedback loop off. The applied bias voltage swept through some range and the resulting current is recorded, producing an $I(V)$ -curve. The first derivative of the $I(V)$ -curve with respect to (wrt) V , $\frac{dI}{dV}$, is proportional to the LDoS of that region of the sample.

When a voltage, $+V$, is applied to between the tip and the sample, the states which are probed correspond to an energy range between the Fermi level and eV . Increasing the applied voltage increases the number of states which are probed by an energy increment of ϵ , up to $eV + \epsilon$. The change in the tunneling current observed from increasing the probing energy by ϵ corresponds to the number of states in that energy range. Hence, $\frac{dI}{dV}$ reflects the LDoS of the surface. This can be seen by taking the first derivative of

Eq.(2.5) with respect to V . The DoS term is replaced by the LDoS, $N_s(E)$ and the Fermi level is set as 0.

$$I_t \propto V \exp(-2\kappa d) \int_0^{eV_{bias}} N_s(E) dE \quad (2.6)$$

$$\frac{dI}{dV}(V_{bias}) \propto V_{bias} N_s(E) dE \quad (2.7)$$

A number of approximations has been used to arrive at this relationship. Firstly, this relationship relies on the approximation that for low bias voltages the tunneling current is linearly proportional to the applied bias voltage. At large bias voltages, this is not the case as the tunneling current no longer follows ohmic behaviour. The DoS of the tip plays an important role in the tunneling current. This is a factor which has been neglected in this calculation for simplicity by assuming that the DoS is constant.

Tersoff-Hamann Simulated STM images

In order to accurately simulate STM images the exact electronic structure of the tip must be known. This is never the case and as such approximations need to be made for the tips electronic structure. One such approximation, proposed by Tersoff and Hamann[14] models the STM tip as a spherically symmetric single “s” orbital. The conductance (dI/dV) between the DFT simulated slab and a fictitious STM tip depends on the overlap of the wave-functions of the tip and the sample. The wave-function decays exponentially into the vacuum and so only the orbital of outermost atom of the tip will contribute significantly to the tunneling current.

A simulated STM image of the DFT model surface is generated in a similar manner to STM images. A voltage and a fictitious current value is selected. The surface is dividing into a grid with each grid point corresponding to a pixel of the resulting image. The “s” orbital tip approaches the model surface with an “applied” bias voltage until the fictitious tunneling current value is achieved. This is repeated for all grid point and a 2D height map is produced with the tip height represented on a colour scale. This

method provides a good approximation to real STM images however the tip orbitals which probe the surface are more likely to be “d” orbitals, which would produce sharper images of the surface.

2.1.2 The scanning tunneling microscope

The scanning tunneling microscope consists of an atomically sharp (tip curvature apex <10 nm) conductive tip which is brought into close proximity to a conductive surface. A bias voltage is applied between the tip and surface. When the tip and surface are within close proximity, typically around 1 nm, the amount of tunneling electrons is sufficient to be detected. A tunneling current is selected and the tip allowed to approach the sample. This current along with the selected bias voltage determines the final height of the tip above the surface following the approach procedure.

This approach procedure is typically done *via* applying high voltages to piezo ceramics. The separation of net charge within the crystal cells of piezoelectric materials allow the piezos to expand/contract when an electric field is applied along the axis of charge separation. Slowly increasing the voltage expands/contracts the piezo element causing the inertial mass to move while the moving mass remains at rest under an applied force due to friction. Quickly restoring the voltage to its initial value causes the moving mass to overcome the frictional force, “slipping”, resulting in its movement across the surface. The inertial mass also moves, but much less due to its relatively higher mass. The process can be repeated to allow for large scale movement. This method of movement is known as a “slip-stick” mechanism.

Once the tip is in the tunneling regime, its lateral position relative to the surface is adjusted using piezos however this time without the slip-stick mechanism. One method for fine piezo control, which is used in the body of this work, relies on a tube consisting of 4 piezo strips. Applying a voltage to each piezo stripe in an appropriate manner enables the tube, and therefore the tip, to bend, resulting in lateral movement on a small scale. This allows the tip to sample any point-like region within a frame size of approximately $2\mu\text{m}$. The movement of these piezos are extremely fine, controllable and

reproducible allowing for the full realisation of the STM's potential. Typical piezoelectric constants for these crystals are in the range of a few Å/V.

A resolution can be selected to determine how many pixels you would like to obtain in your image size. A square frame is typically used for images. The tip scans both left to right and right to left from top to bottom or bottom to top in order to obtain an image. The tip scans and saves both horizontal directions for each image in order to identify possible issues that may arise in imaging from tip/surface inconsistencies.

There are 2 modes in which you can obtain images from the STM, constant current mode (CCM) and constant height mode (CHM). CHM keeps the tip at the height above the surface previously set in the approach settings. The current is then measured at each point and the resulting current map gives an insight into the topographical & electronic structure of the surface. This mode should only be used on atomically flat surfaces as the tip will likely crash due to the tunnelling distance being comparable to just 2/3 steps in the layers of many materials. CCM keeps the current constant by adjusting the height of the tip as it scans across the surface. This mode is very versatile as it allows for large scale images without the risk of crashing the tip into the surface. The disadvantage is that this mode requires a feedback loop system to adjust the tip height. This feedback system has a finite response time which limits the scan speed of the system and introduces errors to the resulting images.

2.1.3 The scanning tunneling microscopy system

The UHV STM system consists of a load-lock, a preparation chamber and an analysis chamber. Samples are first placed into the load-lock at atmospheric pressure and pumped down using a turbo pump until the pressure is within an order of magnitude or two of the preparation chamber which typically has a base pressure on the order of 10^{-10} mbar. Once inside the preparation chamber the sample can be cleaned through annealing and ion sputtering. A LEED apparatus is attached to the preparation chamber allowing for the characterisation of the sample. A number of gas leak valves are also available

for exposure of samples to a gas environment. The pressure is measured using a Bayard-Alpert (BA) gauge. An ion pump maintains the pressure in the preparation chamber and can be assisted by a titanium sublimation pump (TSP). When oxygen and argon are introduced to the system, the gate valve to the ion pump is closed and the valve to the load lock opened, allowing the turbo pump to pump the system. Annealing is achieved using resistive heating alone or in combination with electron bombardment heating. A tungsten filament is located under the sample plate which heats the sample from beneath. The heating stage, where the sample resides is electrically insulated from the STM chamber, applying a voltage across the heating stage allows for thermally emitted electrons from the filament beneath to bombard, and thus heat, the plate. The temperature of the sample is estimated using a K-type thermocouple which is located near the filament. Temperatures above 900 K can be measured using an optical pyrometer. When using electron bombardment this is necessary as the bombarding electrons primarily hit the sample plate resulting local heating of the plate and not the surrounding area in which the thermocouple is located.

Sputtering is conducted by leaking Ar gas into the gas cell of an ion gun which is located in the preparation chamber. Here, it is ionised *via* electron bombardment. The Ar ions are then accelerated through a ring which is typically biased in the range of 0.5 to 2 keV. Typical Ar pressures are in the order of 1×10^{-5} mbar.

The analysis chamber is isolated from these cleaning and exposures in order to ensure a clean and stable gas environment, only when the preparation chamber returns to its base pressure are the two chambers opened to each other using a gate valve. The base pressure in the analysis chamber is in the order of 1×10^{-11} mbar and is maintained with an ion pump and TSP. The stage that the sample plate sits on during scanning can be placed in contact with a large reservoir of liquid nitrogen/helium allowing it to cool. This stage is electrically isolated from the rest of the system and hangs from springs when not in contact with the cooling reservoir. These springs in combination with eddy current damping reduces vibrations. The entire

STM system is placed on 4 pressurised canisters which allow the system to “float”, further isolating the system from vibrations.

2.1.4 Tip preparation/cleaning

To make a tip with a narrow tip radius (on the order of a few nanometers or even a single atom) an electrochemical etching process is used.[11]. A 2 M solution of NaOH is prepared and 100ml of the solution is placed in a small beaker. A tip, typically made of Tungsten, (111), (100) or poly-crystalline is placed in the centre and submerged into the solution to a depth of ≈ 3 mm. A stainless steel cylinder is placed in the NaOH solution and surrounds the tip. A DC bias is then applied between the tip and the shield, with positive bias on the tip. A chemical etching process begins where tungsten is oxidised and dissolves in solution. WO_4^{-2} ions are produced at the anode and water is reduced to H_2 and OH at the cathode resulting in bubbles forming. The tungsten oxide flows down the rod owing to its relatively higher density, protecting the part of the rod which is submerged, without this process the entire rod below the meniscus would be etched away. As the rod gets narrower near the meniscus, the weight of the rod beneath the meniscus applies strain which results in the rod stretching and getting thinner, eventually leading to the rod breaking. The result is 2 rods with a tip apex on the nanometer scale. However the rod which was in the solution is often very thin due to etching and so only the rod which was in air is used. A schematic of the etching process is depicted in Fig.(2.2).

The tip is then cleaned in deionised water to remove any remaining NaOH which may cause further etching, then dipped into isopropanol to remove the water. The tip is quickly loaded into the load lock of the STM system to minimise oxidation of the tip. Once transferred to the preparation chamber a wide variety of further cleaning/shaping options are possible however only a few are available for our setup. It is possible to sputter the tip with argon in the same way samples are, however, glancing angles are typically used. Sputtering can be used to clean the tip of oxides much the same way for samples. The 2nd option for cleaning is a large electric field. The tip is

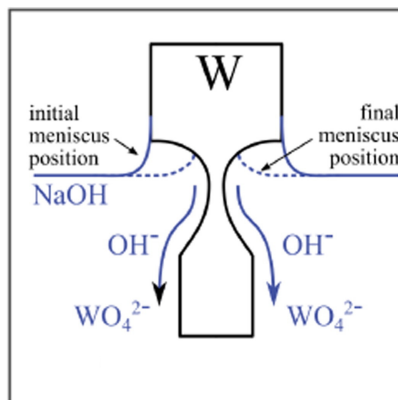


Figure 2.2: **Schematic of etching process for W STM tips.** The W rod is placed in a 2M solution of NaOH. A bias is applied between the rod and an electrode in the NaOH solution. W ions are etched at the meniscus and sink to the bottom of the rod. When the rod reaches a critical thickness, the weight of the section of the rod beneath the meniscus pulls the rod and results in its breaking with a sharp tip.

brought into close proximity (2/3 mm) to a curved filament. A large voltage is applied to the filament and the tip is connected to the ground. The current is monitored as the voltage increases. Typically at around 1.0 kV small bursts of current ($0.5 \mu\text{A}$) are measured and a steady current is obtained at around 1.2 kV. Once a steady current is obtained, the tip has been cleaned and so the voltage is switched off. The small current bursts are from contaminants being removed from the tip. It is also possible to clean the tip *via* an applied electric field when the tip is placed in the STM, however the maximum applied voltage is limited to 10 V. Furthermore applying large pulses close to the sample often leads to contaminants on your surface localised underneath the tip.

2.2 Low-energy electron diffraction

Following Louis de Broglie's proposition in 1924, in which he theorised that particles are wavelike in nature, the possibility of observing particles, such as electrons, undergoing diffraction became apparent. Davisson and Germer confirmed this theory in 1927. Firing low energy electrons at a crys-

talline nickel target produced a diffraction pattern consistent with that of X-rays which Bragg had developed in 1913. Low energy electrons are back-scattered from a crystal lattice, which acts like a diffraction grating, producing a diffraction pattern, similar to that of a monochromatic light source.

Louis de Broglie proposed that the wavelength of a particle, λ , is related to its momentum, p , and the Planck constant h as follows:

$$\lambda = \frac{h}{p} \quad (2.8)$$

The kinetic energy of an electron is obtained from the accelerating voltage:

$$\frac{1}{2}mv^2 = eV \quad (2.9)$$

The momentum of the electron is then:

$$p = mv = \sqrt{2meV} \quad (2.10)$$

The wavelength of the electron is thus proportional to the inverse of the square root of the accelerating voltage:

$$\lambda = \frac{h}{\sqrt{2meV}} \quad (2.11)$$

For a wave to produce a diffraction pattern, the wavelength needs to be approximately that of the spacing of the lattice. For larger wavelengths or smaller lattice spacing, d , the angle of diffraction, θ increases:

$$n\lambda = 2d \sin(\theta) \quad (2.12)$$

where n is a positive integer describing the bright fringes of the interference pattern.

Considering the typical inter atomic distances in a crystal range from approximately $1\text{\AA}$ to $3\text{\AA}$, the corresponding electron acceleration voltage to produce these wavelengths are 150 V and 50 V respectively. Furthermore, the inelastic mean free path is close to a minimum for electrons in this range, seen in Fig.(2.3)[15], making LEED a surface sensitive technique. An electron

filter is also present in LEED apparatus to assist by removing unwanted inelastically scattered electrons. A retarding voltage is applied to a grid which the electrons pass through after being scattered from the crystal, electrons with energies below the retarding potential are filtered out.

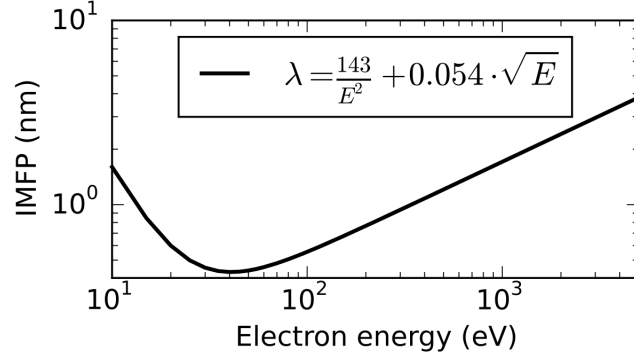


Figure 2.3: **Quantitative electron spectroscopy of surfaces:** A standard data base for electron inelastic mean free paths in all materials. Surf. Interface Anal. 1, 2–11 (1979).[15]. The mean free path is a minimum in the 50–150 V range, making LEED surface sensitive in this voltage range.

Eq.(2.12) indicates that the scattering angle is inversely proportional to the lattice spacing, therefore the diffraction pattern obtained is the reciprocal space Bravais lattice of the surface.

2.3 Density functional theory

2.3.1 Kohn-Sham equations

Kohn and Sham[16] (KS) introduce an approximate energy functional, composed of component energies that when summed approximate the Hamiltonian of the system. The components that cannot be calculated easily are approximated. Kohn-Sham introduce an auxiliary system where the electrons are non-self-interacting. These “electrons” are subject to an external potential known as the KS potential which is defined such that this system’s ground state density is the same as the system which we are trying to solve for. For this to hold, the true ground state density must be equal to the

ground state density of a non-interacting system. This is suspected, but not proven, to be true for all systems, no examples exist to the contrary. This non-interacting system is much simpler than the real interacting system and the ground state wave-functions may be expressed as single particle wave-functions known as Kohn-Sham orbitals. From these orbitals the Kohn-Sham equations can be obtained, however, they are simply stated here:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r) \quad (2.13)$$

ϵ_i is the orbital energy of the KS orbital ψ_i .

$$V_{eff}(r) = V(r) + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc}(r), \quad (2.14)$$

where the exchange correlation term $V_{xc}(r)$ is given by

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}. \quad (2.15)$$

The effective potential $V_{eff}(r)$ is composed of the external potential $V(r)$ and the exchange correlation potential, $V_{xc}(r)$, which depends on the exchange correlation energy, E_{xc} . E_{xc} is comprised of the exchange energy, due to the Pauli principle and the correlation energy, a quantum effect due to the antisymmetry of a many-electron wave-function.

The Kohn-Sham formulation thus succeeds in transforming the N -body problem into N single-body problems, each coupled *via* the Kohn-Sham effective potential. The single-particle Kohn-Sham eigenvalues and orbitals do not have any physical significance and are mere just mathematical tools used to determine the true ground state electron density with the exception that the ionisation energy of the system can be yielded from the eigenvalue of the highest occupied state.

The Kohn-Sham equations are solved in plane-wave DFT codes using self consistent field (SCF) calculations[17]. An initial guess is made for the electron density of the system. This electron density is then used to generate the external potential, $V(r)$. The KS single particle Schrödinger equation

(Eq.2.13) is solved to obtain the wave-functions, called KS-orbitals. These orbitals are then used to determine the new electron density. This process is repeated until the new and old electron densities converge to some threshold. The new and old electron densities may be mixed in order to assist in convergence.

2.3.2 Hellmann-Feynman theorem

A large number of properties depend on the total energy of a system, such as the bulk moduli, lattice constants and phonons to name a few. Other properties however depend more on the derivative of the energy rather than the total energy itself, an important example being the stress/strain in the crystal cell. The dimensions of a unit cell also need to be optimised. Minimising the stress and strain on the cell walls results in a converged unit cell. This can be achieved using perturbation methods such as the Hellmann-Feynman theorem[18]. In classical physics, the force acting on a particle at a distance of r is given by the derivative of the potential energy at that point:

$$F = -\nabla_r U(r) \quad (2.16)$$

The quantum mechanical equivalent of this is:

$$F = -\nabla_r \langle E \rangle \quad (2.17)$$

where:

$$\langle E \rangle = \langle \psi(r) | H | \psi(r) \rangle \quad (2.18)$$

provided that the eigenvectors $|\psi\rangle$ are normalised.

The Hellmann-Feynman theorem relates the derivative of the total energy E wrt some parameter, λ , to the expectation value of the derivative of the Hamiltonian wrt the same parameter as follows:

$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle \psi(\lambda) | \frac{\partial H}{\partial \lambda} | \psi(\lambda) \rangle \quad (2.19)$$

The forces are calculated from the ground state wave-functions. The Born-Oppenheimer approximation states that the electrons adapt instantly to the ionic configuration. The ionic positions are the parameters and the total energy is a function of their coordinates. To solve for the ground state, the total energy should be optimised wrt these coordinates. There are a number of ways to do this optimisation. The gradient of steepest descent is the easiest method to implement and is reliable in finding minima however it can be slow to converge and can get stuck in local minima before finding the minimum. For each ionic position, this method looks at the local energy landscape and takes a step in the line of steepest gradient. The Broyden-Fletcher-Goldfarb-Shanno (BFGS)[19] algorithm builds up a guess for the Hessian matrix. The Hessian matrix describes the local curvature of a multi-variable function, knowing this one can move from a point nearby the minimum directly to the minimum. This leads to an improvement in convergence however is more complex to implement. The exchange correlation energy depends on the derivatives of the electron density (Kohn-Sham orbitals). This term can be approximated in a number of ways, the most common being the local density approximation (LDA)[20]. It approximates the exchange correlation energy by simply taking the values of the electronic density at each point in space. LDA approximations are, in general, based on the homogeneous electron gas model, which assumes that the electron density is the same as a uniform electron gas of the same density. This approximation works best for systems where the electron density changes slowly. LDA can lead to issues in overestimating the correlation energy while underestimating the exchange energy[21]. Another approximation called the general gradient approximation (GGA)[22] attempts to remedy this by taking the gradient of the density into account for each point. This allows for systems, such as molecules, where the density rapidly changes to be accurately modelled. For elemental solids LDA gives lattice constants too small with errors up to between -2.5% and -4%, GGA based approximations perform better[23]. LDA is reported to produce good agreement with bulk lattice constants and bulk moduli of covalently bonded systems, however, the cohesive energies are considerably overestimated. GGA approximations predict overall accu-

rate cohesive energies for a diverse type of crystals and for metals[24]. No approximation can be considered universal as they all under and overestimate various bulk properties and so the ideal approximation depends on the user requirements.

2.3.3 Bloch's theorem

A solid effectively has an infinite number of electrons, to ease the calculations we take advantage of Bloch's theorem states that an electron's wavefunction may be written as:

$$\psi_{j,k}(r) = \mu_j(r)e^{ik \cdot r} \quad (2.20)$$

for an electron within a periodic potential, such as that of a crystal lattice. μ_j is a the potential function with the periodicity of the unit cell. j is the band index and k is the wavevector in the first Brillouin zone.

μ_j can be expanded using a Fourier series in terms of reciprocal space, with reciprocal lattice vectors G such that $G \cdot R = 2\pi m$ for an interger m and real space lattice vectors R . The wavefunctions can then be written as a linear combination of plane waves:

$$\psi_{j,k}(r) = \sum_G c_{j,k+G} e^{i(k+G) \cdot r} \quad (2.21)$$

with $c_{j,G+k}$ being the plane wave expansion coefficients.

At each k-point there will only be a finite number of occupied states and so considering a finite number of electrons is satisfactory, however we require an infinite number of k-points. The electron wavefunctions are almost identical for values of k that are sufficiently close, leading to a finite number of k-points required to properly sample all electrons

The net effect of using Blochs theorem is to reduce the problem of an infinite number of electrons to that of a finite number of k-points, chosen so that the Brillouin Zone is sampled to a reasonable degree.

The wavefunctions can now be expressed in terms of plane-waves for each k-point. The number of these plane waves can be limited to a finite

set. Higher plane wave energies are not typically as important as lower ones as the higher energy waves correspond to the relatively inert core electron. Selecting a cut off energy is common practice. The cut off is typically selected based on computational results so that the total energy of the system does not change significantly.

For a lot of practical applications using plane-wave DFT codes, the all electron model for an atom is an overly complicated system which requires a large amount of computational resources to solve. In order to correctly sample the inner core electrons a large number of plane waves is required (wave-functions oscillate rapidly in the core region). In reality, practically all of the important electronic contributions come from the valence electrons, with the relatively inert core electrons not contributing to physical properties such as bonding. For this reason the inner core electrons are bundled with the nucleus and this system is referred to as the ion core. The potential due to this ion core and the valence electrons is called a pseudopotential[25]. The pseudopotential is compared to an all-electron calculation to ensure that the wave-functions outside of the core are the same, this is norm-conservation. This approximation further reduces the computational requirements of simulating a system.

2.3.4 Calculation types and parameters

Plane wave codes, such as Quantum Espresso (QE)[26], offer a range of calculations to perform. In this section these calculations will be described along with relevant complementary information. The self consistent field (SCF) calculation is used to find the optimised ground state wavefunctions (KS-orbitals) for the atomic configuration and computational parameters provided in the input file using the Kohn-Sham equations and LDA, GGA or similar approximations. The code iterates through this method until the energy difference between steps is within a user defined energy threshold. Like most plane-wave codes, QE implements a mixing factor for the self consistent calculations, here the input and output electron density are combined in some ratio to produce an optimal estimate for the next iterative step.

This factor can play a significant role in the number of steps required to converge the calculation, too low and the calculation takes too long to reach the threshold, too large and it may constantly overshoot the local minimum, oscillating around it and not reaching the threshold. SCF calculations are used for k-point and plane-wave cut off energy convergence testing.

Another factor which needs to be considered for SCF calculations is the electron smearing parameter. In metals problems may arise when a band which is close to the Fermi energy is flat. In the iterative steps for a SCF calculation, the band may move up and down in energy. In 1 iterative step where the band is above the Fermi energy, it is completely unoccupied, if the next step was to lower the band below the Fermi energy it may be completely full, resulting in a large change to the electron density between steps. This can cause the calculation to oscillate between these two steps. A solution to this issue to “smear” the electron energies using Fermi statistics, artificially raising the temperature of the system. The electron Fermi function changes from a Dirac step function to one with Gaussian (or a similar) smoothing, the width/magnitude of which is determined by the smoothing parameter value. With smoothing present electrons may partially occupy the bands, giving a smoother transition between iterative steps, solving the associated oscillation problem. However, by introducing an artificial temperature the integrity of the calculation is brought into question. The KS equations calculate the ground state of a system and by artificially changing the temperature the solution diverges from that of the ground state. As a result, the lowest (minimising smoothing) value for electron smoothing should be used. The Mazari-Vanderbilt[27] cold smearing method is used in this study.

A “relax” calculation involves first conducting a SCF calculation followed by a force calculation using the “Hellmann-Feynman” method with the BFGS algorithm as stated in section 2.3.2. The atomic positions are adjusted appropriately and a SCF calculation is carried out again. This process is repeated until the atomic positions converge within some threshold set by the user. Relax calculations leave the cell parameters unchanged, only the atomic positions are allowed to vary. This calculation is used for relaxing atomic positions for a slab, that is a surface with a vacuum layer.

Variable cell relaxation, “vc-relax”, calculations on the other hand allow for both the cell parameters and the atoms positions to change. The stress/strain in the cell walls is minimised in the same way as for the atoms. This calculation is typically used to optimise parameters for the bulk system. Applying a vc-relax calculation to a slab can result in the vacuum layer collapsing.

The plane-wave cut off energy is an important parameter to consider when using plane wave codes. This value determines the largest Bloch wave to be simulated. Inner core electrons require a large energy to be probed, however as pseudopotentials are used in place of an all electron model, only the outer valence electrons to be sampled. These electrons have lower energies and so plane-wave cut off energies can be optimised to save considerable computational resources.

A pseudopotential is needed for the each atom that needs to be simulated, the Standard Solid State Pseudopotentials (SSSP) library[28] provides a wide range of pseudopotentials for each material, each with the results of a number of convergence tests so that a suitable pseudopotential may be selected with ease. The pseudopotentials are also compared to the all electron calculations in an equation of state plot. When selecting a pseudopotential, the rate and behaviour of convergence with respect to the cutoff energy should be considered as a large cutoff requires more computational resources and one which oscillates may cause issues if the cutoff needs to be adjusted for the specific material being studied. A pseudopotential and associated wavefunction cutoff energy is recommended by the authors of the site for each material, though based on the users needs this may not be suitable. The equation of state plots should be as close as possible in order to ensure that the pseudo potential wavefunctions replicate that of the all electron model as closely as possible.

The number of k-points required to accurately sample the Brilluoin zone depends on the size of the unit cell. If too few k-points are used, some important bands may not be sampled leading to inaccurate results. When the cell size of a system changes, the number of k-points required to sample the cell also changes. Since k-space is the inversion of real space, an increase

in the cell size in a real space corresponds to a reduction in the number of k-points required to accurately sample the Brilluoin zone in that dimension. The ratio of which is inverse, i.e doubling the cell size in the x direction allows for the k-point sampling in that direction to be cut in half. This is a general guideline and some testing of neighbouring k-point values should be evaluated. A suitable range of values for k-point sampling can be determined by multiplying the cell dimension ratios by a series of integers. The number of k-points takes the value of an integer, accordingly the number of the k-points will inevitably need to be rounded to the nearest integer. In cases where this value is close to $\mathbb{Z} \pm \frac{1}{2}$, both of the neighbouring integers may be tested.

Chapter 3

Surface Science of Metals & Metal Oxides

3.1 Surface science

Surfaces play a fundamental role in catalysis reactions and surface structure is crucial in a wide range of applications of nanoscale devices upon which most, if not all, modern technology is based. Bulk crystal structures and properties are well known from a variety of experimental methods such as X-ray diffraction and computational methods such as DFT have the ability to solve bulk systems with relative ease, however, the surface of a material differs both electronically and structurally from the bulk for a number of reasons which are caused by the breaking of crystal symmetry at the surface. The breaking of the crystal symmetry leads to the formation of surface states, lattice relaxations and surface reconstructions. Surface states are electronic states localised at the surface and are a result of the abrupt potential change caused by the transition from crystal to vacuum. While solving the Schrödinger wave equation for a bulk system, the solutions are real; for a finite slab both real and complex solutions exist. The surface states are described by the imaginary solutions. These states decay exponentially into both the crystal and the vacuum.

Lattice relaxations are observed close to the surface, the inter-layer spacing tends to differ to the bulk value as the distance to the vacuum decreases. Surface atoms may rearrange to more energetically favourable configurations, this process is temperature dependent and many reconstructions can be formed for a particular material depending on the preparation temperature and pressure. Surface reconstructions can result in significant changes to the electronic properties of a material as well as complicated surface structures. Famously, Si has been shown to have a complex 7×7 reconstruction which results in metallic properties, whereas bulk Si is an insulator[29]. Surface reconstructions are difficult to predict given the wide array of possibilities. Often, the newly reconstructed surface period is very large, such as the “29” and “44” reconstructions of Cu_2O [30, 31], making computational methods such as DFT resource intensive and often impractical, if not impossible, to compute.

The goal of surface science is to determine as accurately as possible the position and resulting electronic structure of the atoms in the surface region of the unit cell. A number of surface sensitive techniques have been developed in order to achieve this goal, notably STM described in section 2.1, LEED in section 2.2, XPS and ARPES to name a few.

3.1.1 Metal oxide thin films

Thin film metal oxides have found use in a wide range of applications across many fields such as spintronics, where Fe_2O_3 was first used as the magnetic material in magnetic storage devices such as computer hard drives[32]; the semiconductor industry for use in MOSFETs[33], in p-type transparent conducting oxides[34], in memristors[35]; and for thermoelectrics[36] to name a few.

The electrical, magnetic and optical (transmission/absorption) properties of a material can significantly differ when the material is in the form of a thin film. Thin film technologies make use of the fact that the properties can be controlled by the thickness parameter[37]. The choice of substrate for the thin film also has a significant influence on the initial growth orientation of

the thin film along with directly affecting the thin film electronically. The interface between two crystal systems has preferred growth orientations which depend on the lattice mismatch between the film and the substrate. This interface will thus determine the initial growth of the thin film. Minimising the mismatch is energetically favourable and will result in a particular crystal lattice plane growing.

A number of epitaxial relationships exist between the different terminations of crystal structures, however one in particular is used in this thesis and will now be focused on. In the case of the interface between BCC(110) and FCC(111) crystals, 2 epitaxial growth orientations are prevalent, the Nishiyama-Wassermann(NW) and Kurdjumov-Sachs(KS) orientations. The orientation realised depends on the ratio of the nearest neighbour distances, with a preference for the alignment of the most densely packed rows of each crystal plane[38]. The NW orientation has the BCC [001] and FCC $[\bar{1}\bar{1}0]$ directions parallel, while the KS relationship has 2 equivalent orientations, one with the FCC $[\bar{1}\bar{1}0]$ and BCC $[\bar{1}11]$ directions aligned, the other a rotation of the FCC lattice by 5.26° . The most desirable orientation relationship has been determined based on the interfacial energy between FCC(111) and BCC(110) lattices. When the atomic spacing ratio is in the range of $0.83 < \alpha < 0.88$ and $1.02 < \alpha < 1.19$, the NW relationship will appear preferentially, whereas the KS relationship will appear in the region of the atomic spacing ratio $0.88 < \alpha < 0.96$ [38]. Both orientations are displayed in Fig.(3.1).

The interface is a strained region due to the lattice mismatch. This strain can cause the lattice constant of both the substrate and the thin film to change compared to the respective bulk values. The magnitude of the strain increases as the film thickness increases and can be seen up to 100 nm from the interface depending on the lattice misfit, nucleation energy of dislocation and available slip systems as determined by the Schmidt factor[40]. The strain can be relieved by relaxations in the form of dislocations. Larger lattice misfits result in relaxations *via* dislocations at smaller film thicknesses. Lattice mismatches of less than 7% are considered small and films typically grow with one-to-one matching of lattice planes in this case[41].

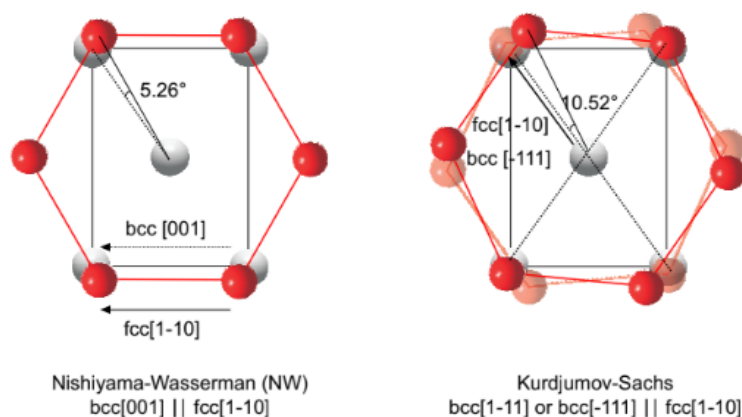


Figure 3.1: **Epitaxial relationships for FCC(111)/BCC(110) interface.**[39] The Nishiyama-Wasserman relationship is depicted on the left, which the Kurdjumov-Sachs is depicted on the right. Two equivalent orientations are possible for the Kurdjumov-Sachs relationship.

3.2 Oxidation mechanisms

The initial oxide layers which form on metal surfaces can protect the underlying metal from further oxidation. The high electronegativity value of oxygen makes it very reactive and for this reason most metals form oxides at room temperature. These oxides come in a wide range of stoichiometries and phases. Oxides which form at low temperatures tend to be amorphous in nature, these structures allow oxygen ions to pass through with relative ease compared to a densely packed crystalline system.

Assuming a clean metallic surface in UHV conditions, oxidation begins when the surface is exposed to molecular oxygen. Oxygen adsorption may occur in two ways, physisorption and chemisorption. Physisorption involves Van der Waals forces weakly binding the oxygen to the surface. Chemisorption involves the oxygen atoms exchanging/sharing valence electrons with the metal surface atoms, forming chemical bonds, resulting in an oxide compound being formed. Chemisorption involves the oxygen molecules disassociating in order to form their new metal bonds. Initially oxide growth is of the form of a number of oxide clusters which form through chemisorption. As the density of these clusters increases, a more energetically favourable option

arises, the clusters coalesce to form a complete oxide layer on the surface. This oxide layer can then act as a barrier to further oxidation. If this is the case, Cabrera-Mott theory describes the process which leads to the oxide layer growing in thickness.

3.2.1 Cabrera-Mott theory

If a barrier to oxygen penetration is present, Cabrera-Mott theory describes the growth kinetics of a thin film oxide layer [42]. The first assumption made in the theory is that electrons can freely pass from the metal to ionise adsorbed oxygen atoms *via* the tunnelling mechanism causing an equilibrium of the Fermi levels of the metal layer and the adsorbed layer. This results in a large, positive, uniform electric field being formed across the oxide layer created by a positive surface charge on the metal and a negative one from excess oxygen ions on the oxide/gas interface. This potential is referred to as the Mott potential and is the driving force for slow ionic transport through the oxide layer, i.e., from the surface to an interstitial site. The Mott potential determines the height of the barrier to ion diffusion through the oxide by lowering the energy barrier relative to the zero potential case. Both metal and oxygen ions may diffuse through the oxide layer in the growth of the oxide film[43]. Metals which oxidise by the Cabrera-Mott mechanism have, or develop, a barrier to oxygen penetration on the surface, while metals which do not oxidise by the Cabrera-Mott mechanism do not have a barrier to oxygen penetration on the surface to begin with or after the oxide has formed. Metals such as Ta, Cr, Ni and Nb exhibit Cabrera-Mott kinetics[44]. A number of studies report Cabrera-Mott kinetics for Cu[45, 46] however linear[47, 48] and parabolic growth[49] has also been observed, the temperature at which oxidation occurs is a factor in the growth mechanism[50, 51]. As the oxide layer increases, the electric field strength diminishes and the ion migration, and thus the film growth, slows down and eventually stops, following an inverse logarithmic rate law:

$$\frac{1}{d} = A - B \ln(t) \quad (3.1)$$

where d is the oxide film thickness, t is exposure time and A and B are fit parameters related to the metal cation formation. In the case of Cu, this thickness is up to 7.3 nm[52].

Studies on Aluminum oxide thin films, while supporting the basic assumptions of Cabrera-Mott theory, indicate a different limiting factor in the thickness of the thin film growth[53]. The absorption energy of oxygen molecules decreases which limits the supply of oxygen to the interface for oxide growth. A secondary effect of this is the breakdown of the mott potential when oxygen does not absorb.

3.3 Oxygen diffusion through an oxide layer

The penetration of oxygen atoms through metal and metal oxide surfaces has received attention from theorists[54, 55]. The energy barrier for oxygen incorporation depends on the oxygen adatom distance to the underlying surface layer and the bond lengths of the atoms within the layer which the oxygen adatom will penetrate, and hence, the substrate electron density. A larger electron density results in a larger barrier. Several factors affect the electron density at the point where the adatom crosses into the substrate, such as the lattice constant, lattice structure and material. In transition metals and their oxides, a 10% increase in lattice constant reduces the barrier by almost 30% [55]. Surface relaxations thus play an important role in determining the substrate electron density.

Several different crystal lattice structures have been studied[54, 55]. The rock-salt structure is very homogeneous and close-packed, leading to high energy barriers. While in the rutile, bixbyite, and spinel structures there are “open channels”, which can be envisioned as vacancies, through which the oxygen can diffuse easily and thus these structures have lower energy barriers for oxygen incorporation [55]. Introducing a defect in the third layer of NbO(111) reduces the energy barrier from 4 eV to 1.2 eV[55]. Furthermore, the presence of an oxide overlayer can increase or decrease the barrier, depending on the induced modification of the metal lattice substrate. For example, in the case of Nb(110), the barrier increases from 1.2 eV to 7.4 eV

after oxidation. Whereas the barrier for incorporation into the Cu and CuO₂ lattices are 0.9 eV and 0.04 eV [54, 55], respectively.

The underlying theory behind inducing an oxygen atom to overcome a potential barrier, such as the one opposing oxygen penetration through a surface, using an electric field is outlined. The applied electric field results from applying bias voltage between two metallic conductors such as a STM tip and a conductive sample. When a conductive metal is terminated by a metal-oxide layer, additional oxygen on the surface must overcome a potential barrier, W , in order to penetrate the oxide layer in order to form an oxide at the interface. The probability of the oxygen adatom overcoming this barrier and penetrating the surface layer to the oxide layer below depends on the frequency of attempts (f , the phonon frequency) to overcome the barrier and the time interval, Δt , in which attempts are made.

$$P = f \Delta t A \exp\left(-\frac{W}{k_b T}\right) \quad (3.2)$$

A is the pre-exponential factor. The electric field generated by applying a negative bias to the tip with respect to the surface reduces this barrier. If the sample metal surface is taken to be a reference point at 0 potential, the potential barrier height reduction can be written as $W - q\psi$, where q is the effective charge of an oxygen ion and ψ is the electric potential at the point of the oxygen ion. It follows that the probability of the oxygen adatom penetrating the surface in the presence of electric field generated by the STM tip is :

$$P = f \Delta t A \exp\left(-\frac{W - q \psi}{k_b T}\right) \quad (3.3)$$

At the typical parameters of tunneling (tip apex is of the order of tens of nanometers according to Scanning Electron Microscope (SEM) experiments and the tip-surface distance, d , is approximately 1 nm) the electric potential can be approximated by a simple model(Fig.3.2) in which we consider the tip and surface as a parallel-plate capacitor. Then the potential at a distance of

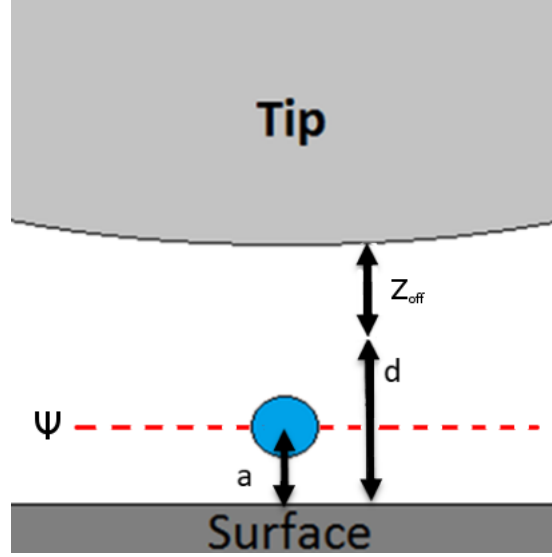


Figure 3.2: **Model of STM tip and surface.** The tip is modelled as a large spherical conductor and the surface is a perfect ground. The tip surface separation is d . The electric potential, Ψ , is calculated at the broken red line, a distance of a from the surface, corresponding to the distance between the oxygen adatom and the topmost metal layer.

a from the plate when a bias of V is applied is given by ψ :

$$\psi = V \frac{a}{d + Z_{off}} \quad (3.4)$$

a corresponds to the distance between the oxygen adatom and the metallic surface. d is the tunneling distance, determined by the tunnel parameters, while Z_{off} is any additional tip-surface distance offset applied. Substituting for ψ in Eq.(3.3), taking the logarithm of both sides and solving for the V gives the following:

$$V = \frac{d + Z_{off}}{q a} \cdot \left(-k_b T \cdot \ln(\Delta t) + W + k_b T \cdot \ln\left(\frac{P}{f A}\right) \right) \quad (3.5)$$

$$\therefore V \propto Z_{off} \quad (3.6)$$

indicating that an increase in applied offset causes the threshold voltage to increase linearly.

3.4 Metal/metal oxide surface science

3.4.1 Molybdenum & its Oxides

Mo

Molybdenum is a BCC transition metal with atomic number 42, it has the 7th highest melting point of all the elements at 2896 K. The unit cell lattice constant is 3.147 Å. The (110) plane is the most densely packed, being 91.8% that of the corresponding hexagonal close packed (HCP) surface[56]. The surface structure is a distorted hexagonal pattern which can be viewed as an elongation of the hcp cell in the [001] direction. The distorted hexagonal is formed from each atom having 4 nearest neighbours and 2 additional neighbouring atoms which are 15.5% further away due to the elongation of the cell. The surface view of a BCC(110) crystal is displayed in Fig.3.3.

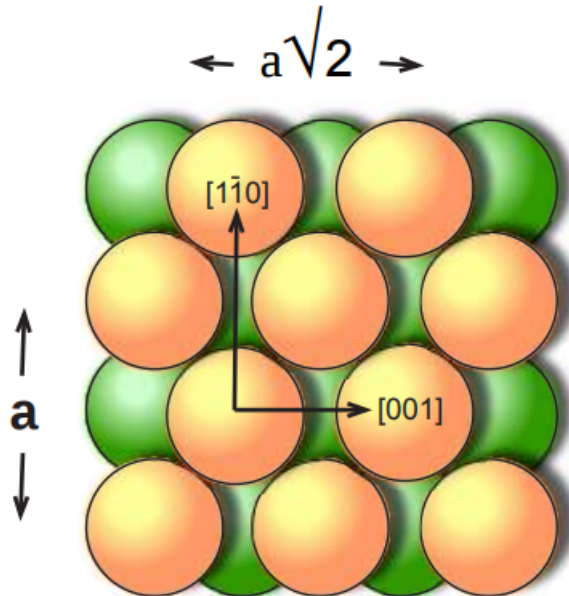


Figure 3.3: **Surface view of the (110) terminated BCC crystal.** The surface structure is a distorted hexagon[57]

Molybdenum does not readily oxidise in air at 300 K, however, oxidation will occur at elevated temperatures[58]. 9 oxidation states exist for Mo, as it

can form a number of different oxide compounds, the highest oxidation state is VI (MoO_3). MoO_3 is a precursor to virtually all other Mo compounds, with the others being formed by reduction of the MoO_3 at elevated temperatures or chemical reduction with H_2 . MoO_3 has an orthorhombic structure with the (010) plane being the most stable[59]. This plane terminates with O ions. MoO_3 is an insulator and is inert at RT. There are many stable oxides between MoO_3 and MoO_2 ; $\text{Mo}_{18}\text{O}_{52}$, $\text{Mo}_{17}\text{O}_{47}$, Mo_9O_{26} , Mo_8O_{23} , Mo_7O_{20} , Mo_6O_{17} , Mo_5O_{14} , Mo_4O_{11} [60]. The MoO_3 unit cell has been understood since 1931[61], it is composed of distorted octahedra with a Mo atom at the centre of each octahedron. The 6 oxygen atoms of a the octohedra are not all equivalent, 2 are triply coordinated, 2 are asymmetrically bonded to 2 neighbouring Mo atoms and 2 are singly coordinated.

MoO_2

MoO_2 crystallises into a deformed rutile structure. Metal atoms are surrounded by 6 oxygen ions to form MoO_6 octohedra which are joined by shared corners. In a perfect rutile structure, the metal ions are equally spaced; however, in MoO_2 , the metal ions form dimers which represents a distortion of the MoO_6 octohedra and thus deformation of the ideal rutile structure. The symmetry of the system is thus lowered from tetragonal (rutile) to monoclinic[62]. The lattice constants of the distorted rutile MoO_2 are 0.486 nm and 0.282 nm for the a and c -axes, respectively [63]. MoO_2 is metallic and chemically stable. The inter atomic spacing of atoms in the (010) plane of MoO_2 is <1% different to that of Mo(110).

$\text{MoO}_2/\text{Mo}(110)$

Epitaxial molybdenum dioxide growth on a Mo(110) single crystal has been achieved by Radican *et al.* [64, 65] and others[66, 67]. A clean Mo(110) surface is initially prepared through annealing in UHV following the procedure established by Haas and Jackson[68]. Once the clean and ordered surface was verified by atomic emission spectroscopy (AES) and LEED respectively, the oxidation process began. The Mo(110) sample was annealed at 1270 K

in a partial pressure of 1×10^{-6} Torr for 1 minute, and resulted in a surface oxide.

Auger analysis reveals that Mo and O are in a ratio of 1:2 indicating the presence of a MoO_2 overlayer[65]. LEED measurements indicate the presence of 2 orthogonal overlayers, vectors perpendicular to the MoO_2 surface normal are aligned in the $[1\bar{1}\bar{3}]$ and $[1\bar{1}3]$ directions of the underlying $\text{Mo}(110)$ plane. These overlayers form a row structure in the $[1\bar{1}\bar{3}]$ direction with a period 17 times larger than that of the underlying Mo layer.

The oxide overlayer is concluded to be MoO_2 . The (010) plane of MoO_2 is parallel to the $\text{Mo}(110)$, and hence, the MoO_2 is (010) terminated. It exhibits an O-Mo-O trilayer structure and forms well-ordered oxide nanorows which appear in STM images as protrusions with depressions in between, an image extracted from Radican[64] can be seen in Fig.(3.4). These rows follow the $[1\bar{1}\bar{3}]$ direction of the $\text{Mo}(110)$ substrate.

Polar metal-oxide interfaces such as this, with oxygen atom terminations are generally the most stable, with adhesive energies an order of magnitude less than that for a non-polar surface. It has also been shown that for transition metal oxides, through a combination of LEED measurements and DFT calculations, that an O-M-O tri-layer structure can be the most energetically favoured[69–72].

The rows in the $[1\bar{1}\bar{3}]$, seen in Fig.(3.4) are the result of a Moiré pattern between the coincidence lattices of the MoO_2 and $\text{Mo}(110)$. The rows have a period of 23 ± 1 Å. High resolution STM imaging of the rows, depicted in the inset of Fig.(3.4), show a series of bright and dim spots, which are concluded to be due to the surface terminated oxygen atoms.

The DFT model of Radican *et al.*[64] altered the MoO_2 unit cell by skewing it by 4° , this reduced the a axis by 3% and increased the c axis by 10%. In doing so, the oxide cell $\text{MoO}_2(010)$ could fit to the $\text{Mo}(110)$ substrate unit cell. An O-Mo-O tri-layer was placed atop a four layer Mo substrate, with all but the bottom 2 Mo layers allowed to relax during the calculations. These calculations indicated the optimised configuration for the interfacial oxygen atoms. There are 4 potential sites for the oxygen atoms, 2 bridge sites, a site on top of a Mo atom, and a 3-fold hollow site. Both bridge sites relaxed to

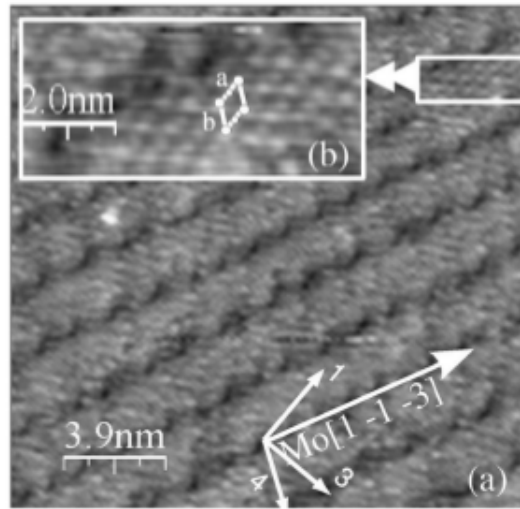


Figure 3.4: **STM image depicting surface structure of $\text{MoO}_2/\text{Mo}(110)$.** The row structure runs in the $[1\bar{1}3]$ direction.[64]

the 3-fold hollow site. Comparing experimental and simulated STM images for the top and 3-fold oxygen sites allows the correct site to be identified. Oxygen in the 3-fold sites resulted in a contrast difference between sites and a row structure forming as seen in experiment, whereas, the top site resulted in little contrast difference and no row structure. This result is further supported from an energetic standpoint, the 3-fold sites have the lowest energy per atom value as calculated from the DFT simulations.

The oxygen atoms on the surface were not observed to be of the same brightness, some appear bright, some dim and some are not visible when imaged with the STM tip at 0.05 V. The model for the 3-fold sites sheds light on these differences. Bright oxygen atoms correspond to O surface atoms which bridge the Mo-Mo dimers, dim O surface atoms bridge between the Mo atoms in each dimer and finally the missing O atoms correspond to the O surface atoms which have just a single bond to the underlying Mo atom.

Okada *et al.*[66] conducted a DFT study with much larger unit cells and allowed the surface to relax. While they also found that the 3-fold hollow site was the most stable, they identified that multiple interfacial oxygen sites

may coexist, namely in both of the bridge sites and the top site. The model is presented in Fig.3.5. Furthermore, simulations using their model produced simulated STM images that also produced some features which are observed to reside between the bright rows in experimental images. These features appear as stripes in the $[11\bar{3}]$ and $[\bar{1}11]$ directions of the Mo bulk. These features were also observed by Krasnikov *et al.*[73].

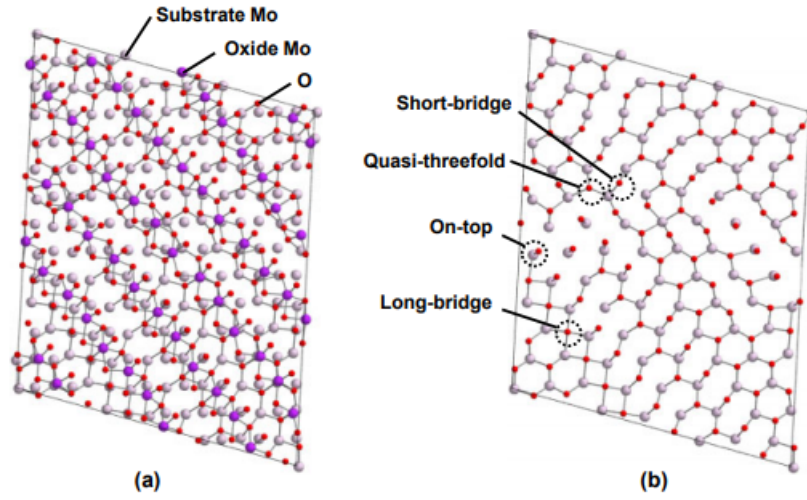


Figure 3.5: **Top view of large scale DFT model of $\text{MoO}_{2+x}/\text{Mo}(110)$ produced by Okada *et al.*[66]**(a) All atoms in the unit cell are indicated, (b) interfacial Mo and interfacial O atoms are indicated to clarify the difference in the kinds of oxygen occupation sites.

$\text{MoO}_{2+x}/\text{Mo}(110)$

Krasnikov *et al.*[73] prepared the MoO_2 surface in a similar fashion to Radican *et al.* and found that allowing it to cool in an oxygen partial pressure lead to an oxygen-rich surface layer. Oxygen adatoms bind to the top of the bright rows in the $[11\bar{3}]$ direction. It was found that these excess oxygen atoms could be removed from the surface if a sufficiently large bias voltage is applied between the STM tip and the surface. Scanning the surface at a low bias voltage (< 1.5 V for $I=1$ nA) allows for an STM image to be recorded without removing oxygen adatoms, the oxygen adatoms on the surface can

then be identified. The tip is then positioned over an adatom, and the feedback switched off so that the tip height above the surface remains constant. A large bias ($\approx 2\text{ V}$) is then applied to the tip for some duration. The surface is once again scanned at the lower bias voltage. Circular regions void of oxygen adatoms are present on the surface at the tip locations where a sufficiently large voltage was applied between the tip and the surface. The adatoms on the $\text{MoO}_{2+x}/\text{Mo}(110)$ surface appears as protrusions in STM imaging, removing them resulting in a darkly contrasted region. Fig.(3.6) depicts 3 images of the $\text{MoO}_{2+x}/\text{Mo}(110)$ following controlled pulsing: (a) “TCD” is “written” on the surface. (b) “NANO” is “written” on the surface. (c) “SFI” is “written” on the surface.

Karasnikov *et al.* investigated the dependence of the pulse time on the threshold voltage, which is the minimum voltage required to remove an individual adatom when the tip is directly over it for a given tip. They showed that the threshold voltage depends on the tip-surface distance and the pulse duration. Regardless of the offset applied to the tip before applying a pulse (up to 1 nm), a pulse duration of 0.5–1 second was sufficient to remove the adatoms. Karasnikov *et al.* conducted their experiments within the tunneling regime. They concluded that inelastic tunneling electrons induce desorption of the oxygen adatoms from the surface to the vacuum.

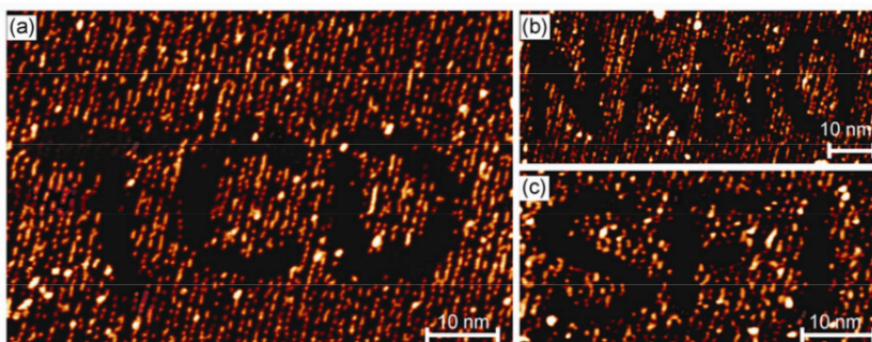


Figure 3.6: **STM images of the $\text{MoO}_{2+x}/\text{Mo}(110)$ surface following pulsing.** Oxygen adatom appears as bright protrusions in STM images, removing them results in a darkly contrasted region. By selectively removing adatoms, one can “write” on the surface. (a) “TCD” - Trinity College Dublin. (b) “NANO” (c) “SFI” - Science Foundation Ireland.

Using the Vienna Ab initio Simulation Package (VASP) simulation package Karasnikov *et al.* modeled both the MoO_2 surface and the overoxidised MoO_{2+x} surface. These calculations produced simulated STM images which showed good agreement with STM measurements when comparing the relative intensities and locations of the protrusions, which are due to the excess oxygen atoms. An interesting observation from the resulting fully relaxed slab with excess oxygen adatoms, is that the molybdenum atom beneath the oxygen adatom relaxes from its position in the Mo lattice plane towards the oxygen layer above which exposes a gap in the Mo layer. The MoO_2 and MoO_{2+x} models are shown in Fig.(3.7c&d) respectively.

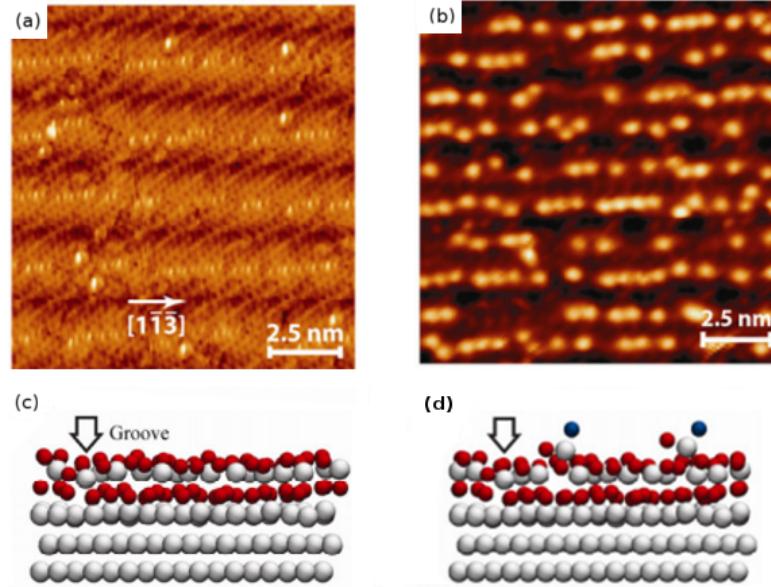


Figure 3.7: **STM images & DFT models of the $\text{MoO}_2/\text{Mo}(110)$ surface.** (a) STM image of the $\text{MoO}_2/\text{Mo}(110)$ surface displaying the bright and dark row features. (b) STM image of $\text{MoO}_{2+x}/\text{Mo}(110)$, the bright features on the bright rows correspond to oxygen adatoms[73]. (c) DFT simulation of $\text{MoO}_2/\text{Mo}(110)$ surface (d) DFT simulation of $\text{MoO}_{2+x}/\text{Mo}(110)$ surface. Note the Mo (white) atom directly below the O adatom (blue) is shifted from its lattice position. Oxygen atoms in the oxide are depicted in red.

The contribution of the electric field to the removal of oxygen adatoms was considered by Karasnikov *et al.*[73]. A simulation of a single MoO_3 cluster with fixed atomic positions for the Mo and two oxygen atoms in

a high electric field was conducted. The electric field was applied in both directions parallel to the Mo-O bond, up to a field strength of $1.25 \text{ eV/\AA}$. The goal was to break the bond between the mobile oxygen atom and the remaining cluster, releasing it to the vacuum. The electric field could not break the Mo-O bond and thus was ruled out as playing a role in the removal of oxygen adatoms.

Fixing the atomic positions meant that the mobile O atom could never pass through the cluster, with this consideration in mind this work aims to determine whether adatom removal outside of the tunneling regime is possible when considering O diffusion through the MoO_{2+x} layer.

3.4.2 Niobium & its Oxides

Nb

Nb is used in a wide range of applications- in high performance metal alloys, the addition of Nb yields desirable increases in properties such as strength and toughness which sees use in pipelines for gas and steel as well as in high-rise buildings. The terminating passive oxide layer of pure Nb and Nb alloys provide corrosive resistant and high melting point protective layers for use in space, nuclear and aircraft applications. Nb has the highest superconducting critical temperature of the elements at 9.3 K and Nb based compounds hold some of the highest superconducting critical temperatures overall.

Niobium is a BCC transition metal with atomic number 41, located one place left of Mo in the periodic table. The unit cell lattice constant is $2.876 \text{ \AA}$ [74]. Niobium, along with molybdenum and other transition metals, has an atypical shell filling order where the final electron occupies the 3d shell instead of filling the 4s shell, resulting in a $[\text{Kr}]4d^4 5s^1$ shell configuration. This extra electron in the d-shell leads to stronger metal-metal bonding which results in a higher melting point, boiling point and enthalpy of atomisation[75]. The next elements in the groups, Ta and W, share these properties, with W having the highest melting point of all elements. As with molybdenum and other BCC crystals, the (110) plane of Nb is a distorted hexagonal lattice.

Niobium oxidises very slowly in air due to an initial protective oxide layer forming which protects the material from further oxidation, the thickness of this layer is reported to be roughly 30Å and can be removed by annealing the sample at 1750 K for 30 minutes at 10^{-9} Torr, followed by a flash at 2150 K[76].

Oxygen is soluble in the Nb lattice at elevated temperatures (> 750 K) and solubility increases up to 2150 K with the oxygen occupying the octohedral sites in the lattice[77]. This dissolved oxygen diffuses from the bulk to the surface when annealed. Once at the surface, if the annealing temperature is not sufficient for the oxygen atoms to desorb from the surface (< 2000 K), an oxide layer (NbO) can form.

Many oxides of niobium exist. Lower coordination oxides are NbO, NbO₂ and Nb₂O₅ with a lot of homologous oxides between NbO₂ and Nb₂O₅. The oxides of Nb typically grow in multiple phases and numerous non-stoichiometric oxides exist. When an oxide layer grows, a wide range of oxides may co-exist and isolating a particular oxide is difficult. The properties of these oxides vary from the metallic NbO to the wide band-gap (insulating) Nb₂O₅, a result of the varying amounts of free electrons in their 3d orbitals due to binding with oxygen 2p orbitals.

NbO

NbO is a cubic metallic metal-oxide with a lattice constant of 4.261Å[78]. The lattice structure resembles that of the rock-salt structure but with one atom of each element missing from the unit cell, leaving a cell with 1 in 4 atomic positions vacant. The coordination of each element is reduced to a square planar geometry. In NbO, Nb atoms are arranged in octohedra, forming clusters of Nb₆, similar to those in pure Nb. These Nb₆ clusters are considered the reason behind NbO's metallic conductivity[79]. Strong covalent bonds are present between metal centres. NbO also has a high melting point at 2200 K (2470°C). Furthermore, NbO shares superconducting properties with Nb, however its critical temperature is much lower at 1.7 K[80]. Modifying the stoichiometry towards a more Nb favoured oxide leads to an increase in

the critical temperature, conversely increasing the oxygen content increases the resistivity. This trend is also true for most other properties such as electrical conductivity and the melting point[81]. The Nb atoms in the (111) plane of NbO has similar interatomic distances to the atoms in the Nb(110) plane, with a mismatch of 4%.

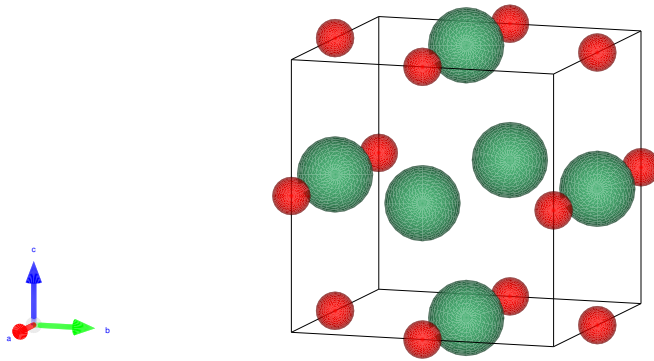


Figure 3.8: **Model of NbO unit cell.** Oxygen atoms depicted in red, while Nb are green. NbO is cubic with a lattice constant of 4.261Å[78]

NbO(111)/Nb(110)

NbO(111) has been reported to grow epitaxially on Nb(110)[39, 82–84]. Annealing an Nb(110) sample at 850 K in an UHV environment liberates dissolved oxygen from the bulk which forms an ultra-thin NbO(111) film at the surface. The NbO(111) oxide layer takes on an interesting surface reconstruction which has received some attention from a number of sources with a variety of experimental methods and some theoretical modelling. In this section, the current knowledge relating to this particular surface termination is reviewed in detail.

Atomically clean Nb(110) samples are difficult to obtain due to the high melting point of NbO of 2200 K. Studies involving cleaning a Nb(110) crystal in UHV *via* argon sputtering and annealing cycles up to 1950 K report that

oxygen is still present on the surface following the procedure. AES measurements give an O:Nb peak height ratio of 0.2 ± 0.02 [82, 83]. This is reported to be a thin film of NbO covering the Nb metal [83]. Photoemission spectroscopy shows two pairs of $3d^{5/2}$ and $3d^{3/2}$ peaks, one pair corresponds to metallic Nb while the other pair of peaks is shifted by 1.4 eV from the metal pair. This shifted pair of peaks is associated with the Nb 3d levels of $\text{NbO}_{x \approx 1}$ as the stoichiometric shift is reported to be 1.8 eV [85]. The thickness of the oxide layer was estimated from the variation in the photoemission intensity of the Nb $3d^{5/2}$ peak of the interface layer as a function of collection angle [85]. Measurements showed that there were 1.4 ± 0.3 monolayers of Nb present in the oxide layer. This concentration of Nb corresponds to an O-Nb-O tri-layer structure with some additional fractional monolayer of Nb atoms.

LEED measurements indicate the presence of a superstructure with two orientations [82]. Large regions of the crystal can be observed to contain just one of these orientations. Focusing on one of these orientations, Arfaoui *et al.* [82] deduced some structural properties of the NbO film. A distorted 6-fold symmetry implies the presence of a distorted NbO lattice with the [110] of NbO(111) parallel to the [111] direction of Nb(110). Four diffraction spots along the Nb [111] direction indicates that the oxide superstructure has a period four times that of Nb. Along one of the [111] directions there is a four period spot in LEED, indicating a superstructure period of four times that of the underlying Nb layer.

There are two possible epitaxy growth relationships between FCC and BCC structures, Kurdjumov-Sachs (KS) and Nishiyama-Wassermann (NW) as discussed in section 3.4.2. Here, NbO is considered to be a defected FCC structure, missing 1/4 of its atoms. Both orientations are presented in Fig.(3.1). NW and KS relationships have been reported for NbO(111)/Nb(110) [82, 86], however, reports supporting NW dominate the literature for the termination of NbO(111)/Nb(110) of interest to this study [39, 84, 87, 88] and is seen again in Fig.(3.10a).

High resolution STM images of NbO(111)/Nb(110) reveal a surface terminated with regular, repeating, small protrusions of approximately 2–3 nm in length, depicted within the blue box in Fig.(3.9). These protrusions are

NbO nanocrystals. Closer inspection of the crystals reveals that they are composed of approximately 6–9 small round features, each of equal size. The model of this structure is depicted in Fig.(3.10b) and follows the rigid and atomic models proposed by Arfaoui *et al.*[82, 85]

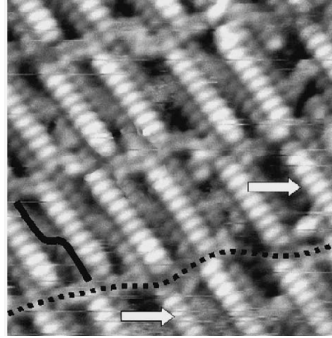


Figure 3.9: **STM image indicating surface structure of NbO terminated Nb(110)**[85]. $7 \times 8.5 \text{ nm}^2$ STM image indicating nanocrystals (White arrows) and the channel separating them (dashed black line). The nanocrystals are composed of a series of approximately 6-9 protrusions.

Each of these round features is thought to be a Nb atom protruding from the surface. The coverage of Nb atoms on the surface is $1/3$ of a monolayer. These terminating Nb atoms occur along the NbO[111] and Nb[110] directions. As inter atomic distances in both crystals are similar (NbO(110): 0.298 nm and Nb(111): 0.286 nm), there exists a small NbO/Nb misfit of 4% along the NbO [110] direction. This misfit has been shown to govern the maximum length of the nanocrystals[82]. There is also a -4% mismatch in the perpendicular [112] direction. Arfaoui *et al.* proposes that the terminating Nb atoms stabilise the NbO nanocrystal on the Nb(110) lattice[85], as the strong interaction between metal atoms expand the nanocrystal along the [112] direction, reducing the lattice strain.

The length of the nanocrystals is largely consistent in the centre of large terraces and only varies significantly near the step edges. The nanocrystals are observed to align in 2 directions as indicated by the LEED measurements. Nanocrystals in the same domain are aligned in parallel and separated by a quantised distance, dictated by the underlying Nb lattice. The minimum distance between nanocrystals corresponds to the spacing between 4 of the

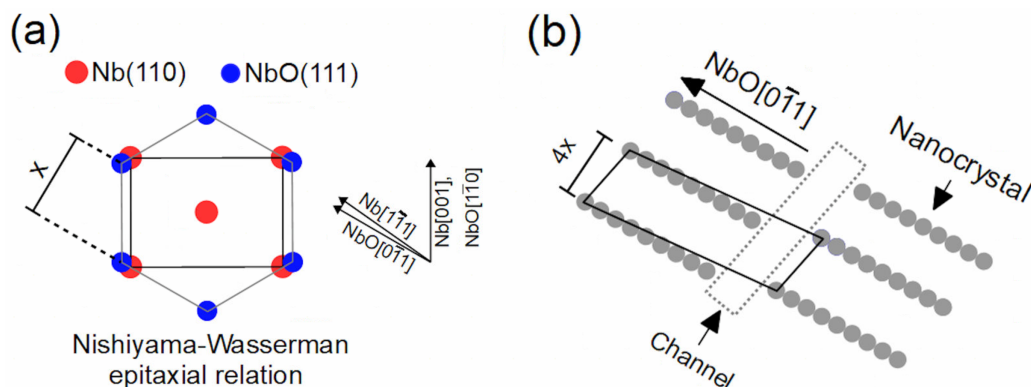


Figure 3.10: **NbO(111)/Nb(110) epitaxial relationship and nanocrystal schematic.** (a) The Nishiyama-Wassermann epitaxial relationship between the Nb(110) and NbO(111) lattices. The schematic depicts the unit cells and not all the atoms therein. The Nb[001] aligns with one of the NbO[110] directions ([110] is chosen in the schematic). The other two NbO[110] directions are rotated by 5° with respect to the two Nb[111] directions of the Nb(110) plane. It is these two NbO directions which are the orientation of the nanocrystals, one of which is depicted in (b). (b) The Nb atoms which terminate the NbO nanocrystals are depicted. The depicted rhombus defines the arrangement of these nanocrystals. Slight variations in the length of and the distance between nanocrystals are commonly observed. The area separating stacks of parallel nanocrystals, termed a channel, is highlighted.

underlying Nb rows in the NbO[112] direction, with subsequent distances increasing by 1 atomic Nb spacing at a time[82]. This period is in agreement with the four-period seen in LEED and the pseudocoincidence of the NbO and Nb lattices.

Adjacent nanocrystals form “strips/bands”, referred to as lamella. The lamella are approximately the same width, due to the fixed length of the nanocrystals, however, due to the nanocrystals’ shift relative to one another they can be irregular in shape. The disordered region separating lamella are referred to as “channels”. Both the lamella and channel can be seen in Fig.(3.9) with green lines on the border of the structures. The schematic model is shown in Fig.(3.10b). It should be noted that nanocrystals in adjacent lamella do not line up with one another, they are shifted by at least

1 substrate Nb row spacing. The exception to this is, again, near the step edges where nanocrystals can be seen to align. The breaking of the regular rod size and orientations at and near the step edges is thought to be the result of relaxations induced by the step edge.

This rigid model provides an insight into the basic structure of the nanocrystal however it has a number of issues. Along with the length of the nanocrystals, the rigid model does not describe the nature of the poorly ordered channel separating the lamella. Arfaoui's STM and LEED results[82] indicated a distorted hexagonal cell, with the NbO layer rotated relative to the underlying Nb layer, this observation implies that a relaxation is taking place, most likely to reduce the stress/strain in the nanocrystals due to the misalignment. With this model in mind, STM images of the small features which the nanocrystals are comprised of, correspond to a combination of the Nb terminating atoms and the bonds to either the underlying Nb row or the nearest neighbour oxygen atoms. NbO is metallic and so it is difficult to discern from pure Nb.

Razinkin *et al.*[84, 89, 90] also conducted STM, X-ray photoelectron spectroscopy and X-ray photoelectron diffraction (XPD) of the NbO terminated Nb(110) surface. STM measurements are in agreement with previous studies. Razinkin determined the thickness of the NbO terminating layer to be 0.5 nm, in agreement with an O-Nb-O tri-layer with an $\approx 1/3$ monolayer termination of Nb. XPS analysis of the O 1s peaks indicates the presence of two chemically nonequivalent states of oxygen; the first, termed O_I is reported correspond to chemisorbed oxygen on the Nb(110) surface while the O_{II} peak corresponds to the oxygen in the NbO terminating layer. XPD experiments allow for the estimation of the structural positions of atoms on the surface. A model of the two distinct oxygen atom locations on the surface was produced using this result and is depicted in Fig.(3.11). The chemisorbed O_I atoms are located on the surface in the channels between the nanocrystals, and the O_{II} atoms comprise the terminating NbO nanocrystals in the Nb[001] direction.

The NbO terminated Nb(110) system is of interest due to its wide range of applications, however it's structure and electronic properties are not fully known, as such further study is required. This work aims to determine the

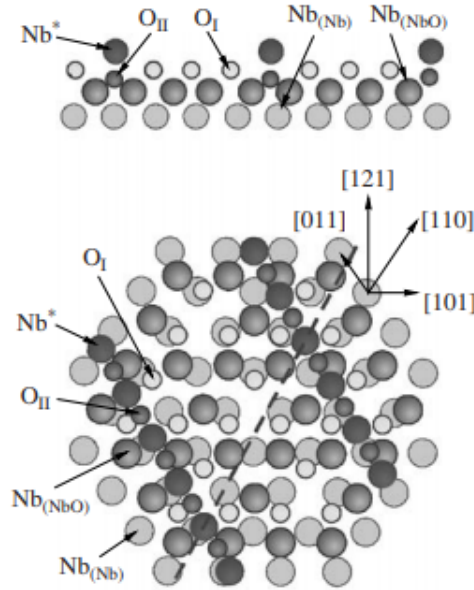


Figure 3.11: **Model of the NbO/Nb(110) surface by Razinkin *et al.*[89]** A FCC Nb monolayer is located on the BCC Nb(110) substrate; the oxygen atoms O_I are located on the surface above the niobium atoms. Nb and O_I atomic monolayers are ordered as in NbO (25% vacancies in both sublattices). Chains of Nb^* atoms form streaks along two NbO[110] directions. Oxygen atoms O_{II} enter the structure of Nb^* streaks, being located between Nb^* atoms below the streak planes.

electronic structure in the 2 distinct regions of the surface, the nanocrystals and the channels, and how their electronic structure dictates further oxidation. The protective nature of the NbO layer is also of interest as it helps to protect further oxidation.

3.4.3 Copper & its Oxides

Cu

Cu is a FCC transition metal with an atomic number of 29. Copper has a lattice constant of $3.597\text{\AA}$ [91] and a melting point of 1357 K. It is ductile and has the second highest conductivity of the elements after silver, combined

with its relative abundance on earth, Cu is universally used as a conductor for high voltage electricity.

Atoms in FCC (111) planes have a coordination number of 6, 3 in each of the neighbouring layers. Three stacking plane orientations exist for FCC structures, due to its 3-fold symmetry, A, B and C. These layers can stack in a number of ways. Stacking in an ABAB... results in the HCP structure, while ABCABC stacking results in the cubic close packed structure. (111) FCC crystals have the largest packing density of crystal with 74.04% of the crystal occupied by atoms. Thus, the (111) surface of an FCC crystal is almost smooth on the atomic scale.

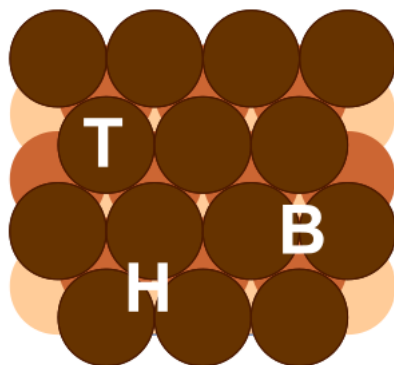


Figure 3.12: **Image of the FCC(111) plane with primary binding locations indicated**[52] This hexagonal surface surface is the most densely packed. 3 primary binding site exist: Top site (T), directly on top of a surface atom. Bridge site (B) halfway between to neighbouring atoms. Hollow site (H): the middle of 3 neighbouring Cu atoms, which is also referred to as the 3-fold hollow site.

Cu is widely used as a template material for thin film growth such as graphene[92–94], Fe[92] and Cl[94]. Cu is also used in the reduction of CO_2 , controlling the surface structure of copper electrocatalysts can guide CO_2 reduction activity and selectivity[95].

Due to its low electrical resistivity and high thermal conductivity, copper is an ideal material for electronic connections in integrated circuits with sub-micron features. Nanocrystalline copper films which share the properties of the bulk are of interest and an active field of research[96], defects in the

crystal thin film need to be optimised to improve the electrical properties of the Cu films[97].

Copper oxides

The two stable oxides of copper are cuprite (cuprous oxide, Cu_2O , Copper(I) oxide) and tenorite (cupric oxide, CuO , Copper(II) oxide). Cu_2O can be formed at low pressure ($\approx 500^\circ\text{C}$, 10^{-4} mbar) whereas CuO forms only at higher pressure ($\approx 500^\circ\text{C}$, 10^2 mbar) [98]. Cupric Oxide(CuO) has a monoclinic crystal structure with Cu atoms in a square planar configuration.

The cuprite, Cu_2O , structure is cubic and has a lattice constant of $4.2696\text{\AA}$ [99]. The Cu atoms arrange in a FCC sublattice and the O atoms in a BCC sublattice. One sublattice is shifted by a quarter of the body diagonal relative to the other. This results in each oxygen ion being surrounded by a tetrahedron of copper ions to give an oxygen coordination of 4 and a Cu coordination of 2. The bulk crystal can be seen in Fig.3.13.

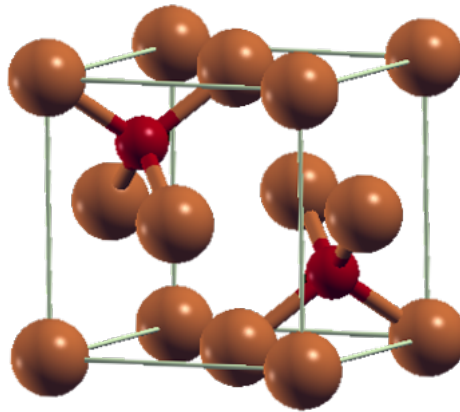


Figure 3.13: **Atomic model of Cu_2O unit cell.** Oxygen atoms are depicted in red while Cu atoms are brown. The lattice constant is $4.2696\text{\AA}$. [99]

The (100) terminated Cu_2O crystal is composed of alternating Cu-O layers, which results in a polar surface. The surface reconstructs in an effort to minimise this polarity. Three surface reconstructions of $\text{Cu}_2(100)$ have been

observed and the particular relaxation realised depends on the preparation procedures[100, 101].

The (111) terminated surface is formed by O-Cu-O tri-layers, resulting in either a stoichiometric non-polar oxygen termination or a non-stoichiometric polar Cu termination. Annealing in an oxygen environment results in the stoichiometric oxygen terminated surface, with the possibility of losing the unsaturated Cu atoms (Cu_U)[100]. The atomic model for the oxygen terminated Cu_2O surface is shown in Fig.(3.14a) alongside a simulated STM image in Fig.(3.14b)[102]. The unsaturated Cu_U atoms appear as bright protrusions in STM imaging. The bright protrusions are separated by 6–7 Å[24, 102]

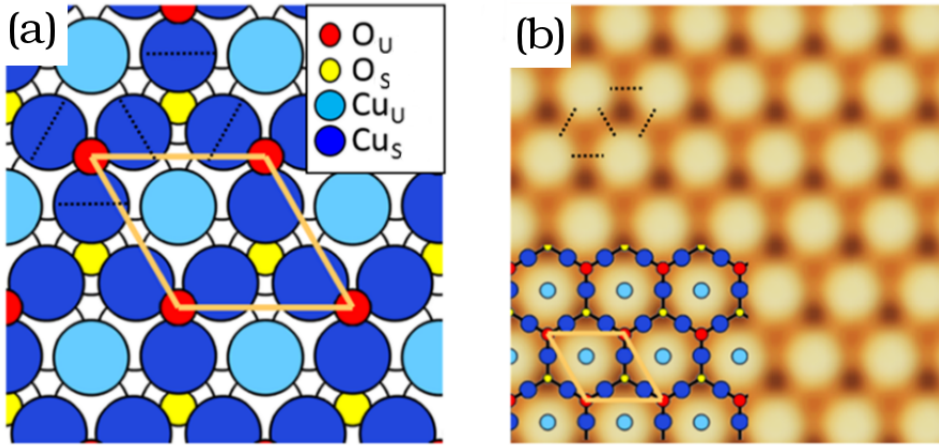


Figure 3.14: **Atomic model & DFT simulated STM image of Cu_2O [102]** (a) Atomic model of bulk $\text{Cu}_2\text{O}(111)$ (b) Simulated STM image of $\text{Cu}_2\text{O}(111)$ with the atomic model overlaid. The protrusions on the $\text{Cu}_2\text{O}(111)$ correspond to unsaturated Cu atoms (Cu_U)

Zhang *et al.*[24] recently produced DFT models the $\text{Cu}_2\text{O}(111)$ structure with Cu_U and O_U vacancies. The resulting simulated STM images were compared to STM measurements with good agreement. The STM image with both Cu_U and O_U is depicted in Fig.(3.15a). The simulated image of the relaxed model with a Cu_U vacancy resulted in a depression at the vacancy location, Fig.(3.15c). The oxygen vacancy seen in Fig.(3.15d) resulted in the contraction of the 3 unsaturated Cu atoms surrounding the vacancy to contract, reducing the inter atomic spacings from 5.1 Å to 4 Å. Brightly con-

trasted triangular clusters are formed in Fig.(3.15e), closely matching those of STM measurements which show a contraction from 6.5Å to 4.7Å.

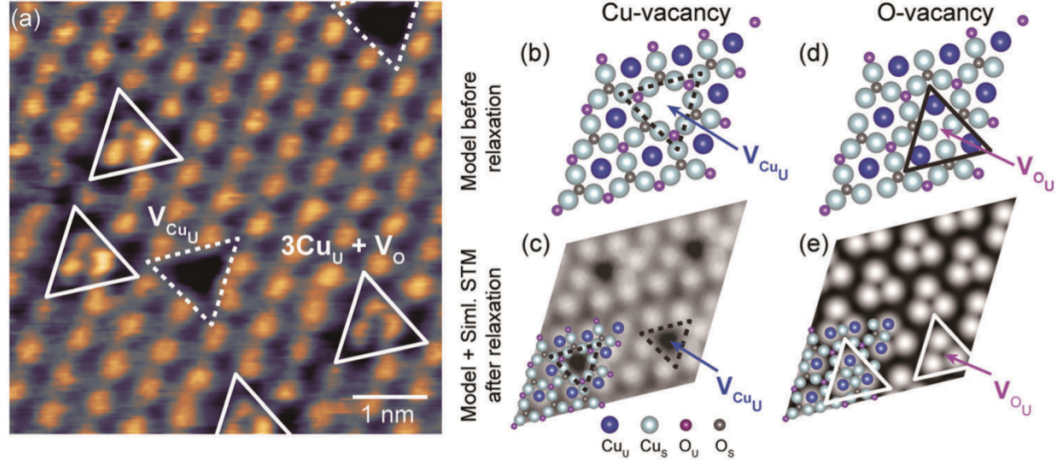


Figure 3.15: **Experimental and simulated STM images of $\text{Cu}_2\text{O}(111)$ with Cu and O vacancies.**[24](a)STM image of the $\text{Cu}_2\text{O}(111)$ surface with a number of vacancies. (b) Atomic model of unsaturated Cu (Cu_U) vacancy. (c) Simulated STM image of unsaturated Cu (Cu_U) vacancy, resulting in triangular depression. (d) Atomic model of unsaturated O (O_U) vacancy. (e) Simulated STM image of unsaturated O (O_U) vacancy, resulting in relaxation of the neighbouring Cu atoms towards the vacancy.

Onsten *et al.* presented the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ reconstruction of $\text{Cu}_2\text{O}(111)$ [100] on a bulk $\text{Cu}_2\text{O}(111)$ crystal. This surface is characterised by large protrusions, referred to as P1, separated by 11Å, close to the expected value, 10.46 Å. No internal structure of this feature was observed. Where P1 features were vacant from the surface, another smaller protrusion was observed and is referred to as P2. These features are separated by 6–7 Å and approximately 3 of these features occupy the same area as the P1 feature. The P2 features were attributed to the (1×1) $\text{Cu}_2\text{O}(111)$ surface. P1 features were reported to be due to oxygen vacancies, as was presented by Zhang seen in Fig.(3.15e). The $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ reconstruction is thus an oxygen deficient $\text{Cu}_2\text{O}(111)$ layer, with 1/3 of the unsaturated O atoms removed.

Onsten [100] proposes a model, in which the P2 features are due to the unsaturated Cu atoms matching the model of Thi Ly *et al.*, presented in

Fig.(3.14). The P1 features were then attributed to the 3 surface Cu atoms surrounding the unsaturated oxygen vacancy (O_U) atom contracting, resulting in large triangular protrusions, as presented by Zhang *et al.* and seen in Fig.(3.15e).

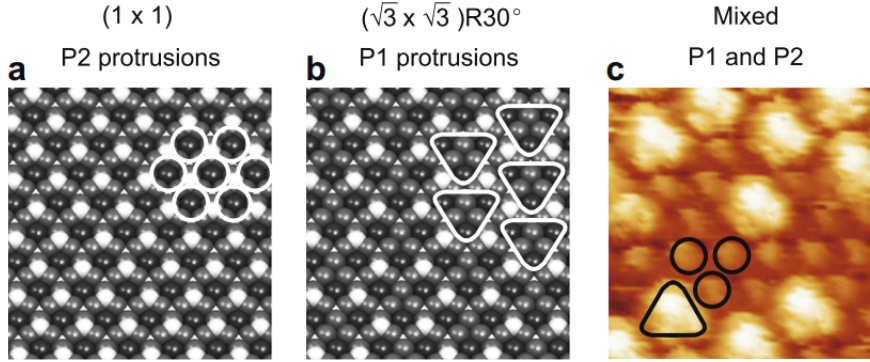


Figure 3.16: **Atomic model for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction of $\text{Cu}_2\text{O}[100]$** Small protrusions (P2) correspond to the unsaturated Cu atoms of $\text{Cu}_2\text{O}(111)$ and are separated by 6 Å, large protrusions are due to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction and are separated by 11 Å.

DFT calculations[103] indicate that the oxygen terminated (111) surface undergoes only minor relaxations, where the oxygen atom relaxes towards the bulk exposing the Cu atoms beneath. Whereas, for the Cu terminated surface, extensive relaxation occurs in order to minimise the surface polarity. The predicted lowest energy structure in high O_2 pressure is the Cu_2O (111) surface with the unsaturated Cu atoms vacant. At low O_2 pressure the Cu_2O (110) surface with a CuO-like surface reconstruction is predicted to be the most stable, however, it has not been observed experimentally. [104, 105]

Initial oxide growth on Cu(111)

The clean Cu(111) surface has the lowest surface energy for copper and is the least reactive of the low-index Cu surfaces. Oxygen binds preferentially to the FCC 3-fold hollow site at low coverage (<0.75 ML) and does not form any ordered overlayer structures below 170 K[106]. At temperatures in excess of 170 K, molecular oxygen is not detectable[107].

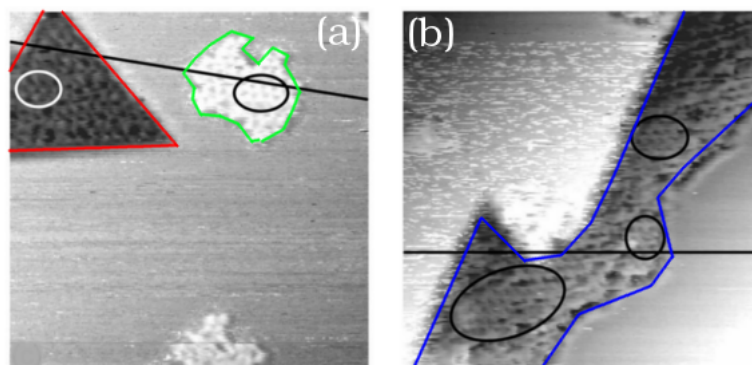


Figure 3.17: **Oxides on Cu(111) following oxidation at 300 K**[30]. Matsumoto *et al.* demonstrated 3 types of oxide structures on Cu(111). (a) Red lines indicate the boundary of the pits which contain the “in-terrace” oxide. Green lines indicate the boundary of the oxide islands referred to as the “on-terrace” oxide. (b) Blue lines indicate the “step” oxide, some ordered structure is observed, indicated by black ovals.

Higher coverage at 300 K results in the formation of an amorphous oxides. These come in 3 distinct varieties, “in-terrace”, “on-terrace” and “step” oxides[30] shown in Fig.(3.17). The green lines indicate the oxide islands which sit atop Cu(111) terraces and are referred to as the “on-terrace” oxide. The red lines indicate the step edges around a vacancy island. The oxide formed within these vacancy islands is referred to as the “in-terrace” oxide. Cu atoms have diffused from these locations leaving triangle shaped pits in the terrace, 1 atomic layer in depth. The triangular nature of these vacancy islands reflects the 3-fold symmetry of the surface. These triangular pits grow in size with oxygen exposure and can form even without a previous surface defect[30]. The blue lines indicate the location of the “step-oxide”, which forms at the step edges as a result of diffusing Cu atoms from the “in-terrace” oxides. Some ordered structures have been observed within the step oxide, however, it is confined to small areas. Copper is one of a handful of metals which do not form ordered oxides at RT[108]. Oxidation at elevated temperatures (> 600 K) leads to ordered overlayers (very few other elements are similar). The O-metal structure which forms at the onset of oxidation is often distinctly different from the bulk-like oxide which forms upon a monolayer of coverage[108].

In the initial stages of oxide growth, the Cu(111) surface reconstructs resulting in corrugated surface overlayers. These disordered overlayers provide channels for oxygen diffusion through the oxide layer, which assists in the formation of the first bulk-like oxide layer[109?]. While Cu(111) has a high barrier for oxygen atom penetration due to the close packed nature of the lattice, the reconstruction induced by oxygen atoms accommodates further oxidation by creating a channel for oxygen atoms to diffuse through.

Cu₂O(111) is widely reported to grow epitaxially on Cu(111) by annealing in an oxygen partial pressure. The surface unit cell of Cu₂O is 2.35 times larger than that of Cu(111), resulting in a mismatch of 17.5% between Cu₂O(111) and Cu(111) lattices[109]. This large mismatch results in a number of long-range quasi-hexagonal structures forming in the initial oxide growth phase. “29” and “44” superstructures have been experimentally observed[30, 110], which have unit cells “29” and “44” times larger than 1×1 Cu(111), respectively. A computational study of the “29” superstructure has been conducted[31], however, the “44” structure has not been examined due to the considerable size of its unit cell. The model of the “29” superstructure includes a number of oxygen adatoms. These superstructures act as the initial template layer for further oxide growth. As the oxide thickness increases, the strain reduces and bulk-like Cu₂O(111) is obtained.

Yang *et al.*[111] found that defects occur in the initial oxide growth stage of the “44” superstructure. Fig.(3.18a) presents the clean Cu(111) surface. Following an exposure of 100 L, a defective Cu₂O(111) “44” superstructure was formed, seen in Fig.(3.18b). Following another exposure of 180 L the surface is still somewhat defective, Fig.(3.18c). Finally, after a 200 L exposure a complete layer of the Cu₂O(111) “44” superstructure was formed, Fig.(3.18d).

The CuO is predicted to have a relatively low barrier to oxygen diffusion through the oxide layer to the underlying interface with Cu(111)[54, 55]. This may allow oxidation to be induced by the STM tip. Furthermore, with a single monolayer of oxide, it may be possible to directly observe the effect of induced oxidation. Oxide growth on Cu(111) has received a lot of attention in the literature, the study of the initial oxide growth has not. The

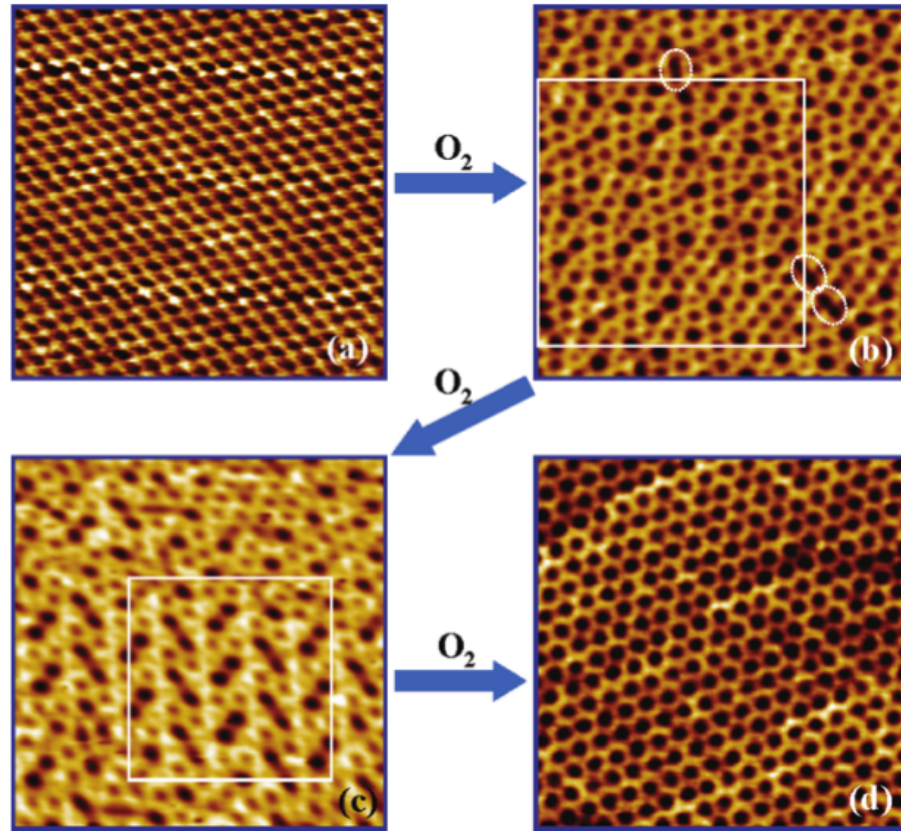


Figure 3.18: **STM images of initial $\text{Cu}_2\text{O}(111)$ growth on $\text{Cu}(111)[111]$** (a) The clean $\text{Cu}(111)$ surface (b) The surface following a 100 L oxygen exposure, a defective $\text{Cu}_2\text{O}(111)$ “44” superstructure is formed. Some defects are indicated by white ovals. (c) Following a further exposure of 180 L the surface is still defective though some order is beginning to appear. (d) After a further exposure of 200 L a complete layer of $\text{Cu}_2\text{O}(111)$ “44” is formed on the surface of $\text{Cu}(111)$. (a) $5 \times 5 \text{ nm}$, 1 V, 100 pA (b-d) $10 \times 10 \text{ nm}$, 1 V, 100 pA.

few studies which have been conducted shed light on a wide range of oxide stoichiometric and structures. The properties these structures exhibit are of general interest.

Chapter 4

$\text{MoO}_{2+x}/\text{Mo}(110)$

4.1 Introduction

Molybdenum is a crucial element in many high-performance alloys and steels[112, 113]. Its compounds are utilized in a wide variety of applications such as; fertilisers[114] and catalysts [115]. Molybdenum oxides are important catalysts, catalytic applications include hydrotreating of oil to reduce the sulphur, nitrogen and aromatics content, yielding cleaner more efficient fuels [116]. MoO_2 is a conductor which has been reported to act as a catalyst in several different reactions including the dehydrogenation of alcohols [117], the reformation of hydrocarbons [118, 119] such as biodiesel [120] and is used for the partial oxidation of aviation fuel [121]. The catalytic activity shown by MoO_2 is due to the transfer of nucleophilic oxygen ions from the oxygen sub-lattice to the catalytically active surface where they are then consumed to sustain the redox cycles [122]. The oxygen content is an important factor in catalytic activity. For example, the catalytic activity of MoO_x in converting methanol to formaldehyde is determined by its oxygen coordination [123]: MoO_2 is a poor catalyst in comparison to MoO_3 . The presence of Mo^{6+} is the critical factor in obtaining a high formaldehyde yield rate. The ability to control which MoO_x species is present on the surface has important applications for oxidation and reduction reactions. Finally, MoO_2 can also be used as a template for the growth of nanostructures[124].

The work on oxygen adatom removal from the MoO_{2+x} surface carried out by Karasnikov *et al.* was conducted in the tunneling regime where the contribution from inelastic electron tunneling is believed to dominate that of the electric field. This belief may not be valid given new experimental and computational evidence. In this work, results from experiments where the STM tip is pulsed while outside of the tunneling regime are presented. These results indicate that oxygen adatoms can be removed from the surface by the electric field between the STM tip and sample. A number of experimental results are simulated using FEM calculations and the simulations, which only consider the electric field, show good agreement to the experiment results. Furthermore, the results indicate that the oxygen adatoms do not desorb from the surface but instead penetrate the topmost Mo layer of the O-Mo-O tri-layer structure, to the oxide beneath.

4.2 Experimental details

Sample preparation

Preparation of the $\text{MoO}_2/\text{Mo}(110)$ surface was conducted in the same manner as Radican *et al.* [64]. An atomically-clean single crystalline $\text{Mo}(110)$ (Surface Preparation Laboratory Moscow) surface was prepared by in-situ annealing at 1275 K. The preparation chamber used in experiments has a base pressure of 5×10^{-11} mbar at 300 K. The sample was heated by electron beam bombardment and temperatures were measured using an optical pyrometer (Ircon UX20P, emissivity 0.35). The clean $\text{Mo}(110)$ surface was verified by LEED and STM measurements before oxidation. The sample was oxidised using O_2 gas with 99.998% purity, at 1250 K in an oxygen partial pressure of 1×10^{-7} mbar for 2 minutes after which the oxygen valve was closed and the sample was then allowed to cool to room temperature. The pressure during the cooling process was of the order of 10^{-10} mbar. This process results in a clean $\text{MoO}_2/\text{Mo}(110)$ surface termination. The $\text{MoO}_2(010)$ surface, which is depicted in Fig.(4.1a), exhibits an O-Mo-O trilayer structure and forms well-ordered oxide nanorows which appear in STM images as

bright rows with dark rows in between. These rows follow the $[1\bar{1}\bar{3}]$ direction of the Mo(110) substrate in agreement with the work of Radican *et. al*[64]. and Okada *et. al*[66]. detailed in 3.4.1.

In order to obtain oxygen adatoms on the MoO₂/Mo(110) surface, the sample was then exposed to an oxygen environment of 1×10^{-7} mbar for 2 minutes at room temperature. This results in the formation of an oxygen-rich MoO_{2+x}/Mo(110) surface exhibiting oxygen adatoms which is depicted in Fig.(4.1b). The preparation procedure described here differs slightly to that of Karasnikov *et al.*[73], which is detailed in 3.4.1, differing in the point in time in which the surface is exposed to oxygen. This method was found to give a greater oxygen adatom surface coverage. Oxygen adatoms appear as small protrusions (bright dots) on the MoO_{2+x} surface and make up the vast majority of the observed features. The oxygen adatoms reside on the bright rows of the MoO₂ surface. They can be seen in greater detail in the images presented in Fig.(4.3).

During the development of the oxidation procedure to obtain the MoO_{2+x}/Mo(110) surface, the MoO₂/Mo(110) surface was exposed to increasing doses of oxygen and there is a strong link between the number of these small protrusions and the dose of oxygen which the surface was exposed to. The MoO₂ surface is illustrated in Fig.(4.2a). In Fig.(4.2b) we present the surface after an initial exposure to oxygen for 40 seconds at a partial pressure of 1×10^{-7} mbar which results in a ~ 0.3 ML coverage. Fig.(4.2c) displays an increase in the number of bright features following a longer exposure to oxygen (80 seconds total) at the same partial pressure, the coverage is ~ 0.6 ML. Fig.(4.2d) displays the surface with a close to complete surface coverage which occurs after 2 minutes at the same partial pressure. Prolonged exposure at this pressure does not result in a noticeable increase in the surface coverage. Surface coverages were determined by counting individual bright features for each exposure time and the surface density compared to that of the near complete surface coverage. Only these small bright features in Fig(.4.1), attributed to O adatoms, which can be easily distinguished from others, were the subject of the following pulsing experiments.

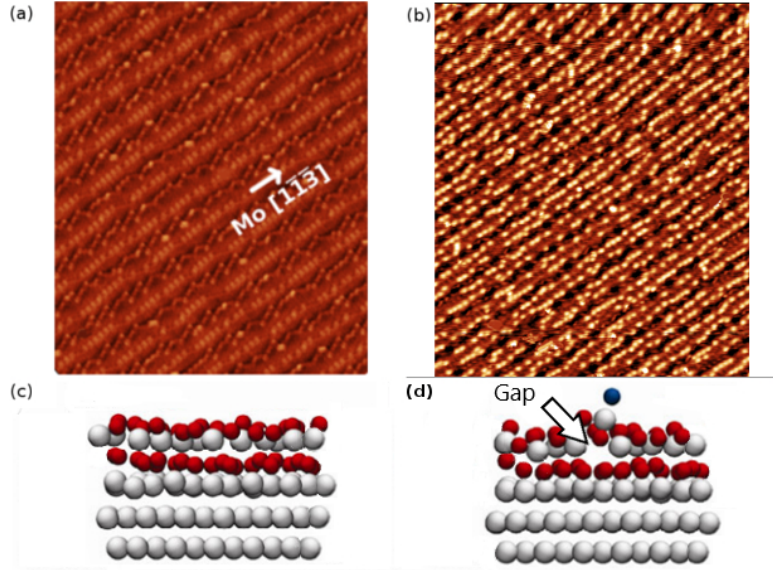


Figure 4.1: **STM images & DFT models of the MoO_2 and MoO_{2+x} surfaces.** (a) STM image of the $\text{MoO}_2/\text{Mo}(110)$ surface displaying the bright and dark row features. (b) STM image of $\text{MoO}_{2+x}/\text{Mo}(110)$, the bright features on the bright rows correspond to oxygen adatoms. (c) DFT simulation of $\text{MoO}_2/\text{Mo}(110)$ surface (d) DFT simulation of $\text{MoO}_{2+x}/\text{Mo}(110)$ surface. Note the Mo (white) atom directly below the O adatom (blue) is shifted from its lattice position.

Pulsing experiment details

Pulsing involves applying a bias, for some period of time, between the surface and the tip. The duration of the pulse influences the probability of removing an adatom[73] up to a saturation point. A saturated pulse duration for the following experiments was selected as 500 ms. Increasing the pulse duration above this value does not cause a significant change in the pulses' effectiveness at removing an adatom. The magnitude of the applied bias voltage and the tip-surface distance influence the probability of removing oxygen atoms and the size of the area from which the adatoms are removed. These relationships are explored in this work.

Prior to applying a pulse, the surface is scanned at a bias voltage low enough as to not remove any adatoms. For example, not in excess of 1.5 V for a tunneling current of 1 nA. Based on the adatom location in the previous

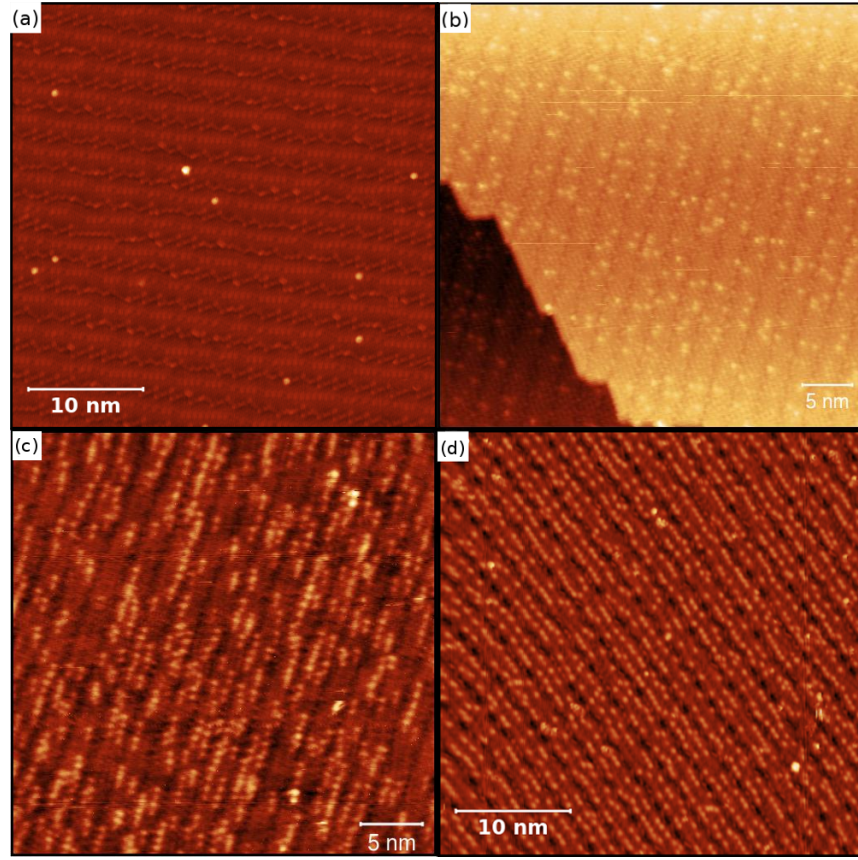


Figure 4.2: **Oxidation of the MoO₂/Mo(110) surface resulting in MoO_{2+x}/Mo(110)** STM images exhibiting increasing bright protrusion density with an increasing oxygen exposure. (a) The clean MoO₂/Mo(110) surface exhibiting the row structure. (b) The MoO_{2+x}/Mo(110) surface with ~ 0.3 ML coverage of oxygen adatoms, the adatoms bind to the row structure. (c) The MoO_{2+x}/Mo(110) surface with ~ 0.6 ML coverage of oxygen adatoms. (d) The MoO_{2+x}/Mo(110) surface with a close to complete coverage of oxygen adatoms on the row structure.

image, the tip is then positioned directly above an oxygen adatom and a pulse is applied. Care is taken to ensure there is minimal drift and pulsing occurs immediately after the lines which resolve the adatom have been scanned. Following pulsing, the surface is scanned again to determine if the adatom has been removed. The surface polarity is positive throughout results presented here, unless otherwise stated.

In the tunneling regime the thermal influence of the tunneling current, inelastic electron scattering and the electric field generated between the STM tip and the surface contribute to the removal of oxygen adatoms. In order to isolate the contribution of the electric field, a vertical offset is applied to the STM tip to remove it from the tunneling regime for the duration of the applied voltage pulse. The vertical offset is not the absolute tip-surface distance but is the distance the tip is moved from its initial position in the scanning tunneling regime. In order to ensure consistency in this height, the initial scanning bias voltage and tunneling current were kept constant throughout all experiments (bias voltage = 1 V, tunneling current = 1 nA) and a tip offset of 1 nm (sufficient to remove the tip from tunneling regime) was used unless otherwise stated. The minimum voltage required to remove an adatom at a particular off-set is referred to as the threshold voltage.

The tip stability was verified by approaching the tip into the tunneling regime and switching the feedback off. No significant changes in the tunneling current were detected during a 100 second interval. The error in applying a vertical offset is estimated to be no more than 0.1 Å. All experiments were performed 30 hours after filling the STM with liquid nitrogen, ensuring that the temperature is stable, and therefore, no significant thermal drift is present. The accuracy of the tip can be verified by scanning an area before and after pulsing and comparing the target position (the position selected on the first(before) STM image) and the real position (the position adatoms are removed from on the second(after) STM image). The target and real positions are within 1 Å, this high level of precision can be observed in Fig.(4.3c) where selected individual adatoms are removed from the surface leaving their neighbours in place.

4.3 Experimental results - Pulsing

Resolution of pulsing

Applying a single voltage pulse (positive sample bias) with the STM tip when outside of the tunneling regime can lead to a number of oxygen adatoms being

removed from the surface at once when the bias voltage is sufficiently large, as seen in Fig.(4.3a). In this image we do not observe an increase in the density of oxygen adatoms in the vicinity of the pulsed area, indicating that there is no lateral diffusion. This can also be viewed in the work of Krasnikov *et. al* [73] where larger scale images are presented. No tunneling current is present during a bias pulse due to applying a sufficiently large vertical offset between the tip and surface. The diameter of the circular area from which oxygen adatoms are removed depends on the magnitude of the pulse voltage for a given tip-surface distance, the white circle is the result of a 3.5 V pulse and the larger green one of a 4.5 V pulse. Individual adatoms can also be removed even when neighbour adatoms were separated by just 5 Å. The high resolution of oxygen adatom removal is depicted in Fig.(4.3b) & Fig.(4.3c). A single low voltage pulse is applied to each adatom highlighted in Fig.(4.3b) resulting in their removal, seen in Fig.(4.3c). Oxygen adatom removal was only observed at positive sample bias. Given that the oxygen adatom is negatively charged and the surface is at positive polarity, the applied electric field imparts a force on the adatom acting towards the bulk.

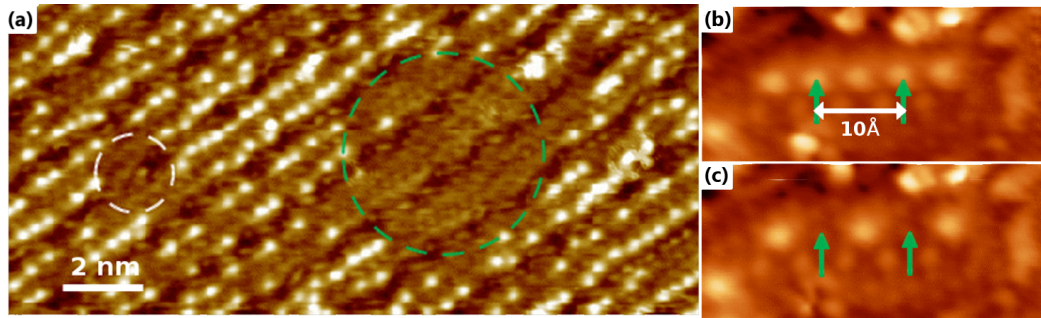


Figure 4.3: **STM images indicating the high resolution of adatom pulsing.** (a) Oxygen adatom removal *via* pulsing at $V = 3.5$ V (white circle) and $V = 4.5$ V (green circle) (b) STM image of a row of oxygen adatoms on the MoO_{2+x} surface, before single pulses are applied to each atom highlighted in green. (c) Individual adatoms are removed from the surface following pulsing, while their neighbours remain in place. The peak to peak distance between adatom features is 5 Å, demonstrating the high resolution of this method.

Intermediate state

After pulsing is performed the oxygen adatom is either removed from the surface or still in its original location on the surface, depending on the magnitude of the bias pulse. However, on occasion pulsing has been observed to change the relative height of the oxygen adatom as observed by STM. In Fig.(4.4), three STM images and three lines profiles are presented. From left to right the STM images correspond to before pulsing (Fig.(4.4a)), after one pulse (Fig.(4.4b)) and after a second pulse is applied in the identical position (Fig.(4.4c)). The sequence of line profiles (Fig.(4.4d-f)) illustrate that the adatom is not fully removed from the surface after the initial pulse, but sits in an intermediate state (Fig.(4.4e)). This intermediate state is suspected to be a higher Mo oxide compound that lies within the topmost molybdenum layer. After a second pulse is applied (Fig.(4.4f)) the adatom is fully removed from the surface and is suspected to go into the oxide layer. This intermediate state has only been observed on a few occasions, when the pulsing bias is close to the threshold voltage, in contrast to the oxygen removal phenomenon. This may be due to the intermediate state having a small potential barrier to transition to the next subsurface state. The change in relative height of the feature may be due to a change in the adatom position and/or a change in the electronic state of the adatom, through ionisation or a chemical reaction resulting in an oxide compound being formed.

Removal spot size Vs. Applied voltage

The minimum voltage required to remove an adatom is referred to as the threshold voltage, which depends on conditions such as the tip-surface separation. The threshold voltage for the removal of oxygen adatoms can be measured in two ways. Firstly, by systematically increasing the bias voltage and monitoring the increase in the spot diameter, a non-linear dependence is obtained as indicated by the black circles in Fig.(4.5). The threshold voltage is estimated by extrapolating the bias voltage from this relationship to a minimum spot size of 0.5 nm, which corresponds to a single oxygen adatom atom being removed. This method gives a qualitative estimate of the threshold

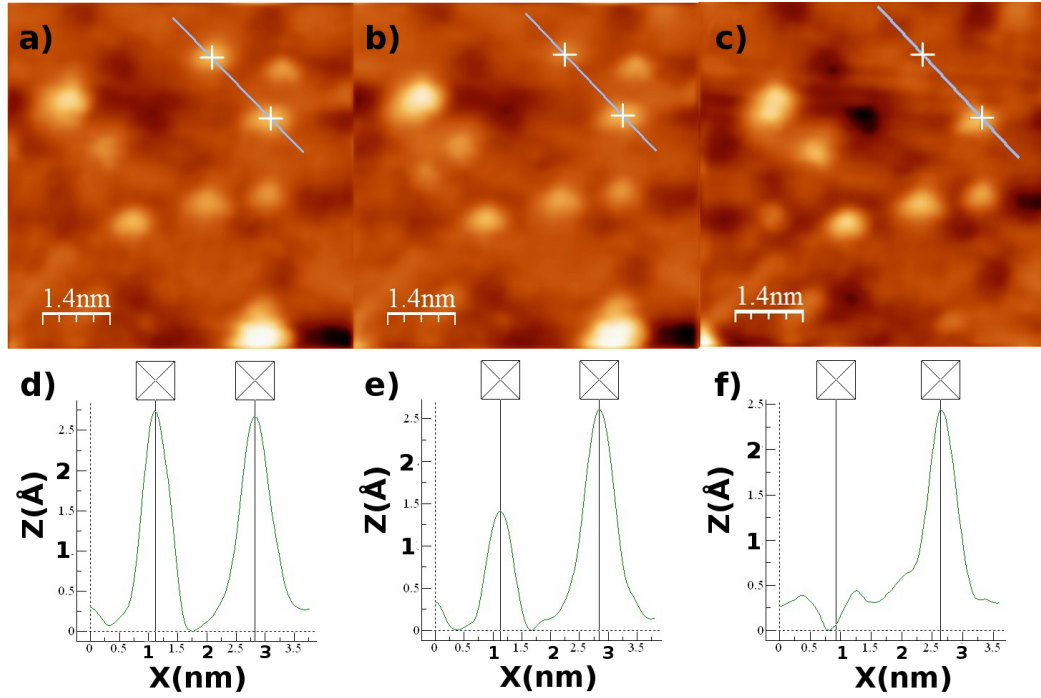


Figure 4.4: **Pulsing experiments indicate the existence of an intermediate state.** STM images of the $\text{MoO}_{2+x}/\text{Mo}(110)$ oxide surface. Fig.(a) and Fig.(d) correspond to the STM image and line scan respectively before a pulse is applied to the adatom positioned at the cross at the top of the STM image presented in (a), its relative height decreases as seen in (b) and (e). Another pulse is then applied to the same adatom. Finally in (c) and (f) it is clear that the aforementioned adatom has been removed from the surface.

voltage. Secondly, the threshold voltage can also be estimated by measuring the pulse voltage at which the probability of removing an adatom is roughly 50%. 30 individual pulsing experiments were performed at different points on the surface. For each experiment, the pulse voltage was increased until adatom removal was achieved, with the surface being scanned before each voltage increment. The grey crosses in Fig.(4.5) depict the probability of adatom removal as a function of the pulse voltage. The probability that an oxygen adatom will be removed by applying a pulse sharply increases at the threshold voltage. Both methods indicate that a pulse voltage of approximately 3.3 V, represented by the vertical dashed line in Fig.(4.5), is required

to remove an individual adatom for the particular scanning parameters used in this experiment. While the adatom removal process is probabilistic in nature it has a strong voltage dependence. Using the applied bias as a criterion for the spot size is therefore a reasonable procedure. The probability curve (grey crosses in Fig.(4.5)) sharply rises at the threshold voltage, indicating that the error associated with taking a single value (threshold voltage) instead of the probability is quite small, about 0.2-0.3 V. This is especially so at higher voltages where variance in probability is averaged out due to the large number of adatoms being removed upon pulsing.

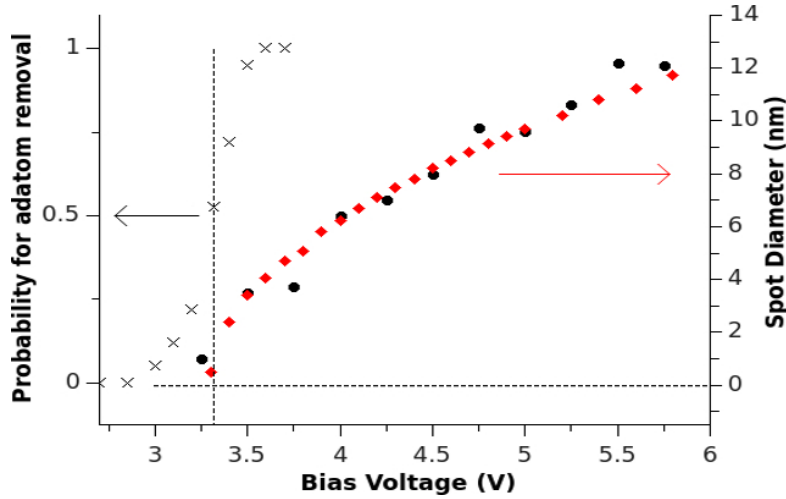


Figure 4.5: **Dependence of spot size and the probability to remove an adatom as a function of applied pulse voltage.** **Grey crosses:** The probability to remove an adatom increases sharply at the threshold voltage. **Vertical dashed line:** The threshold voltage corresponds to removing an adatom with a probability of 0.5 or the minimum spot size of 0.5 nm. **Black circles:** Experimentally, the spot diameter increases as the applied bias voltage is increased. **Red diamonds:** FEM simulations of the relationship between the spot diameter and applied bias voltage are in agreement with the experimental result.

Threshold voltage Vs. Applied offset

The red triangle in Fig.(4.6) demonstrates the dependence of the tunneling current on the applied offset, note the absence of a tunneling current after an

offset of approximately 0.5 nm is applied. The dependence of the threshold voltage on the tip-surface distance has been explored. An offset has been applied to the tip and the pulsing voltage has been increased until adatom removal is observed. Subsequently, further offsets have been applied and once again the threshold voltage is found. The threshold voltage for the removal of oxygen adatoms increases as the distance between the surface and tip increases as shown in Fig.(4.6) by the black circles. This relationship has two distinct regions, reflected in the change of slope, indicated by the dashed vertical line at an offset of 0.5 nm. Below an offset of 0.5 nm the tunneling current contributes to adatom removal whereas at an offset above 0.5 nm the tunneling current does not contribute to the removal of the oxygen adatoms. The linear relationship between vertical offset and threshold voltage with no tunneling current is in agreement with that of the electric field mechanism theory, seen in Eq.(3.6), which predicts a linear relationship. In the absence of a tunneling current oxygen adatom removal is only observed at positive bias voltage (applied to the surface relative to the tip). The direction of the electric field is thus towards the tip, meaning a negatively charged ion, such as oxygen, will experience a force towards the surface.

Barrier to oxygen penetration

To penetrate the surface, an oxygen adatom needs to overcome a potential barrier, W . The magnitude of this barrier can be modified by applying an electric field. If the probability of an oxygen adatom being removed follows the relationship in Eq.(3.3), measuring the threshold voltage as a function of the pulse length, Δt , will yield a linear relationship. Such an experiment has been performed at 121 K and 81 K and is depicted in Fig.(4.7). Turning to Eq.(3.5), the intercept of the V vs $\ln(\Delta t)$ graph contains two terms. The temperature dependent term provides only a small contribution, as the intercept only changes by ~ 0.1 V for the measurements at 121 K and 81 K, and hence, this term is omitted. Therefore, the intercept provides an approximate value for $W \cdot \frac{d+Z_{off}}{aq}$. Considering that the slope provides a value for $k_b T \cdot \frac{d+Z_{off}}{aq}$, an approximate value for W is determined to be 0.45 eV.

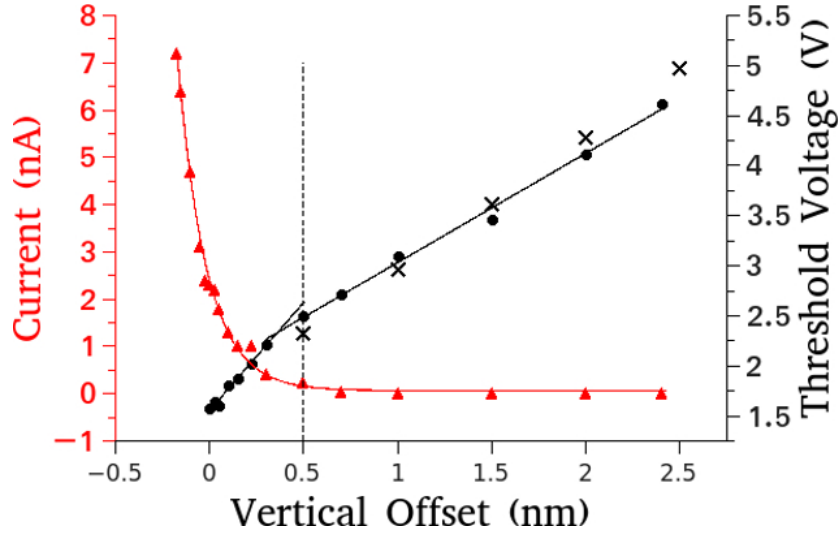


Figure 4.6: **The dependence of the tunneling current and threshold voltage as a function of tip-surface offset. Red triangles:** The dependence of tunneling current on applied offset indicates that at a tip offset of 0.5 nm is sufficient to remove the tip from the tunneling regime; **Black Circles:** Experimental relationship between the threshold voltage and tip offset is linear and divided into two regions by the dashed line which corresponds to the end of the tunneling regime; **Black crosses:** FEM simulations ($V = 0.43$ V) of the threshold voltage and vertical offset, using only an electric field, closely agree with the experimental relationship outside of the tunneling regime.

4.4 Finite element method simulations

Simulation details

FEM simulations[125] of the electric field generated between the tip and surface have been performed in order to shed light on the mechanism behind the removal of oxygen adatoms from the $\text{MoO}_{2+x}/\text{Mo}(110)$ surface. In the FEM model, the tip is approximated as a conductive sphere and the MoO_2 terminated surface a perfectly flat metallic plane. An electric potential is applied to the tip and the electric potential between tip and surface can then be determined. The electric potential at any point can be then calculated as a function of tip-surface distance, tip radius of curvature and bias voltage. This allows one to estimate the trends of the experimentally observed rela-

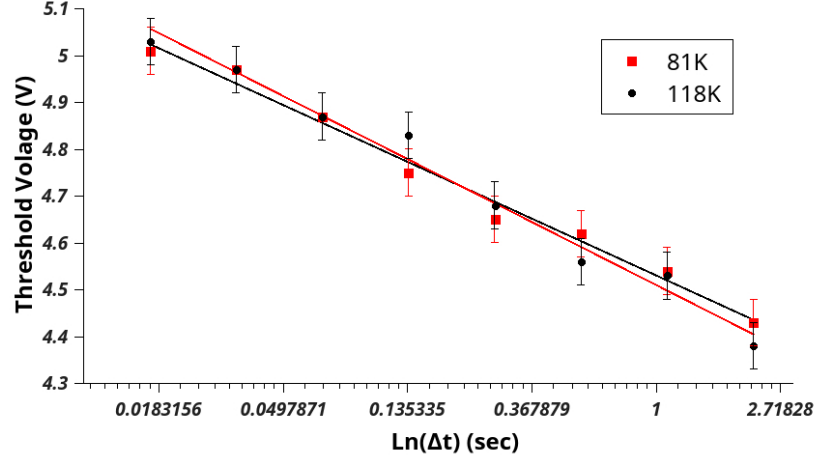


Figure 4.7: **Threshold voltage dependence on temperature.** The dependence of threshold voltage on the duration of bias voltage pulse measured at two temperatures: red and black circles correspond to 81 K and 118 K respectively. The dependencies are fitted by linear functions. Yields an estimate for the barrier to penetration W of 0.45 eV.

tionships, such as the threshold voltage for the removal of oxygen adatoms as a function of tip-surface distance. In these simulations the electric potential is calculated at a distance of 0.4 nm above the first Mo layer of the O-Mo-O tri-layer, corresponding to the approximate position of the oxygen adatom, according to relaxed slab results from the DFT simulations conducted by Krasnikov *et al.*[73] seen in Fig.(4.1d).

The tunneling gap, the distance between the adatom and the tip before an offset is applied, used in the simulation was 0.8 nm. In total, a tip-surface distance of 1.2 nm is used prior to an offset being applied. This distance is then used as a zero point when calculating offsets in the simulations, for example, an offset of 1 nm in Fig.(4.6) corresponds to a total tip-surface distance of 2.2 nm. A “tip” diameter of 30 nm is used in the simulations. The tip diameter and tunneling gap were selected based on the simulations of spot size vs. applied bias voltage. Initial guesses based on scanning electron microscope measurements were used and later refined based on comparison to experimental results.

The tangential component of the force acting on the adatom is negligible due to the metallic conductivity of the surface, and hence, only the component of force perpendicular to the surface is considered. Using this principle, the electric field between the tip and the surface is simulated in order to get an estimate for the electric potential experienced by the oxygen adatom when a pulse is applied. The lack of lateral diffusion of oxygen adatoms in STM images taken from experiment support this reasoning.

In order to simulate the relationship between the spot diameter and the applied bias voltage, which used a vertical offset of 1 nm, an experimental reference point is required to set the threshold voltage for the simulation. The point corresponding to a 1 nm offset for an applied bias voltage of 3.3 V was taken from the threshold voltage vs. applied offset experiment, black circles in Fig.(4.6). Using this offset and bias voltage the electric potential is calculated in the plane parallel to the surface, containing the point of the adatom's position. The model is presented in Fig.3.2. The distance between the adatom and the topmost Mo layer is 0.4 nm, this value is obtained from the relaxed DFT models of the $\text{MoO}_{2+x}/\text{Mo}(110)$ presented by Karasnikov *et al.*[73]. This potential corresponds to the threshold potential, the minimum potential required to remove an adatom.

Bias voltages exceeding this threshold voltage are then simulated and their electric potentials in the same plane are calculated. The spot size is determined by calculating the region in the plane for which the magnitude of the potential of the applied bias voltage exceeds the magnitude of the potential of the threshold voltage. An example of this is demonstrated in Fig.(4.8), where a line profile has been taken through the center of the plane. This spot width calculated here corresponds to the diameter of the spot in which adatoms are removed with a high probability, the adatoms at the edge have a removal probability of 0.5 while those closer to the centre of the spot have a higher probability.

To simulate the dependence of the threshold voltage on the tip-surface distance, the electric potential directly below the tip at the adatom height of 0.4 nm above the surface is calculated as a function of the applied bias voltage for various tip-surface offsets. 6 offset values were simulated starting

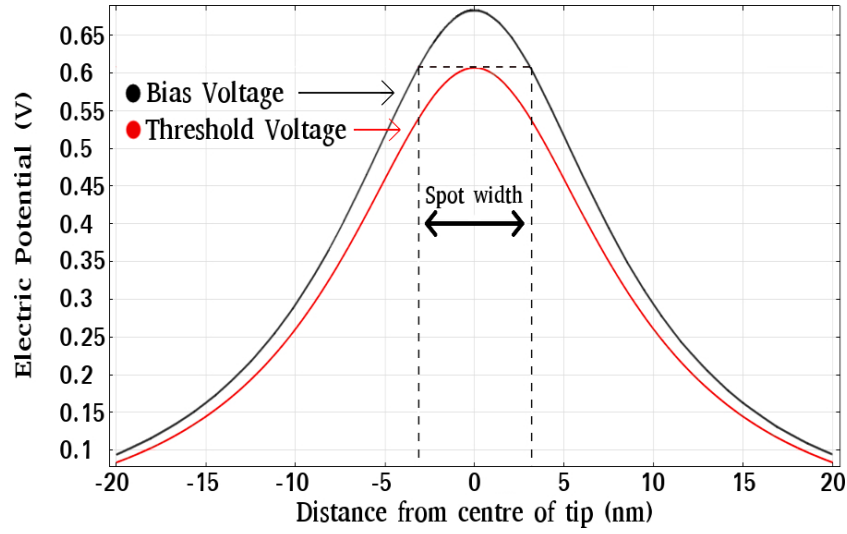


Figure 4.8: **FEM simulations of electric potential at the adatom height above the surface.** The spot diameter is determined by finding the diameter of the circular region in which the applied bias voltage (black) exceeds the threshold voltage (red). The threshold voltage value of 3.3 V for a 1 nm tip-surface offset is taken from experiment.

at 0.5 nm and every 0.5 nm up to 3 nm. The results for offsets of 1, 2 and 3 nm are shown in Fig.4.9.

The dependencies of the electric potential, Ψ , on the applied bias voltage for various tip offsets can be interpolated, so that an arbitrary value of Ψ may be selected and the corresponding bias voltage required to generate said potential, at different tip offsets, determined. Comparing the resulting Ψ vs. applied bias dependencies for a wide range of values of Ψ to the experimental results will indicate whether the electric field can replicate the experimental results and also enables an estimate of potential required for the adatom to transition below the surface. This will yield an estimate, as the dependency of the removal of an adatom as a function of applied bias voltage is probabilistic in nature, data points indicated by grey crosses in Fig.(4.5).

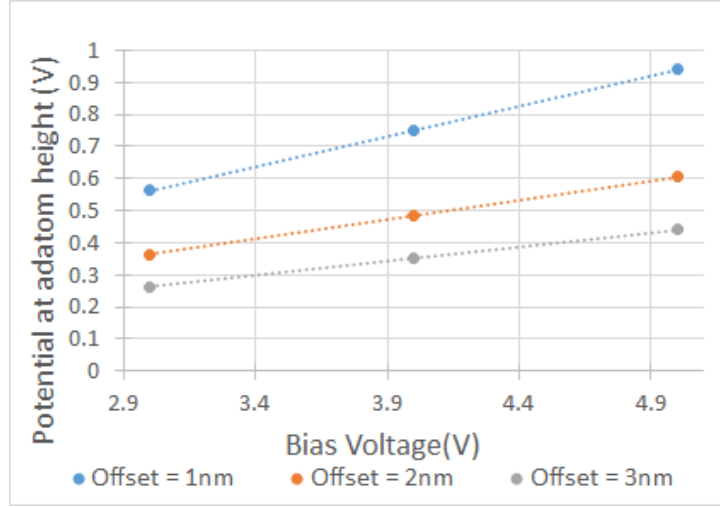


Figure 4.9: **FEM simulation of the electric potential experience by the adatom as a function of applied bias for different tip-surface offset.** The electric potential is calculated as a function of applied bias, at a point 0.4 nm above the surface, directly beneath the centre of the tip for 3 tip-surface offsets: 1, 2, 3 nm. The

Simulation results

Fig.(4.10) illustrates an example of the electric potential (black curve) calculated along a line, parallel to the surface, at the adatom height above the surface. The corresponding probability to remove an oxygen adatom from the surface (red curve) calculated using Eq.(3.3) is shown in Fig.(4.10). The pre-exponential factors are set such that the probability curve peak is normalised to 0.5, which coincides with the probability of removing one adatom at the threshold voltage. Although the spatial distribution of the potential curve demonstrates the broad peak located below the STM tip apex with a full width half maximum (FWHM) of approximately 15 nm, the FWHM of the probability curve is much narrower. The FWHM of the probability curve is approximately 1 nm. Considering the adatom directly below the tip apex has a probability of 0.5, i.e. threshold, the probability of its nearest neighbours, which are at most 0.5 nm away, being removed is at most 0.25. This serves to highlight that the electric field can give rise to extremely high-resolution removal of oxygen adatoms and is in good agreement with the

resolution of individual oxygen adatoms removal observed in experiment, see Fig.(4.3) and Fig.(4.4).

A reference threshold value of 3.3 V for an offset of 1 nm was taken from the threshold voltage vs. applied offset experiment, black circles in Fig.(4.6), to simulate the relationship between the spot size and the applied bias voltage. The spot size in which adatoms are removed is calculated as the area in which the applied electric potential exceeds the threshold electric potential in the plane of the adatom, parallel to the surface. An example of this calculation can be found in the methods section. The comparison between these computational results and the experimental results can be seen in Fig.(4.5). To simulate the relationship between the applied offset and the corresponding threshold voltage, the electric potential at the position of the adatom is calculated as a function of applied bias voltage, this is repeated for different tip offsets. Interpolating the data allows one to select a potential value and determine the bias voltage required to generate the potential in question at various tip-surface offsets. A potential value of 0.43 V best fits the experimental data. The black crosses in Fig.(4.6) depict the calculated linear relationship between the threshold voltage and the tip-surface distance, which is in good agreement with the experimental findings (black circles). The FEM results, obtained solely from applying an electric field, are in agreement with the experimental results, indicating that the process of oxygen adatom removal from the $\text{MoO}_{2+x}/\text{Mo}(110)$ surface can be realised without the influence of tunneling electrons.

4.5 Discussion

When out of the tunneling regime, oxygen adatom removal is only observed when a positive bias is applied to the sample. Given that the oxygen adatoms are negatively charged and that the electric field acts perpendicular to the surface due to its conductive nature, the net force on the adatoms acts perpendicular and towards the surface. Large surface area scans before and after pulsing indicate that the density of adatoms in the regions surrounding the pulsed areas does not change upon pulsing outside of the tunneling regime,

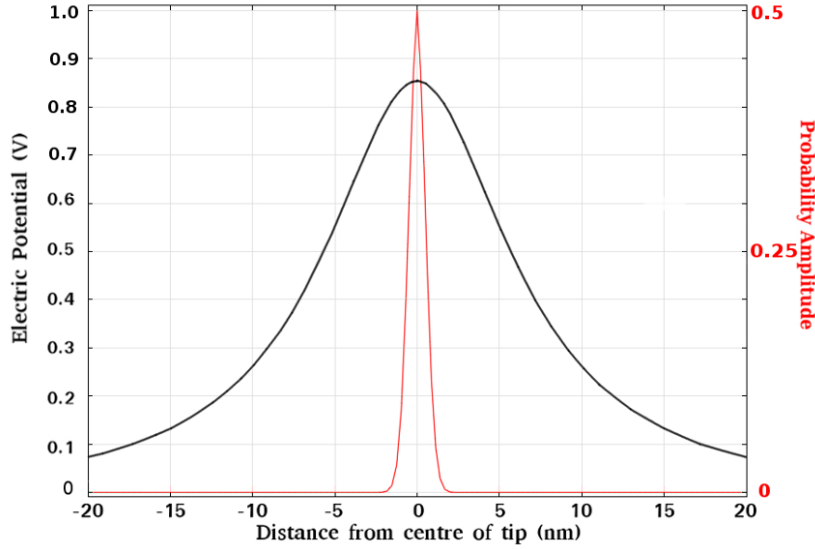


Figure 4.10: **FEM simulation of probability amplitude of removing an adatom at the threshold voltage.** The electric potential curve (black) corresponding to the threshold voltage, is used to generate the probability amplitude shown in red using Eq.(3.3) where W is set to equal the peak value of the electric potential and the pre-exponential factors set so that the probability peak is a maximum at 0.5. This probability curve then closely represents the probability to remove an adatom at the threshold voltage. This curve supports the narrow spot diameter of ≈ 1 nm observed in experiment when adatoms are removed from the surface.

indicating there is no lateral diffusion in this regime. Pulsing at high voltage/current in the tunneling regime can lead to lateral diffusion, likely due to local heating of the surface due to inelastic electron tunneling.

Oxygen adatoms have been observed to transition to an intermediate state before being fully removed from the surface. This state occurs when pulsing close to the threshold voltage and results in a reduction in the apparent height of the oxygen adatom in STM images, indicating that either, the oxygen adatom is now within the surface layer or has changed its electronic state, likely due to chemical bonding.

Pulsing of the MoO_2 surface without any adatoms did not result in any oxygen atom transitioning below the surface. The relative ease (barrier calculated to be 0.45 eV) at which oxygen adatoms on the MoO_2 surface can pene-

trate the surface is concluded to be due to how the adatoms modify the nearby MoO_2 lattice. Density functional theory (DFT) calculations have previously been performed in order to understand the structure of the molybdenum dioxide layer [65] and the over-oxidised MoO_{2+x} surface [73]. These calculations can shed light on the observation of the removal of oxygen adatoms *via* pulsing with the STM tip. The simulations, seen in Fig.(4.1c) and Fig.(4.1d), indicate a deformation of the lattice structure of the topmost molybdenum layer immediately around the oxygen adatom. The molybdenum atom below the oxygen adatom relaxes from its position in the molybdenum layer to the oxide layer above it, changing its oxygen coordination. This deformation results in the opening of a “channel” in the topmost molybdenum layer for the adatom to pass through. It is suggested that defected structures such as this, reduces the barrier for an adatom to penetrate into the underlying oxygen layer as the electron density is reduced in that region. Ion transfer in a crystal lattice under an applied electric field is characteristic of ion conductivity and electrodiffusion. Oxygen mobility through vacancies is the basis of oxide ion conductivity in numerous fluorite, perovskite and pyrochlore systems [126]. The activation energies for such ionic conductivity’s were found to be in the range of 0.7 to 1.6 eV [127], which is of the same order of magnitude as the potential barrier height obtained in our experiments (0.45 eV).

The FEM model simulating the electric field effect yields convincing results despite its simplicity. Disparity in the curve profile of the spot diameter vs. applied voltage plot (Fig.(4.5)) between the FEM simulation and experimental results are suspected to be due to the differences in the simulation parameters such as the tip shape. Furthermore, the surface is neither perfectly flat or conducting, which would lead to a different potential energy being present in the vicinity of the surface. The value for the adatom-surface distance, a , in the simulations was intuitively taken as the distance between an oxygen adatom and the topmost molybdenum layer, this assumes the potential barrier is a maximum in the plane of the molybdenum layer, referred to as the crossing point. However, in a non-uniform system, such as this one where the oxygen adatom deforms the topmost molybdenum lattice structure, the crossing point may not lie in the same plane as the topmost

molybdenum atoms. Variations of charge distribution on the atomic scale can affect the spatial distribution of the electrostatic field generated by STM tip which can influence the potential barrier. Nevertheless, the simulation is in good agreement with the experiment, suggesting that our model, which is based solely on the electric field, is correct.

The simulation of the MoO_3 cluster, conducted by Karasnikov *et al.*, which ruled out the electric field as contributing to the removal of oxygen adatoms did not consider the possibility of the oxygen adatom penetrating the surface. The configuration of the MoO_3 cluster used in the simulation made it virtually impossible for the oxygen atom to pass through the cluster. Due to the extremely high energy barrier there is practically no way for the oxygen adatom to pass through the Mo atom save perhaps by tunneling (this would require much higher energies than available in this experiment). Furthermore, only the adatom was free to move, the other 3 atoms were fixed so no relaxation was possible.

Interestingly, the change in slope for the threshold voltage as a function of tip-surface offset differs by a factor of two, between the two regimes: One where the tunneling current contributes to adatom removal and one where the electric field is solely responsible for adatom removal. The slope in the tunneling regime is twice that of outside the tunneling regime, indicating that more energy is required to remove adatoms within the tunneling regime. This is an interesting observation and more work is required to understand the underlying mechanism.

The oxygen adatoms on the $\text{MoO}_{2+x}/\text{Mo}(110)$ surface demonstrate high mobility. Pulsing the oxygen adatoms with the STM tip leads to the removal of the adatoms from the surface. This only occurs at positive sample bias and is observed in the absence of the tunneling current. The bias polarity dependence, the absence of lateral surface diffusion and the presence of an intermediate state indicates that the adatom penetrates the topmost Mo layer due to the electric field. FEM simulations of the electric field generated between tip and surface accurately describe the experimental results, indicating that the electric field is solely responsible for the observed removal of the oxygen adatom, which is pushed below the terminating layer. DFT

calculations show that the oxygen adatom modifies the underlying Mo layer structure, which in turn opens up a channel in the Mo layer, which can reduce the energetic barrier for the adatom to transition to the oxygen layer below.

The atomic resolution capability of this method of oxygen adatom removal is due to the exponential dependence of the probability to transition on the applied bias voltage. The minimum spot diameter in which adatoms are removed from the surface is quite small, just 0.5 nm in diameter. The potential barrier for oxygen adatom incorporation into $\text{MoO}_{2+x}/\text{Mo}(110)$ was found to be approximately 0.45 eV. This localised mechanism allows for the implantation of atoms without strongly influencing the substrate.

Chapter 5

NbO terminated Nb(110)

5.1 Introduction

Niobium has the highest superconducting transition temperatures ($T_C = 9.2\text{ K}$) of all the elements[128] and finds application in superconducting radio frequency particle accelerators[129] , superconducting quantum interference devices (SQUIDS)[130], infrared photodetectors[131] and Cooper-pair transistors[132]. Niobium and/or niobium oxide takes a prominent place in the tunnel barriers of single electron transistors[133] and Josephson junctions[134] . The presence of oxides clearly influence the tunneling characteristics in such devices. Niobium oxides find further relevance as catalysts[135]. For example, small amounts of $\text{Nb}_2\text{O}_{5-y}$ and NbO_2 can increase the catalytic activity of transition metals in redox reactions[135] . Niobium surfaces readily oxidise and niobiums superconductivity transition temperature drops by approximately 1 K per percent oxygen impurity[136]. Dissolved oxygen resides predominately in interstitial octahedral sites[137]. Recently it has been shown that oxygen can only be removed entirely at temperatures above 2700 K[138]. Sputtering can remove oxygen from the surface region, however, annealing as low as 470 K results in diffusion of dissolved oxygen to the surface[138].

NbO formed on the surface of Nb is extremely stable [84, 85, 139] and limits further oxidation [140, 141]. The barrier for oxygen diffusion through

the NbO(110) oxide layer is very high, 3.9 eV[54, 55], 5.5 times that of Nb. Thus once an NbO film is formed on the surface oxidation proceeds very slowly. The thickness of the NbO layer has been previously estimated from the variation in the photoemission intensity of the Nb $3d^{5/2}$ peak of the interface layer as a function of the collection angle[85]. Measurements showed that there were 1.4 ± 0.3 monolayers of Nb present in the oxide layer. This concentration of Nb corresponds to an O-Nb-O tri-layer structure with some additional fractional monolayer of Nb atoms. The NbO layer which forms on the surface acts as an interface between Nb and the higher valence oxides, dictating their initial growth. The electronic structure of this NbO layer and the role it plays in the initial stages of oxide growth on NbO terminated Nb(110) is investigated.

5.2 Experimental details

A Nb(110) single crystal was used in this study. Measurements were performed across two UHV systems, a STM system and a XPS system. The XPS and STM experiments were performed separately on the same (110) terminated niobium single crystal. The crystal was exposed to atmospheric conditions between experiments. Throughout this chapter the STM results are presented and the corresponding XPS measurements, obtained after applying similar preparation procedures, were qualitatively discussed. Furthermore, LEED measurements used in both chambers indicate that the surface unit cells are the same qualitatively. For STM measurements the ambiently oxidised crystal was annealed at 1150 K for 1 hour in UHV, while for XPS measurements the ambiently oxidised crystal was annealed at 1050 K for 20 minutes in UHV. The annealing process both cleaned the surface and resulting in the NbO termination of the Nb(110) crystal.

5.3 Experimental results

5.3.1 Atomic structure & characterisation

Fig.(5.1a&c) depict the two planes of the surface structure. A large scale STM image is depicted in Fig.(5.1b). High resolution images of the terrace structures, which are depicted in Fig.(5.1d&e) demonstrate that both terrace structures exhibit the same surface reconstruction. This reconstruction is the characteristic NbO terminated Nb(110) described in 3.4.2, which will be focused on shortly. The terrace structure observed in Fig.(5.1c) is atomically flat in the $[001]$ Nb direction. These terraces are typically up to 500 nm in length ($[001]$) and the width ($[\bar{1}10]$) of the terrace varies. This structure exhibits a row-like structure. The terrace structure observed in Fig.(5.1a) also has a terrace edge parallel to the $[001]$ direction, however it exhibits a terrace in the $[\bar{1}11]$ direction too, resulting in a series of narrow steps. The coexistence of the two terrace structures, which increases the surface area, implies the step-like terrace structure is energetically favourable. The step-like structure can facilitate relaxation of the strain induced by the misfit between NbO(111) and Nb(110), resulting in a lower surface energy.

The step-like terrace structure (Fig.(5.2a)) will now be focused on. Fig.(5.2b) depicts the two nanocrystals domains of NbO terminated Nb(110). The presence of NbO is further evidenced by XPS measurements depicted in Fig.(5.2d), where NbO is the only oxide observed. The long range order of this structure is demonstrated by low energy electron diffraction (LEED) measurements depicted in Fig.(5.2e). LEED measurements were conducted in both the XPS and STM UHV systems and the resulting diffraction patterns are qualitatively the same. The LEED image is characterised by the superposition of a Nb(110) and a NbO(111) diffraction pattern (red circles), indicative of the Nishiyama-Wasserman epitaxial relation, seen in Fig.(3.10a). The spots from the oxide and substrate layer coincide in the Nb $[001]$ direction, which is the vertical axis on the LEED screen. The spots are misaligned in the other directions in agreement with the Nishiyama-Wasserman model. It is not possible to discern substrate from oxide spots, one unit cell

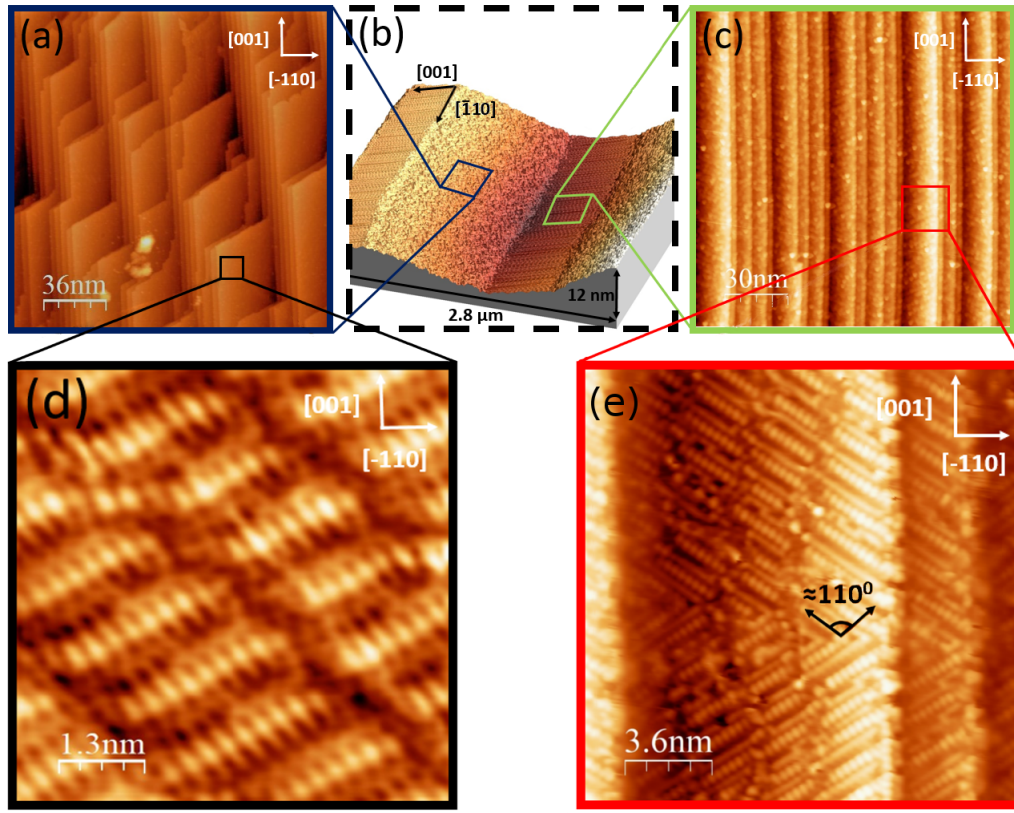


Figure 5.1: **STM measurements of NbO terminated Nb(110).**(b) illustrates large scale image of the surface. Two type of terrace structures are present, depicted in (a) and (c). In (c) the row structure is flat along the Nb [001] direction while in (a) the structure is exhibits terrace edges running in both the [001] and $[\bar{1}11]$ directions. High resolution images of the two different terraces structures (d) & (e) illustrate that both exhibit the NbO terminated Nb(110) surface reconstruction. (a) $170 \text{ nm} \times 170 \text{ nm}$, $V = 1.2 \text{ V}$ and $I = 74 \text{ pA}$ (b) $2800 \text{ nm} \times 2800 \text{ nm}$, $V = 0.97 \text{ V}$ and $I = 350 \text{ pA}$ (c) $150 \text{ nm} \times 150 \text{ nm}$, $V = 0.97 \text{ V}$ and $I = 141 \text{ pA}$ (d) $6.5 \text{ nm} \times 6.5 \text{ nm}$, $V = 0.5 \text{ V}$ and $I = 80 \text{ pA}$. (e) $18 \text{ nm} \times 18 \text{ nm}$, $V = 0.61 \text{ V}$ and $I = 102 \text{ pA}$.

is inicted in blue. Other spots in the LEED image result from the superstructures on the surface. While the Kurdjumov-Sachs epitaxial relationship has been reported, the resulting LEED diffraction pattern would consist of the superposition of a Nb(110) and two NbO(111) diffraction patterns[142]. A high resolution image of the nanocrystals is presented in Fig.(5.2c). The nanocrystals are typically 2–3 nm in length and are composed of approxi-

mately 6–9 protrusions, which are considered to be Nb atoms. The channel which separates the nanocrystals is also evident. The model for this structure is depicted in (3.10b). These STM, XPS and LEED measurements support previous observations of this termination[39, 84, 85, 88].

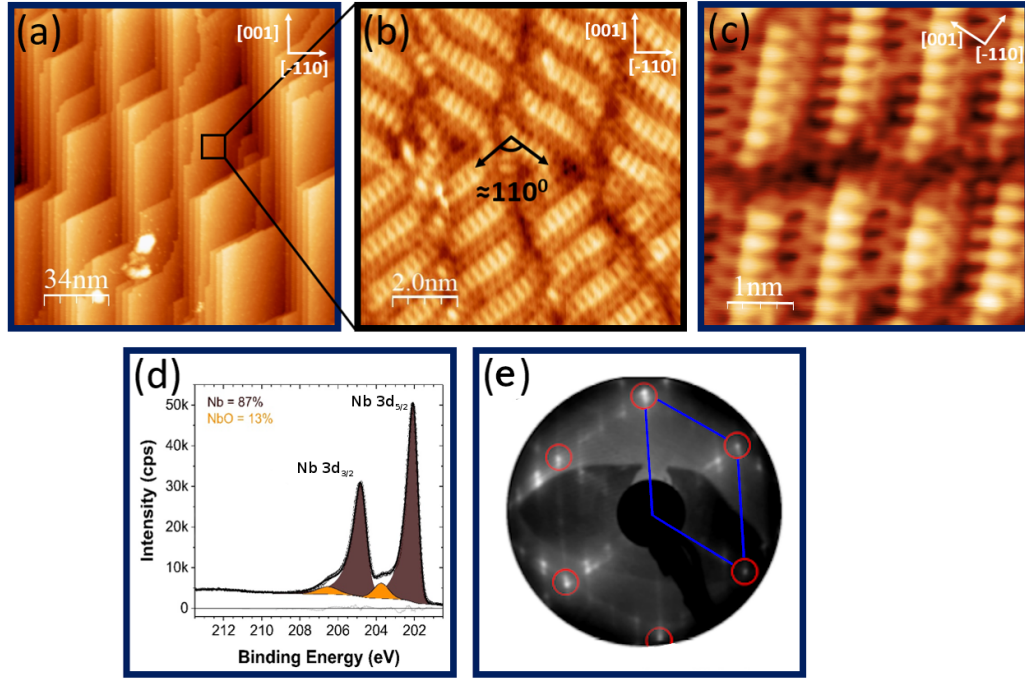


Figure 5.2: **STM, LEED and XPS measurements of NbO terminated Nb(110).** (a) illustrates the terrace structure. (b) high resolution image illustrates the NbO(111)/Nb(110) nanocrystal termination. In (b) the two domains are evident. In (c) a high resolution STM image of the nanocrystals is presented (d) Similar treatment during XPS measurements illustrate that the only oxide present is NbO. (Beam source energy: 1486.7 eV, probe depth ≈ 10 nm) (e) LEED measurement of surface. Red circles indicate NbO and Nb spots which coincide along the Nb[001] direction (vertical axis). Unit cell indicated in blue. (a) $170 \text{ nm} \times 170 \text{ nm}$, $V = 1.2 \text{ V}$ and $I = 74 \text{ pA}$. (b) $10 \text{ nm} \times 10 \text{ nm}$, $V = 2 \text{ mV}$ and $I = 61 \text{ pA}$. (c) $4.4 \text{ nm} \times 4.4 \text{ nm}$, $V = 2 \text{ mV}$ and $I = 92 \text{ pA}$.

STS measurements were conducted using a 64×64 point grid on the area of the surface presented in Fig.(5.3a). A series of terrace edges in the Nb(110) can be observed to run vertically through the centre of the image. 10 $I(V)$ -curves measurements were taken at each point of the grid and their

values averaged to produce a single $I(V)$ -curve for each point. $I(V)$ -curves are measured in the following way: the tip is initially positioned at a grid point and the tip-surface distance is determined by the scanning parameters in the constant current mode (CCM). Once the tip height is stable, the feedback controlling the tip-surface distance is switched off. The bias voltage is then swept between -2 V and 2 V to obtain the $I(V)$ -curve at a constant tip-surface distance. Following the 10 measurements being taken at each point the feedback is switched on and the tip moves to the next point in the grid, where the procedure is repeated. The CCM scanning parameters used to determine the tip-surface distance were $V = 1.3\text{ V}$ and $I = 50\text{ pA}$. Therefore, for every $I(V)$ measurement the current at 1.3 V was 50 pA . As the tip-surface distance remains constant, variation in the tunneling current at different voltages are due to differences in the electronic structure.

Fig.(5.3c) and Fig.(5.3d) illustrate the $I(V)$ and $\frac{dI(V)}{dV}$ (numerical derivative of $I(V)$) spectra of two points on the grid indicated by the green and the blue stars in Fig.(5.3a). The green star corresponds to a spectroscopy point positioned on a nanocrystal and the blue star corresponds to the channel between the nanocrystals, which is highlighted by the white rectangle in Fig.(5.3a&b) and is depicted schematically in Fig.(3.10b). While the termination is conducting throughout, the two points are inequivalent. Most notable is the higher DoS between 1 and 2 eV above the Fermi level ($+1$ to $+2\text{ eV}$ in the spectra) at the nanocrystal site. This difference in DoS between the nanocrystals and the channel is illustrated in the current map presented in Fig.(5.3b). The tunneling current from each spectroscopy point at $+2\text{ V}$ is plotted using a grey scale, where brighter points indicate a higher tunneling current. This current map is characterised by bright lines corresponding to the terraces edges and the channels which run between rows of nanocrystals. Fig.(5.3f) shows the in-equivalence of the nanocrystal and the channel at difference bias voltages ranging from $0 - 2\text{ V}$. 8 points along a line in the $\frac{dI(V)}{dV}$ grid, indicated by the red line in Fig.(5.3b) are depicted. This line intersects 2 nanocrystals and the channel between them. For example, points 1 and 2 correspond to the first nanocrystal, while 4 and 5 correspond to the channel. The colour reflects the $\frac{dI(V)}{dV}$ at that bias. At $1.5 - 2\text{ V}$ it is clear that the

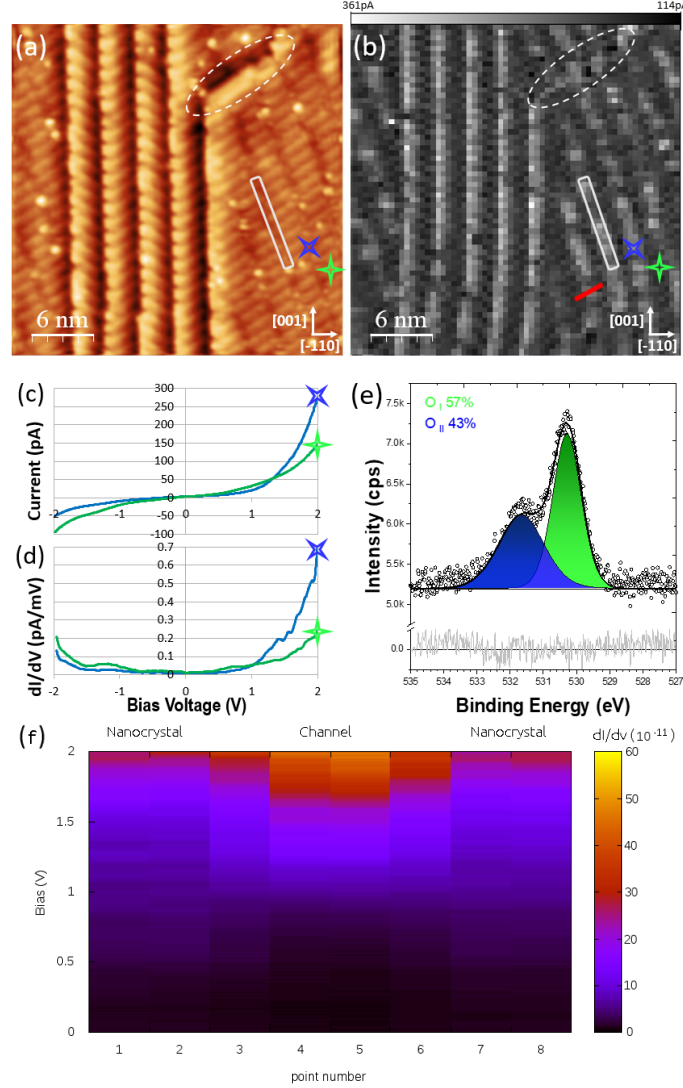


Figure 5.3: **Grid spectroscopy of NbO terminated Nb(110).** (a) (30×30 nm $V = 0.3$ V and $I = 105$ pA): STM image of the NbO(111)/Nb(110) nanocrystal termination. (b) depicts the tunneling current value taken at each spectroscopy point on the grid at 2 V. A channel (between nanocrystals) is indicated by the white rectangle in (a) and (b)). (c) & (d) illustrate individual $I(V)$ and $dI(V)/dV$ spectra of two points on the grid highlighted by the green and blue stars in (a) and (b) positioned on a nanocrystal and a channel respectively. (e) O 1s spectra indicating the presence of two oxygen chemical states. (f) STS spectra of each point (1-8) along the red line in (b) which intersects two nanocrystals and the channel between them.

channel has a significantly higher LDoS, while in the region of 0.5-1 V, the nanocrystal has a slightly larger LDoS.

It is also interesting to note that the terrace edge parallel to the nanocrystals (highlighted by the dashed ovals in Fig.(5.3a&b)) does not exhibit as high a DoS compared to the terrace edges which coincide with the edge of the nanocrystals. This indicates that the presence of the nanocrystal edges are in part responsible for the high DoS of the terraces running in the [001] direction. This is understood in terms of relaxation of the misfit-induced strain, which is easier at the edge of the nanocrystal; Arfaoui *et al.* commented that a larger nanocrystal length could be stabilised at the edge of a terrace, likely due to the reduced strain[82].

Analysis of the O 1s peak, depicted in Fig.(5.3e), can provide insight into the different electronic character of the nanocrystals and channels. Two components, one at 530.3 eV (O_I) and one at 531.7 eV (O_{II}), indicate the presence of two nonequivalent oxygen chemical states. These measurements support those performed by Razinkin *et al.* [84]. One can speculate that the differing surface electronic structure is related to the distribution of the two oxygen states, one in the nanocrystal and one in the channel. This is corroborated by Razinkin *et al.* who observed an increase in the O_I/O_{II} ratio when the incident angle was reduced. This indicates that the “highest” features, the nanocrystals, have a higher O_I/O_{II} ratio compared to underlying layers. This is in agreement with the STS in which the nanocrystals and channels, which are at different heights, exhibit different electronic character. This is suggested to correlate to the different O_I/O_{II} ratio.

Referring back to the terrace structures depicted in Fig.(5.1) with the STS results in mind; In the terrace structure presented in Fig.(5.3a), we observe a sequence of narrow steps, the width corresponding to that of 1 nanocrystal (≈ 3 nm). The orientation of the nanocrystals on each narrow terrace alternates between the two nanocrystal domains. This is not observed on the row-like terrace structure (Fig.(5.1b)) and is suggested to be energetically favourable. Furthermore, the STS of the step edges reveals that the step edges in the [001] and $[\bar{1}11]$ (dashed oval in Fig.(5.3b)) have a non-equivalent electronic structure. This correlates to the orientation of

the nanocrystal with respect to the terrace edge: The terrace edges in the $[\bar{1}11]$ direction are parallel to the nanocrystals, whereas the terrace edge in the $[001]$ direction are close to perpendicular to the nanocrystals, with the nanocrystals terminating at this edge. This is reflected in the colour of the current map (Fig.(5.3b)). The row-like terraces structure only contains the $[001]$ terraces edges, while the second terrace structure contains both. This once again shows the in-equivalence of the terrace structures.

5.3.2 Low dosage oxidation of NbO terminated Nb(110)

The NbO(111)/Nb(110) crystal was exposed to low dosages of molecular oxygen in order to investigate the interaction of oxygen with the termination at the atomic scale. The protective nature of the termination was also investigated. Exposure was performed at 78 K while the sample was in the STM chamber.

Fig.(5.4a) demonstrates a region of the surface following exposure to an oxygen partial pressure of 5×10^{-10} mbar for 30 seconds resulting in protrusions on the surface (indicated by arrows). These protrusions, attributed to physisorbed oxygen, are distributed randomly and are not correlated with the substrate. Pulsing individual protrusions with the STM tip up to ± 7 V within the tunnelling regime did not result in their removal from the surface. This surface with additional oxygen was annealed at 1500 K for 30 mins and flashed at 1700 K for 10 seconds in UHV. This results in the formation of clusters less than 1 nm in size, the vast majority of which reside in the channel between the nanocrystals (Fig.(5.4c)). Chains of up to 10 separated clusters are observed to form within the channels. A high resolution STM image of these clusters is presented in Fig.(5.4d). The clusters are characterised by five distinguishable atom-sized features. Small variations in terms of the number of atoms and the cluster shape are observed. The large scale image shown in Fig.(5.4b) shows the oxide clusters forming rows in the channels between nanocrystals following multiple exposures and annealing cycles.

The NbO terminated Nb(110) forms upon UHV annealing either the oxidised (ambient or otherwise) surface or the oxygen-free surface, which con-

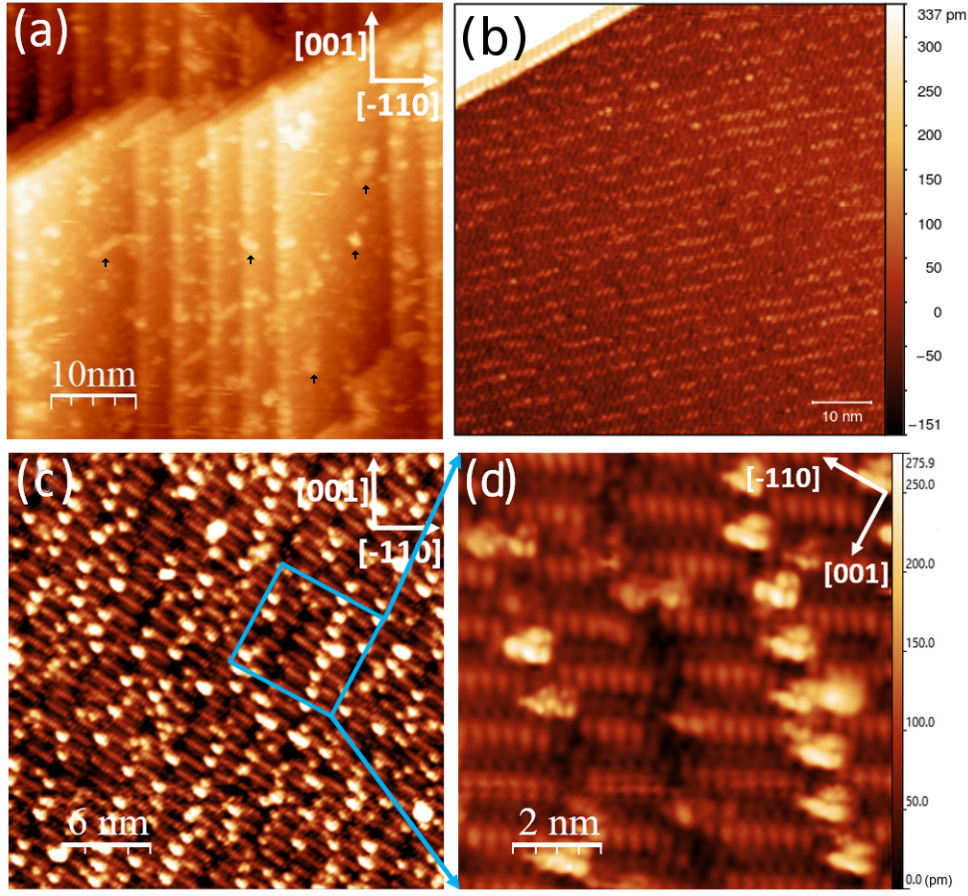


Figure 5.4: **Low dosage oxidation and subsequent of NbO terminated Nb(110).** NbO terminated Nb(110) was exposed to a small dose ($P_{O_2} = 5 \times 10^{-10}$ mbar for ≈ 30 s) of molecular oxygen at 77 K. The bright randomly positioned features in (a) are attributed to oxygen. Annealing the surface in (a) to 1700 K results in the formation clusters ≈ 1 nm in diameter seen in (c) and (d), which form chains of up to 10 separated clusters. These clusters reside in between the niobium nanocrystals of NbO terminated Nb(110). (b) Displays a large scale image of the surface where the clusters can be seen to fill the channels. High resolution STM image (d) demonstrates the features consist of 5 resolved atom-sized features. However, small variation in size and number of atom-sized features are observed. (a) 50×50 nm, $V = 1.4$ V and $I = 68$ pA. (b) $70 \text{ nm} \times 70 \text{ nm}$, $V = 1.4$ V, $I = 60$ pA. (c) 30×30 nm, $V = 0.4$ V and $I = 66$ pA. (d) 10×10 nm, $V = 0.01$ V and $I = 62$ pA.

tains oxygen dissolved in the bulk. Annealing these crystals up to 1900 K does not result in the formation of the oxide clusters. Arfaoui *et al.*[85] and Razinkin *et al.*[84] also annealed the niobium crystal free of surface oxygen at 1200-2200 K and 2000 K, respectively and observed the NbO(111)/Nb(110) nanocrystal termination identical to that in Fig.(5.2) without the presence of the clusters. The clusters therefore only form following the oxidation and subsequent annealing of the NbO(111)/Nb(110) termination. The clusters are observed to reside within the channels between the nanocrystals. While the exact nature of these clusters and their formation is currently not understood one can hypothesise a mechanism for their formation. During annealing, absorbed oxygen which is randomly distributed on the surface may diffuse and find a more stable configuration in the channels where an oxide compound can form.

The grid spectroscopy of NbO terminated Nb(110) provides insight into the nucleation position of the clusters. Between 1 & 2 eV above the Fermi level, the channels in between the nanocrystals exhibit a considerably larger DoS compared to the nanocrystals. It is currently unclear why the clusters reside in this specific electronic environment. However, by considering both the conductivity and enthalpy of the niobium oxides a hypothesis can be put forth. The conductivity of the different niobium oxides reduces from metallic NbO to semiconducting NbO₂ and finally insulating Nb₂O₅. In turn, the enthalpy of formation for NbO, NbO₂ and Nb₂O₅ is -415 kJ/mol, -780 kJ/mol and -911 kJ/mol, respectively[143]. Therefore, the conductivity increases as the enthalpy decreases. One can hypothesise that the adsorbed oxygen will preferentially reside in the area of higher conductivity, which corresponds to a lower enthalpy of formation of an oxide, as is observed. The enthalpy also decreases as the oxidation state decreases. The model of Razinkin *et al.* concluded that oxygen in the channels has a lower oxidation state than oxygen in the nanocrystals[84]. It is noted that at low positive bias voltages and negative bias voltage, the centre of the nanocrystals exhibit a slightly larger DoS than the channels, which can be seen in Fig.(5.3f) for low bias voltages. However, the magnitude of the difference is considerable smaller than that observed between +1 eV and +2 eV

Pulsing these clusters with the STM tip within the tunneling regime did not result in their removal or diffusion from the channels, indicating their stability and the protective nature of NbO terminated Nb(110).

5.4 Discussion

Two terrace structures are evident, the row-like terrace structure and the step-like terrace structure. Both terrace structures exhibit the characteristic NbO terminated Nb(110) nanocrystals. The relative energetics of these terraces is of interest. While the step-like structure certainly has a lower surface energy, the exact difference to the row-like structure is unknown. The step-like structure's lower surface energy is hypothesised to be the result of terracing in the $[\bar{1}11]$ direction which may reduce the misfit strain of the NbO layer to the underlying Nb(110). DFT calculations could be employed in order to model these two terrace structures and determine their surface energies. The step-like structure was also observed to regularly exhibit terrace widths in the $[\bar{1}11]$ direction of exactly 1 nanocrystal, the orientation of which alternates between the two nanocrystal domains terrace by terrace. The alternating orientation appears to be energetically favourable. Understanding this observation is also of interest and will be pursued through further experimentation and with DFT calculations.

The characteristic NbO nanocrystals exhibit a significantly different LDoS to the channels which separate them. This difference is the DoS is suspected to be due to chemically different oxygen atoms in each structure. Furthermore, this difference in the LDoS is shown to dictate the initial oxide growth on the surface, with oxygen clusters forming exclusively in the channels between the nanocrystals. While atomic models exist for the nanocrystal structures, DFT calculations could provide quantitative information about the substructure, particularly the different oxygen states and how their electronic structure determine the initial oxide layer formation. The two types of terraces, one aligned parallel to the nanocrystals and one aligned parallel to the nanocrystals exhibit a different LDoS, this may be due to the nanocrystal structure, however, it may also relate to the energetics of the two terrace

structures as one terrace direction, which is exclusive to the step-like terrace structure, has a lower LDoS. The NbO terminating layer protects the underlying Nb(110) bulk from oxidation. Pulsing oxygen adatoms and oxide clusters on the surface with the STM tip could not remove them. The initial oxide clusters which form in the channels between the nanocrystals raises some questions; why do the oxygen atoms adsorbed on the surface form an oxide in UHV conditions instead of desorbing from the surface, as one would expect given that the clean NbO is prepared by annealing in UHV (reducing) conditions.

Chapter 6

Oxidation of Cu(111)

6.1 Introduction

Cu oxides exhibit a high activity at low temperatures[144], as such, they are used as catalysts in commercial settings for the dehydrogenation of alcohols[145, 146], used in the production of Nylon[147] and the synthesis of methanol[148]. Cu oxides are actively being investigated for use in the oxidation of CO to CO₂[149–151], critical in catalytic converters, in preventing the poisoning of Pt electrodes in fuel cells[152] and for the conversion of propylene oxide to CO₂[153]. Cu nanomaterials can also be used for the reduction of CO₂[154]. Unsaturated Cu atoms in the Cu₂O support the dissociation of H₂O, used for water splitting[155, 156]. Oxygen vacancies are reported to increase the rate of dissociation [156]. There is some debate over the active sites for Cu oxides with some evidence supporting both Cu₂O and CuO sites[144, 150, 151].

Ronay and Nordlander[54, 55] calculated the barrier to oxygen penetration clean Cu(111) to be 0.9 eV, whereas for Cu₂O the barrier is just 0.04 eV. The Cu₂O provides little to no resistance to the oxidation process, therefore, once the initial oxide layer has formed, the oxidation rate becomes parabolic[108]. Oxygen adatoms have been reported on Cu on Cu₂O and an investigation to determine the incorporation barrier experimentally was conducted. However, in the process of producing the Cu₂O thin film, a number of interesting defects were observed on the surface which are discussed in Ap-

pendix A, along with a number of sub-monolayer oxides which are discussed in this chapter. Pulsing of oxygen adatoms on $\text{Cu}_2/\text{Cu}(111)$ has yet to be realised.

While oxides such as the “29” and “44” $\text{Cu}_2\text{O}(111)$ -like superstructures (section 3.4.3) have been observed at close to a monolayer of coverage, oxide structures which form prior to these structures have not received much attention. The initial stages of oxidation are of interest for the theoretical understanding of the oxidation process. The oxides which initially form on $\text{Cu}(111)$ prior to a monolayer of coverage are investigated in this chapter.

6.2 Surface preparation

A $\text{Cu}(111)$ single crystal (99.999% purity) was used over the course of this study. The clean $\text{Cu}(111)$ surface was prepared by argon sputtering and annealing cycles. LEED measurements between cycles monitored the progression of the surface. Argon beam energies ranging from 150 eV to 1 keV were used during the sputtering process, with the energy decreasing with each cycle. Each cycle had a 20 minute duration. The argon partial pressure was 5×10^{-5} mbar for each sputtering cycle. Each sputtering cycle was followed by an anneal cycle. The annealing temperature was 750°C as measured by a pyrometer (emissivity = 0.25) and a thermocouple located beneath the filament and the sample plate. Annealing steps lasted 20 minutes. The electron beam voltage was 0.3 kV which results in an e-beam current of 35 mA. Cycles were repeated until an ordered $\text{Cu}(111)$ surface, as demonstrated by LEED, was observed. The ordered LEED image is presented in Fig.(6.1a).

Annealing the sample at temperatures up to 950°C for 1 hour did not result in a noticeable improvement of the surface structure as judged by LEED and STM measurements, it did however result in the heating stage surrounding the sample to discolour. The colour matches that of the Cu sample, indicating that at 950°C Cu atoms desorb from the crystal surface and form a thin film on the heating stage.

Following the preparation procedure the $\text{Cu}(111)$ was exposed to an oxygen partial pressure while the temperature of the sample varied from $\approx 78 -$

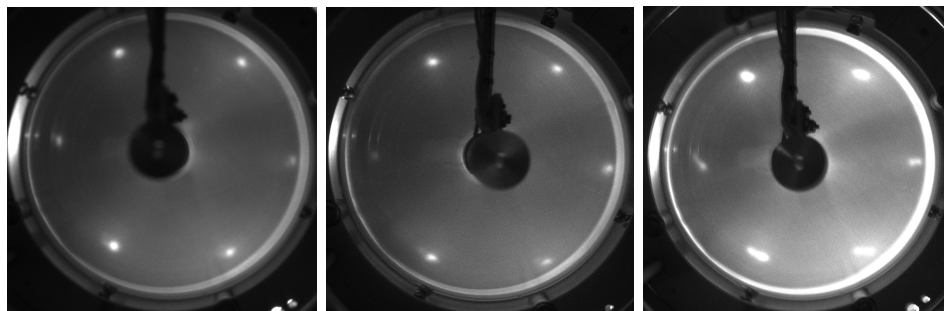


Figure 6.1: **LEED images of the Cu(111) surface** (a) The Cu(111) surface following the preparation procedure. (b) The surface following a 50 L exposure to oxygen at 750 K. Spot broadening is observed. (c) The surface following a 150 L exposure to oxygen at 750 K. Each spot is observed to have split.

850 K. LEED and STM measurements were conducted with the aim of investigating the initial stages of oxidation. All STM measurements take place at ≈ 78 K.

6.3 Experimental results

Oxidation at low temperature

The sample was cooled to 78 K in the STM chamber before being promptly moved to the preparation chamber and exposed to an oxygen partial pressure of 1×10^{-9} mbar for 15 minutes (1 Langmuir) before returning to be cooled in the STM chamber. The background pressure prior to exposure was 1×10^{-10} mbar. STM images of the surface reveal a small number of protrusions which have a brightly contrasted Friedel Oscillation (FO) along and considerably more features with a darkly contrasted FO centre. No oxide-like structures, such as those in the following oxidation sections, were observed. The defects which perturb the electron density resulting in these FOs are investigated in the appendix A.2.

Oxidation at 300 K

The Cu(111) sample was exposed to an oxygen partial pressure of 1×10^{-7} mbar for 15 minutes (90 Langmuir) at room temperature (300 K) following the preparation procedure, employed to obtain a clean copper surface, outlined above. The background pressure prior to exposure was 1×10^{-9} mbar. STM measurements indicate that the surface is partially oxidised and that three types of surface oxides are present on the surface, in agreement with Matsumoto *et al.*[30] The three types of oxides can be seen in Fig.(6.2) and each oxide domain is highlighted by colour. In keeping with the nomenclature of Matsumoto *et al.*, the green lines indicates the “on-terrace” oxide, the red line indicates the “in-terrace” oxide and the blue lines indicate the “step-oxide”. The oxides observed appear to be disordered, with the exception of a small region of the “step” oxide depicted in the inset of Fig.(6.2). This ordered oxide exhibits a distorted hexagonal structure with a period of ≈ 1.6 nm. These results are consistent with the work of Matsumoto *et al.* which is detailed in section 3.4.3.

Oxidation at 750 K

The sample is cleaned by annealing before being exposed to an O_2 partial pressure of 5×10^{-8} mbar for 50 minutes, corresponding to an exposure of 150 Langmuir, at 750 K. The sample is post-annealed at 850 K for 5 minutes in vacuum. LEED measurements taken before and after are shown in Fig.(6.1a&c). Following the annealing cycle, the hexagonal symmetry observed in LEED before oxidation, is still present, however, the spots are broader, indicating that the surface has undergone some change. The LEED image in Fig.(6.1b) corresponds to an exposure of 50 Langmuir.

STM measurements reveal a surface with a diverse oxide structure, depicted in Fig.(6.3). Cu(111) terraces (yellow) are still present on the surface as indicated by LEED. A new type of oxide structure is observed in place of some of the Cu(111) terraces, indicated by **I** in Fig.(6.3). The oxide which resides on the terraces in islands (green) and at the terrace edges (**II**) appear similar in STM images and their relative heights above the terrace is

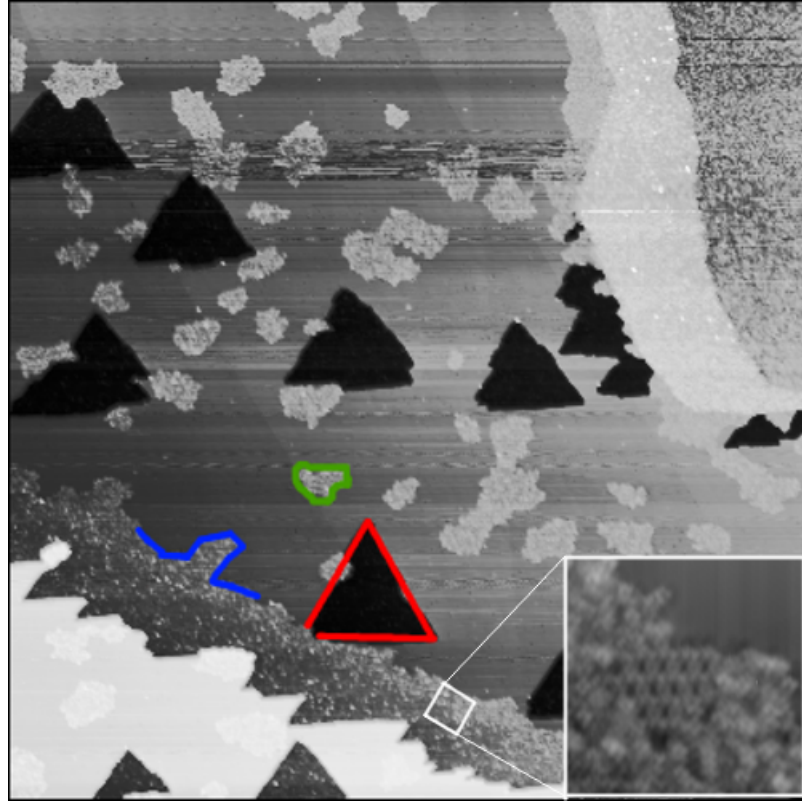


Figure 6.2: **STM image of the Cu(111) surface following oxygen exposure at 300 K.** Three oxides are observed following oxygen exposure at 300 K. the brightly contrasted islands, highlighted in green are the “on-terrace” oxides. The red line indicates the triangular pits in the Cu(111) terrace, which contain the “in-terrace” oxides. The blue line indicates the edge of a part of the “step-oxide” which forms at the Cu step edges. A small region of ordered oxide structure within the “step” oxide is depicted in the inset.

equal, unlike the “on-terrace” and “step” oxides observed at 300 K which are distinct[30]. The cyan/blue line indicates the boundary between the oxide at the step and the terrace upon which it sits. A height difference of 63 pm is observed. The pink line indicates the terrace edge, a height of approximately 190 pm, similar to those observed between Cu(111) terraces in previous experiments (200 pm). Oxides are only observed on this new type of terrace, no oxides, island or step like, are observed on Cu(111) terraces. The “in-terrace”

(red) oxide is not as prominent as for 300 K, it has only been observed in a few locations and is generally significantly smaller in size.

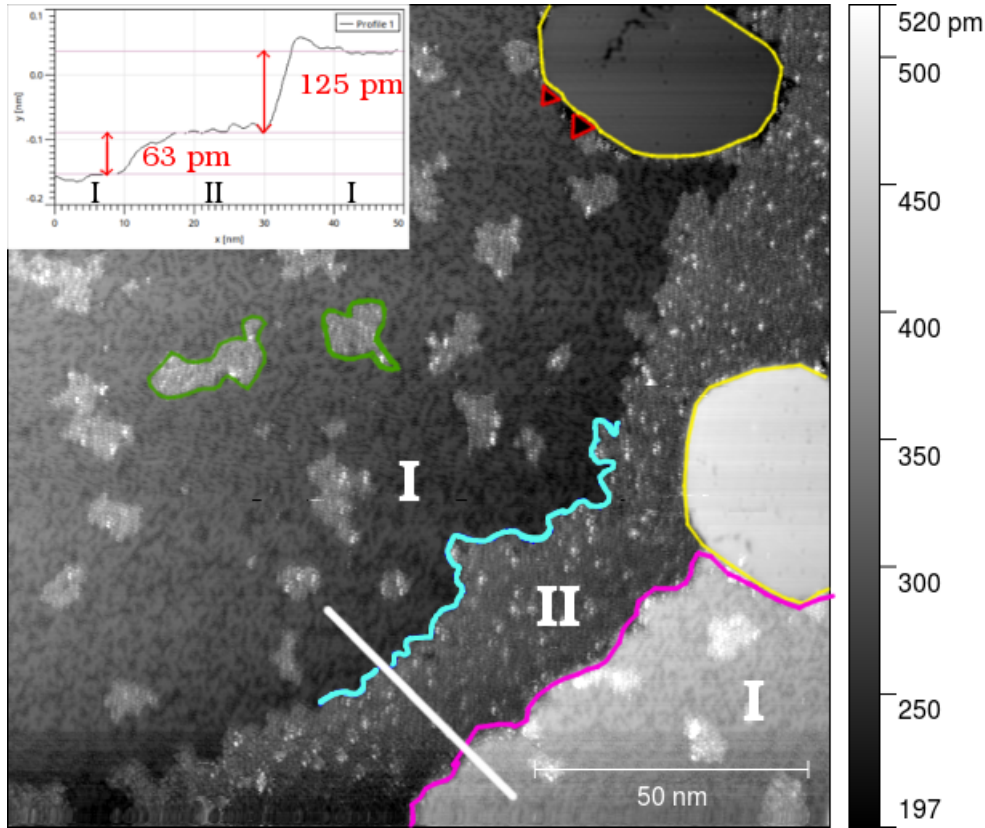


Figure 6.3: **Large scale STM image exhibiting different oxides structures following oxidation at 750 K.** Region I indicates the “inhomogeneous” oxide structure. Region II is the oxide which resides at the terrace edges (indicated by pink line). The boundary between the oxide at the step edge and the terrace upon it sits is indicated by the cyan/blue line. Green indicates the oxides which form islands on the terrace and appear similar to the oxide at the step edges. Cu(111) terrace islands are highlighted in yellow. Adjacent region I terraces differ in height by 190 pm, closely matching that of Cu(111) terraces.

A high resolution image of the new oxide structure is present in Fig.(6.4), along with an enlarged image of a small subsection. The new oxide structure has two main features, a “flat” component which resembles the Cu(111) terraces, in the sense that it is homogeneous, and small round protrusions, indicated by the white arrow in the inset image. The round features are

5.5 Å in diameter and are numerous on the surface, forming “chains”. The relative height difference between the flat region and the round features, is approximately 18–30 pm, indicating the difference is due to an electronic effect rather than a purely topographical one as Cu step heights are approximately 200 pm. This is also supported by the relative height difference to the adjacent Cu(111) region which is a part of the same Cu terrace. The height profile is shown in Fig.(6.4) and indicates that the Cu(111) region is 20 pm above the new oxide. These features may be the first oxide structures which form on Cu(111) before overlayer structures such as the ordered “29” or “44” superstructures, described in section 3.4.3, form. The structure seen in the pink box in Fig.(6.3a) is henceforth referred to as the “inhomogeneous” oxide.

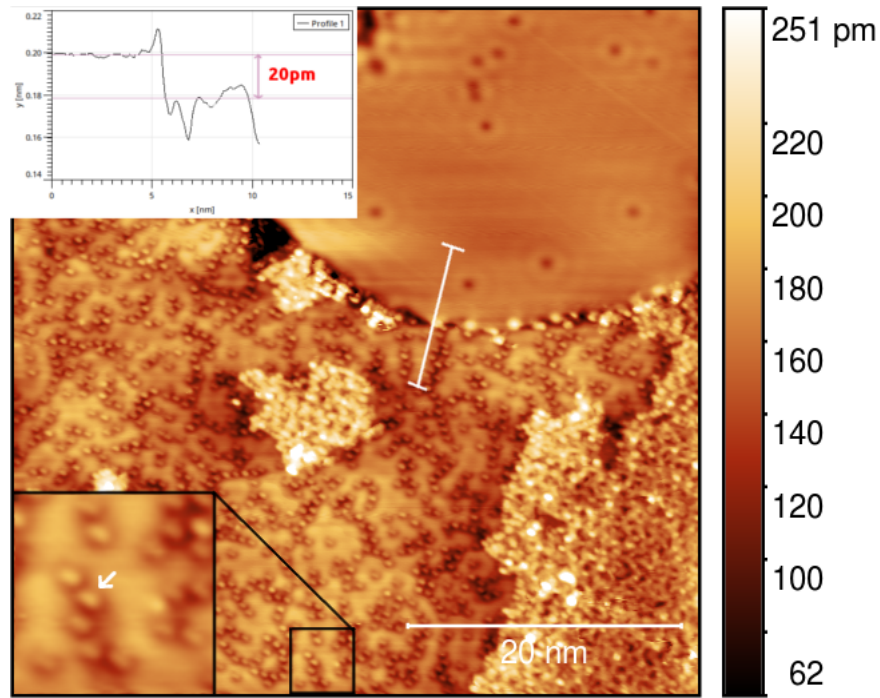


Figure 6.4: **High resolution STM image depicting the “inhomogeneous” oxide following oxidation at 750 K.** This oxide is composed of a flat region resembling Cu(111) with small round features, (white arrow), forming chains within the terrace. The line profile indicates a 20 pm height difference between the Cu(111) island and the “inhomogeneous” oxide.

Oxidation at 850 K

The surface was once again cleaned of oxides prior to oxidation following the preparation procedure detailed in section 6.2. The oxygen exposure was identical to that of 750 K, however the annealing temperature during oxidation was 850 K. The sample was also post annealed at 850 K for 5 minutes. LEED measurements following this oxidation procedure are presented in Fig.(6.1c). It is clear from the splitting of the hexagonal spots in LEED, that the surface structure has changed.

STM measurements exhibit two ordered oxides on the surface alongside the “inhomogeneous” structure and the Cu terraces observed in the previous sections. Fig.6.5 displays a region of the surface, $50\text{ nm} \times 50\text{ nm}$ in size. “Inhomogeneous” oxide regions are labelled **I** and the oxide which resides at the step, **II**, as previous denoted at 750 K. The boundary between a large Cu(111) terrace and the oxide structures is indicated by the yellow line. The terrace edges of the “inhomogeneous” structure are indicated by the pink lines and the boundary between the oxide at the terrace edges and the terrace which is resides by blue. Each “Inhomogeneous” oxide terrace contains an oxide at its step edge. The width of this step oxide (**II**) varies to the small regions depicted in Fig.6.5 to large widths in excess of 100 nm (not presented) which comprise significant portions of the terrace. The island oxide which was present on the terraces at 750 K are no longer evident. Given the similarity of the step and island oxides at 750 K and the large increase in the size of the step oxide (**II**) coinciding with the disappearance of the island oxides at 850 K, a statement can be made about the growth of the oxide from the terrace edges. At the elevated temperature (850 K), the oxide which comprised the island oxides has sufficient energy to diffuse on the surface, coalescing with the oxide at the terrace edges (**II**) and resulting in the significant growth of the oxide structure. At 750 K oxides were stable in both configurations, at the terrace edges but also in islands, limiting the growth at the step edges. The step heights between regions **I** and **II** at 850 K closely resemble the steps heights between the regions at 750 K with

blue and pink boundary lines, indicated in Fig.6.5, being 70 pm and 130 pm respectively, resulting in a Cu(111)-sized terrace height of 200 pm.

The oxide (**II**) which resides at the edges of the “inhomogeneous” terraces (**I**) are shown to be ordered in the inset of Fig.6.5. The period of the structure, which demonstrates a hexagonal symmetry, is approximately 1 nm, 4 times larger than that of Cu(111). A tip event occurred between obtaining the main image of Fig.6.5 and the inset image, altering how the surface appears in STM images. This change is also reflected by a change in appearance of the “inhomogeneous” terrace. The small round features in the bottom of the inset image are contrasted brighter than the surrounding Cu component of the layer, contrary to how they appear in the main image of Fig.(6.5) and Fig.(6.4). This change in tip state is observed numerous times over the course of this study and consistently resulting in the same 2 variations of the inhomogeneous structure and the ordered oxide structure. Thus, the terrace edge oxide (**II**) observed at 750 K, Fig.(6.3) likely contains the same ordered structure as at 850 K in Fig.6.5.

The second ordered oxide structure observed following oxidation at 850 K is observed upon the same terrace as the smaller structure. Fig.6.6 presents 3 images of the same terrace taken sequentially over a 6 hour time period, beginning with (a). In Fig.(6.6a) a large ordered oxide region is present to the right of the image, the period of the bright features is measured to be 1.6 nm. From the enlarged image of this structure, presented in the inset, the protrusions appear to display a 3-fold symmetry. Fig.(6.6b) and Fig.(6.6c) also displays this large periodicity structure with the addition of another ordered structure indicated by the white boxes. This structure has a period close to 1 nm, approximately that of the terrace edge oxide (**II**) structure presented in the inset of Fig.(6.5) and changes appearance (tip effect) in the same manner between Fig.(6.6b) and Fig.(6.6c) and so the structures are identical. The terraces are composed of the terrace edge oxide (**II**) with small regions of a larger periodic structure.

High resolution images of the larger structure, within the white box in Fig.(6.6a), reveals internal structure to the large protrusions, depicted in Fig.6.7. The large protrusions seen in Fig.(6.6a) are confirmed to exhibit

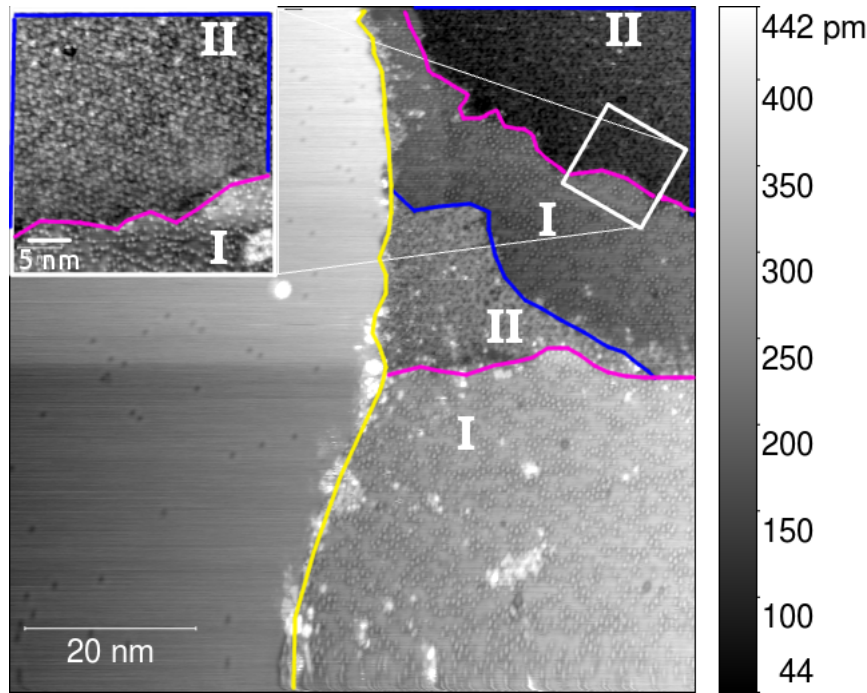


Figure 6.5: **STM image of the surface following oxidation at 850 K.** A Cu(111) terrace is in the region to the left of the yellow line. The “inhomogeneous” oxide(I) terrace edges are indicated by the pink lines and the boundary between the terrace edge oxide (II) and the “inhomogeneous” terrace (I) on which it sits is indicated in blue.

a 3-fold symmetry, with 3 additional atomic-sized features present on each protrusion. Two of these atomic-sized features are protrusions which appear similar in contrast and size, the third is similar in size however is darkly contrasted (depression). These atomic-sized features form a triangle. The distance between triangles is 1.6 nm, matching that of the large scale image and indicating that these triangular structures appear round at lower resolution. There is a difference in the distances between the atomic-sized features. The inset of Fig.6.7 presents an enlarged image of the triangular structures. The distance between the two atomic-sized protrusions from the same triangular structure is $\approx 7.5-8 \text{ \AA}$ (blue line). The distance between bright atomic-sized features in adjacent triangular structures is always greater than for the inter-triangular distances, by approximately $0.5-1 \text{ \AA}$ (pink). The distances between the atomic-like protrusions and the depression, within the same triangular

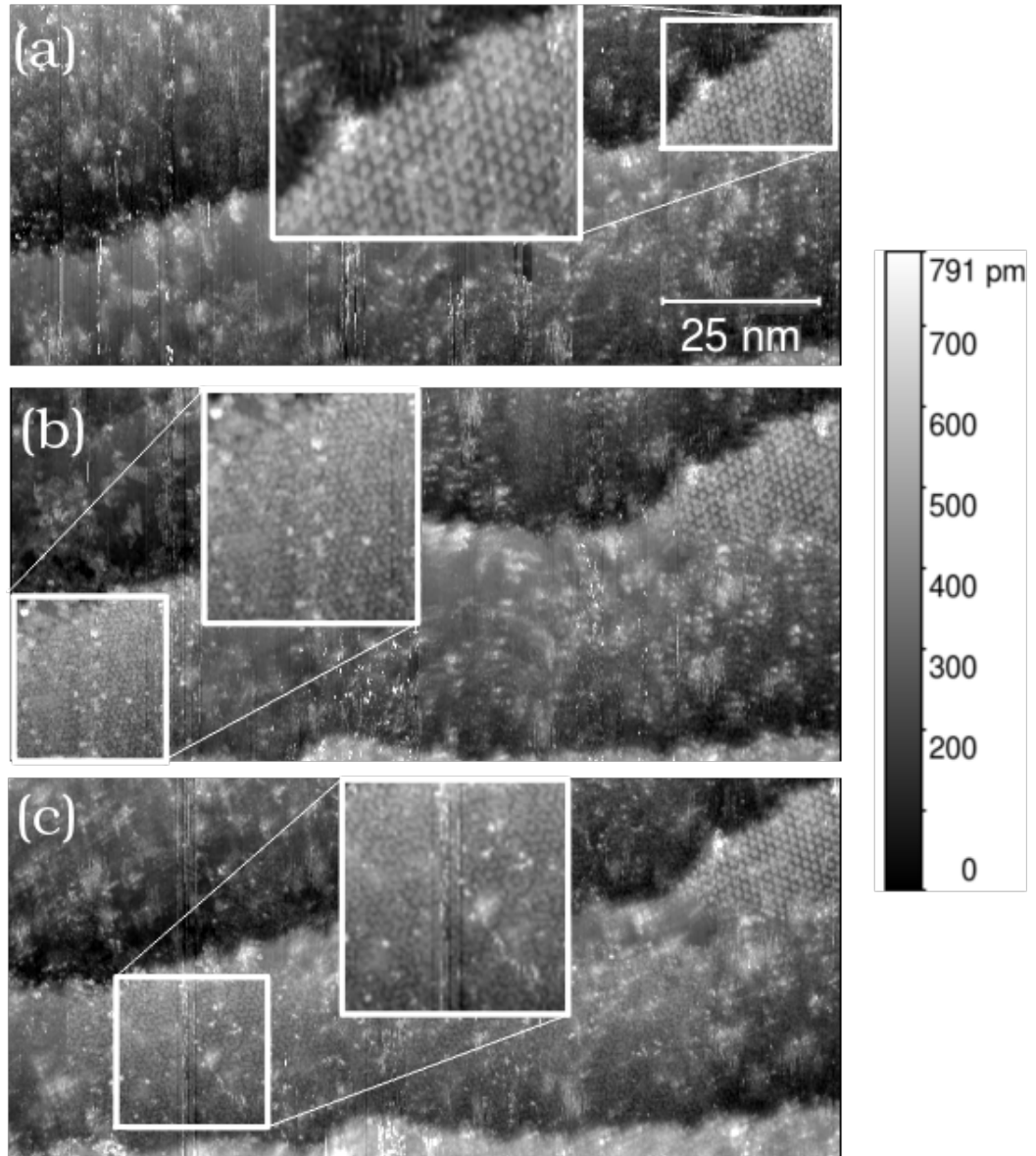


Figure 6.6: **STM images of Cu(111) following oxidation at 850 K exhibiting two distinct ordered structures.** (a) A large periodic (1.6 nm) structure is present and enlarged within the white box. (b) While the large structure is still present, another ordered structure with a period of 1 nm is present. (c) The structure seen in (b) no longer appears ordered however it can be seen to extend across the majority of the terrace.

structure is $\approx 7.5 \text{ \AA}$ (red line) and $10 \text{ \AA}$ (yellow line). The atomic-sized depression always occupies the same point on the triangular structure. The triangular structures are all orientated the same way. The regions where the corners of the triangular structures meet are darkly contrasted. The region between the sides of the triangular structures (below yellow line) is brightly contrasted, on a similar scale to the centre of the triangular structures.

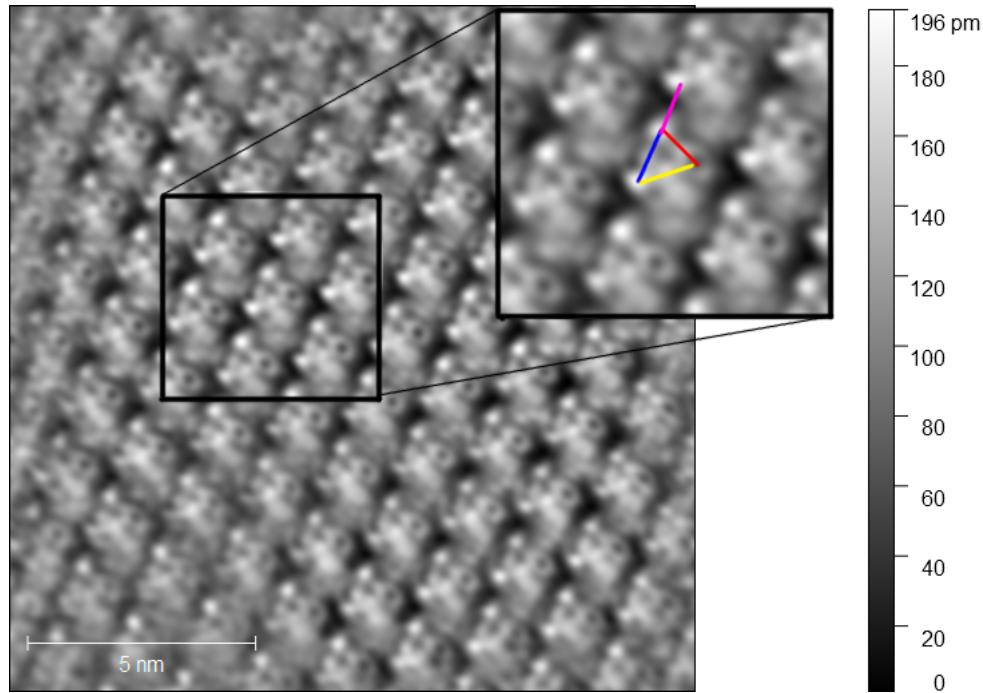


Figure 6.7: **Filtered high resolution image of the large scale ordered structure seen in Fig.(6.6a)** The internal structure of the protrusions has been resolved. 3 atomic-sized features are present, two protrusions and 1 depression. The inset shows the structure in more detail and indicates the distances between features. Red = $7.5 \text{ \AA}$, Yellow = $10 \text{ \AA}$, Blue = $0.75 \text{ \AA}$, Pink = $0.85 \text{ \AA}$. Distances were calculated on an unfiltered image.

While it is clear that the atomic-sized depression is inequivalent to the two atomic-sized protrusions, the protrusions are also inequivalent. The STM image presented in Fig.(6.8a) shows the surface with the 2 seemingly equivalent atomic-sized protrusions obtained with a bias voltage of 1.5 V and a tunneling current of 100 pA . The STM image presented in Fig.(6.8b) uses the same bias voltage of 1.5 V , however, the tunneling current is 50 pA . One of the

atomic-sized protrusions is no longer resolved. The atomic-sized depression is still present along with the other protrusion.

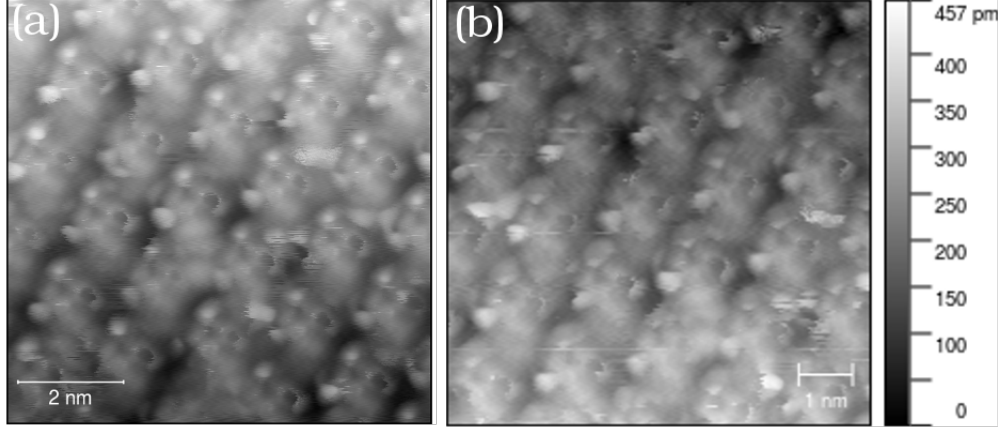


Figure 6.8: **High resolution STM images indicating an inequivalence in the atomic-sized protrusions.** (a) STM image, $V=1.5$ V, $I=100$ pA indicating the presence of both atomic-sized protrusions and the atomic-sized depression. (b) STM image, $V=1.5$ V, $I=50$ pA exhibiting only one atomic-sized protrusion and the atomic-sized depression.

The period of the smaller oxide structure is 1 nm while the larger one is 1.6 nm, approximately 4 and 6.3 times that of the underlying Cu(111) lattice. Neither structure matches that of the $\text{Cu}_2\text{O}(111)$ -like “29” or “44” superstructures which are reported to grow as the initial oxide layer is formed on Cu(111) as discussed in section 3.4.3. Given that the oxygen exposure (150 L) used to achieve this structure is relatively low and a sub-monolayer oxide coverage is observed with STM measurements, these oxides may be distinct from those previously reported.

The larger of the two oxide structures bears resemblance to the $\text{Cu}_2\text{O}(111)$ ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction reported by Onsten *et al.*[100] (Fig.(3.16) in section 3.4.3), more specifically the reconstructed surface with 1/3 unsaturated oxygen (O_U) vacancies reported by Zhang *et al.*[24](Fig.(3.15a&e) in section 3.4.3). The vacancies induce relaxation of the 3 unsaturated copper (Cu_U) atoms, which appears as bright protrusions in STM imaging, towards the vacancy, resulting in triangular structures forming. A key difference between this structure and those of the literature is the differences in period, the

in-equivalency of the (Cu_U) (contrast and spacing) atoms and the relative orientation of these triangular structures to one another. Zhang *et al.* produced a model where the triangular structures due to the O vacancy are orientated with corners pointing to sides of neighbouring triangular structures, whereas for the oxide we observe, the corners facing each other. The space between triangular structure is homogeneous for Zhang's model whereas a contrast difference is observed in experiment. The period of the internal structure is approximately 0.8 nm, close to that of $\text{Cu}_2\text{O}(111)$, the larger oxide structure may be a Cu_2O -like oxide with an incomplete or defective surface coverage.

6.4 Discussion

A variety of oxides were observed on the Cu(111) surface following low dosage oxidation at temperatures ranging from 78 K to 850 K. The sample is scanned at ≈ 78 K. The oxide coverage is low across all experiments, large un-oxidised Cu(111) terraces are presented on the surface. At 300 K clean Cu(111) terraces are present, along with terraces containing oxides. Three types of oxide are observed on these terraces. "Step" oxides which reside at the Cu(111) terrace step edges, "on-terrace" oxides which are oxide islands on the Cu(111) terraces and the "in-terrace" oxide which is formed within the Cu(111) terrace. These oxides are disordered with the exception of some small regions within the step-oxide, which exhibit a distorted hexagonal structure.

At 750 K, another type of oxide is observed on the surface, referred to as the "inhomogeneous" oxide. This oxide strongly resembles Cu(111) terraces in appearance and terrace height, with the addition of small protrusions forming "chains" within the structure. Cu(111) terraces are 20 pm above the "inhomogeneous" oxide terrace, indicating an electronic difference. Oxides only exist on these "inhomogeneous" terraces, indicating an energetic preference for the oxides to be in close proximity to one another. Oxides which form small islands on the "inhomogeneous" terraces and at the corresponding terrace edges appear to be the same. This oxide is shown to be ordered, with a hexagonal symmetry and a period of 1 nm. This oxide is different to that observed at the steps at 300 K.

At 850 K the ordered oxide which appeared at the terrace edges on the “inhomogeneous” terraces at 750 K is significantly larger, the oxide islands are no longer present. It would appear that the oxide islands and the terrace edge oxide observed at 750 K have coalesced at 850 K. The increase in thermal energy is sufficient for the atoms which compose the oxide islands to diffuse to the terrace edges where they are more stable. This ordered oxide structure is very sensitive to the tip condition. A second, larger, ordered oxide is apparent following oxidation at 850 K. This oxide structure has a period of 1.6 nm. High resolution STM images of this structure reveal a 3-fold symmetry. The period of both ordered structures is close to integer multiples of the underlying Cu(111) lattice. Structural models of both structures are planned with the potential for DFT calculations in the future.

At the sub-monolayer order, many oxides exist and are complex in nature. It appears energetically favourable for oxides to grow on top of one another, evident from the segregation of clean terraces and oxide structures. Many oxides are stable on the surface at lower temperatures, but at higher temperatures these oxides coalesce and take the form of ordered structures and the “inhomogeneous” oxide structure. STS experiments could distinguish between the different oxides which appear similar in STM images. Further oxidation of the sample at the same oxidation temperatures would allow for the monitoring of the growth and the formation of the initial oxide layer. The transition between the experimentally observed oxides and those presented in the literature with a coverage of 1 ML or more, may be of interest.

Chapter 7

Discussion & Conclusions

In this thesis, both the initial stage of formation and structure of ultra-thin oxides on Mo, Nb and Cu were investigated. Their physical and electronic structure was analysed in order to understand: (1) the structure and stability of ultra-thin oxides of Mo(110) and Nb(110) and (2) the initial stages of oxidation of Cu(111). STM measurements are used to characterise the surface and probe the ability for oxygen adatoms to penetrate the oxide layer for Mo and Nb.

Oxygen adatoms on $\text{MoO}_{2+x}/\text{Mo}(110)$ can be removed from the surface by applying a bias pulse between the STM tip and the surface. While adatom removal is observed within the tunneling regime, adatom removal is also observed outside of the tunneling regime, where only the electric field contributes to the removal process. FEM simulations using only an electric field replicate the experimental dependence of the threshold voltage on the tip-surface distance. Adatom removal is only observed at positive sample bias outside of the tunneling regime, indicating the oxygen adatoms are “pushed” into the surface by the electric field. An intermediate state, one where the adatom has not fully penetrated the surface, is observed. The electric field produced between the STM tip and the sample is concluded to induce the penetration of oxygen adatoms into the terminating oxide layer. The magnitude of electric field potential experienced by an adatom in order to be removed was estimated to be 0.43 V from FEM simulations and exper-

imental results. The size of the region which adatoms are removed from is shown to depend on the magnitude of the bias applied between the tip and surface. FEM simulations produced a dependence with reasonable agreement to the experimental data. Carefully adjusting the pulse voltage allows for a great deal of control over the spot size with a minimum resolution of 0.5 Å, corresponding to the removal of one adatom. DFT calculations of the $\text{MoO}_2/\text{Mo}(110)$ and $\text{MoO}_{2+x}/\text{Mo}(110)$ indicate that the oxygen adatom induces a relaxation of the underlying Mo atom from its lattice position in the O-Mo-O tri-layer to the oxygen layer above, exposing a channel. Theoretical work presented in the literature suggests that channels such as these can significantly reduce the barrier for oxygen incorporation through an oxide layer. Applying an electric in the vicinity of an adatom can further reduce this barrier, to the point when the oxygen adatom can penetrate the surface layer. The dependence of the threshold voltage on the pulse duration yielded an estimate for the potential barrier of oxygen penetration through the surface to be 0.45 eV, closely matching that from FEM simulations. While the evidence suggests that oxygen adatoms penetrate the surface, other possible mechanisms for the experiential observations exist. Adatoms may be ejected from the surface via desorption to the vacuum when a sufficiently large voltage pulse is applied to the tip outside of the tunneling regime. Potential barriers in the surface region may be significantly altered in the presence of a large electric field, this may lead to a situation beyond that of simple barrier height reduction and result in adatom desorption from the surface. The O-Mo-O trilayer may contain vacancies, which, in a similar manner to those induced by oxygen adatoms, may offer a channel by which to penetrate the surface either occupying the vacancy or diffusing to the underlying O layer.

The NbO layer terminating Nb(110) is a protective oxide layer which presents a barrier to oxygen incorporation that pulsing could not overcome. This ultra-thin layer also exhibits a tri-layer structure. Two terrace structures are present on the surface, one of which is flat in the Nb[001] direction, the other exhibits terracing in both the Nb[001] and $[\bar{1}11]$ directions. Terracing in the Nb[001] is hypothesised to relieve the misfit strain between the NbO terminating layer and the underlying Nb(110) bulk. NbO nanocrystals,

which have been reported previously, terminate the surface of both terrace structures. These nanocrystals form ladder like stacks, typically 2–3 nm in length and are separated by a narrow channel. STS measurements indicate a significantly higher LDoS in the channels above 1 V and XPS measurements indicate the presence of two oxygen chemical states in the oxide layer. Similar results from the literature indicates that one of these oxygen states is localised on the surface, i.e. in the channel. The different LDoS between the nanocrystals and the channels are strongly suspected to be due to the different oxygen states present on the surface.

STS measurements also indicate a higher LDoS along the terrace edges which run in the Nb[001] direction, similar to that of the channels. However the terraces which run in the Nb[$\bar{1}11$] direction do not exhibit as large an increase in the LDoS, indicating that the terrace edge may not be the reason behind the increase in the LDoS. Interestingly the nanocrystals terminate the step edge in the Nb[001] direction, whereas the nanocrystals are parallel to the terrace edges in the [$\bar{1}11$] direction, indicating the termination of the orientation of the nanocrystal with respect to terrace edge may be responsible for the inequivalence. The lower LDoS observed on the terrace edges in the [$\bar{1}11$] direction may contribute to the lower surface energy exhibited through terracing in this direction. The terraces in the [$\bar{1}11$] direction consistently exhibit a terrace width of 1 nanocrystal, the orientation of which alternates terrace by terrace. This is suspected to be energetically favourable given its prominence on the surface.

Oxygen clusters which form on the surface following oxidation and subsequent annealing are confined to the channels between the nanocrystals. As the exposure increases the oxygen clusters grow in size and fill the channels, exhibiting a row structure on the surface. The NbO layer dictates the initial growth of the additional oxide layer. NbO is predicted to have a high barrier opposing oxygen incorporation in comparison to other transition metal oxides, which was observed experimentally, with no pulsing experiments succeeding in inducing adatom or cluster penetration in or outside of the tunneling regime. Unlike Molybdenum, the O-M-O tri-layer which forms on Nb is stable. The densely packed nature of the NbO terminating layer may be the

reason behind this stability, without a channel for oxygen to diffuse through, the potential is too large to surmount by pulsing.

The initial stages of oxide growth on Cu(111) was investigated using STM measurements. A small dosage of oxygen was exposed to the sample over a range of annealing temperatures from 78 K to 850 K resulting in sub-monolayer coverage for each exposure. At low temperatures a number of disordered oxides exist on the Cu(111) surface along with clean terraces. These oxides exist at the terrace edges and on the terrace in the form of islands. A small region of order can be observed within the terrace oxide on occasion and this ordered oxide displays a distorted hexagonal symmetry. At 750 K the step and island oxides are similar in appearance in STM imaging. Clean Cu(111) terraces are evident on the surface, however the terraces which oxides exist take on an inhomogeneous appearance. It is energetically favourable for oxidation to occur in localised regions, however oxides exist in different forms, indicating that at 750 K the energy is not sufficient for the oxides to coalesce into the most stable, ordered, form.

At 850 K, oxide islands are no longer evident on the surface, the oxide which was stable at the terrace edges is observed to have grown significantly in width. It would appear that at 850 K there is sufficient energy for the oxide islands to diffuse, the diffusion then halts when the oxide is at the step edge. This oxide exhibits a hexagonal symmetry with a period of 1 nm. A larger ordered oxide structure is also evident. This structure exhibits a hexagonal symmetry with a period of 1.6 nm. The period of both ordered oxide structures are close to integer multiples of the underlying Cu(111) lattice. High resolution STM images reveal that each protrusion which makes up the 1 nm period structure, exhibits a substructure which is triangular in shape. This subsurface resembles that of a $\text{Cu}_2\text{O}(111)$ -like oxide layer which is found in the literature however some key differences exist. Most notably this structure displays several in-equivalencies within the triangular substructures. Non-identical atom-sized features occupy each corner of the triangular protrusions, with varying inter-feature spacing. Furthermore, the orientation of the triangular structures relative to one another is different than that of the literature. Elements of the oxide structure, such as the

triangular structure resemble oxygen vacant Cu_2O defects, indicating that this oxide may be a defective oxide layer with $1/3$ missing O atoms. This result is not surprising considering the low oxygen exposure and resulting sub-monolayer coverage on the surface.

7.1 Future work

The wide use of ultra-thin film metal oxides in many industries ensures that research into their physical and chemical properties will continue for a long time to come. There is a continuous drive to make metal oxide films more efficient in their wide variety of applications. In order to do so, detailed knowledge of their properties on the atomic scale is required, particularly for catalysis and modern electronics and photoelectronics. In this thesis, fundamental work relating to the surface structure of some select metal oxides and the impact the structure has on the initial oxidation process has been presented, however, much more can be achieved. The ability to induce oxygen diffusion through the surface of $\text{MoO}_{2+x}/\text{Mo}(110)$ using an electric field opens the possibility for ion implantation into other oxides or similar structures with open channel for diffusion. The resolution, spot size on the order of $0.5 \text{ \AA}$, of this method makes it suitable for the production of electronic and optical devices where the properties of the device are governed by a single atom or defect, such as qubits for application in quantum computing[157]. While this study has assisted in identifying the mechanism behind the removal process, aspects such as understanding where exactly the oxygen ion diffuses is still not fully understood. DFT calculations may be able to provide insight. The adatom removal process inside of the tunneling regime is another aspect of this mechanism which requires further investigation. The tunneling current modifies the process making it relatively more difficult to remove adatoms than with the electric field alone. How exactly this occurs remains to be seen. Memristors are devices whose resistance depends on the current that has previously flown through, in oxides this is achieved through oxygen vacancy diffusion. MoO_2 has been shown to exhibit memristor properties[158] and so the work here may be of interest to those in memristor research on

the atomic scale. Molybdenum oxides are used as catalysts in an array of applications and exhibits selectivity depending on the oxidation state. It may be possible through ion implantation to artificially induce oxidation and thus change the oxidation state of a Mo atom in the surface oxide layer. This could potentially lead to catalytic selectivity on controlled areas of the surface, using the nano-scale lithographic properties of this method of ion implantation.

The superconducting properties of Nb are of great interest in the production of high temperature superconductors, Josephson junctions and single electron transistors. NbO has a much lower superconducting critical temperature than Nb. The growth of the NbO oxide layer reduces and eventually destroy the superconducting properties of Nb. However, NbO, even as an ultra-thin film, protects the underlying Nb bulk from further oxidation. Without the ability to penetrate the NbO layer, oxide clusters form on the surface exclusively within the channels between the nanocrystals. While atomic models for the NbO tri-layer exist, no DFT models have been produced to date. A relaxed model would contribute significantly to the understanding of this surface from the exact nature of the NbO nanocrystals to the disordered channels between the nanocrystals. The NbO nanocrystals and the channels between them exhibit a different LDoS, currently suggested to be due to the presence of two different oxygen chemical states residing in each location. DFT simulations of the surface structure would allow for a simulated LDoS of the surface. Comparison to experiment would yield concrete evidence of the source of the disparity in the LDoS. The higher LDoS observed in the channels may be the reason behind the oxide clusters formation here upon oxidation and subsequent annealing. Monitoring the change in the oxygen state concentrations, using XPS, as the oxide clusters fill the channels can provide more information on the location of the different oxygen states and the nature of the oxide clusters. The terraces of NbO also exhibit interesting properties, which appear to be due, at least in part, to the nanocrystals. The two terraces observed on the surface exhibit different LDoS, this may be due to the relative orientation of the NbO nanocrystals to the terraces. The terraces also exhibit a proffered minimum terrace width,

corresponding to the length of one nanocrystal. Furthermore, terracing in one of the directions is thought to relieve the strain from the lattice misfit between NbO and Nb(110). The energetics of the terraces may also be determined using DFT simulations. Nb oxides, such as NbO₂, are used in redox reactions as a catalyst[135], understanding the growth mechanisms of higher valence oxides such of these may be of interest for these reactions. The NbO terminating layer has been shown to dictate the initial growth orientation of additional oxides.

Cu oxides see use as a catalyst in a host of applications from water-splitting for photoelectric devices, methanol and formaldehyde production used in the nylon industry, the reduction and oxidation of CO₂ which sees important use in catalytic converters and is a hot topic given the current climate. All of these processes require an active site for chemical reactions to occur, increasing the number of these sites and their selectivity is strongly desired. Cu oxide lags behind silver in some applications such as water splitting[155, 156], however due to its relative abundance and lower cost there is a strong desire to improve Cu based catalysts to the point of equalling or bettering the capabilities of the other noble metals. Producing new Cu oxide structures may be a way to achieve this task. The initial sub-monolayer ordered oxide structures which have been observed to form on Cu(111) require more experimental and theoretical work to understand. Their atomic structure is unknown, DFT simulations could be employed alongside experimental STM images to determine the structure. XPS and similar surface sensitive techniques may be used to determine the composition of the surface oxide layer, in particular, the number of unsaturated Cu atoms[159] is of interest in catalysis. Monitoring the growth of the oxide layer and how it transitions from the sub-monolayer structures to the near monolayer structures previously reported on is of general interest to those studying oxidation from first principles. Exposing the surface to increasing amounts of oxygen and monitoring the growth with STM, LEED and other techniques is required. The reactivity of these oxide structures may be of interest in the field of catalysis. Upon understanding the structure of these oxides, experimental work in combination with DFT calculations can provide insight into

their effectiveness as a catalyst and in use for selective reactions. The goal of the study was initially to probe the barrier for oxygen adatom penetration through an oxide layer, this task has yet to be achieved. Further oxidation of the Cu(111) is required to achieve an ultra-thin film of Cu₂O(111), pulsing experiments may then begin. While no theoretical comparison for the barrier of MoO₂ exists, and the NbO barrier proved too large to surmount, Cu₂O(111) provides an oxide layer which may be probed and can be directly compared to the work of Ronay & Nordlander[54, 55]. The oxide structures observed at a sub-monolayer coverage may also be interesting from the point of view of inducing oxidation using the electric field or tunneling current generated between the STM tip and the surface when a large bias is applied. Additional oxygen adatoms may be added at low temperature, outside the energy range at which ordered oxides form, pulsing these adatoms may produce an oxide structure.

Appendix A

Cu(111) Surface Defects

A.1 Introduction

Point defects will always exist in some number within a crystal, even with idealised preparation procedures. These defects may be vacancies, substitutional impurities, interstitial impurities, self-interstitial or a combination of these defects. These defects produce distinct surface states which may or may not be desirable. Defects on the surface come into direct contact with any thin film grown upon the substrate, therefore their interaction with thin films and more importantly ultra-thin and monolayer films, may be significant. These thin films inherently have defects and impurities which arise from the substrate and growth/deposition conditions. Identifying the defects and characterising them so that a distinction can be made between undesirable and desirable defects will prove useful in determining how they impact the electronic properties and growth of a system[160]. Examples of desirable impurities come from the p-type and n-type semiconductors which rely on impurities to alter the carrier concentration[161, 162]. Graphene has been shown to contain a number of cluster defects in which pentagonal cells are present alongside the regular hexagonal graphene ones[163].

The (111) surfaces of the noble metals: Au, Ag, Cu have surface states composed of electrons which form a quasi-2D free electron gas. In a pure metal, the electrons move through the solid with no scattering occurring.

These electrons are scattered when they encounter the change in potential due to a defect, in the surface layers of these metals, resulting in standing waves on the surface, called Friedel oscillations(FO)[164, 165]. For an electron to scatter, an empty state must be available. Given that all the states below the Fermi energy are occupied for these metals, only electrons with energies near the Fermi surface can scatter into unoccupied states. The period of these standing waves is called the Fermi wavelength. Taking the Fourier transform (FT) of STM images which resolve FOs on the surface directly yields images of the 2D surface Fermi contour[166]. Cu(111) was one of the first materials observed to exhibit FO and a Fermi wavelength of 15 Å is reported[167]. Defects on Cu(111) have been observed in the literature, however, quite often only the Friedel oscillation (FO) resulting from the defect is resolved, making it near impossible to identify the underlying defect. Throughout the literature the nature of inherent defects on Cu(111) has only been speculated, with S and CO impurities being candidates[168, 169]. Cu atoms on Cu(111) are reported as having a brightly contrasted FO centre[165], FOs with depressions in their centres were also observed but the corresponding defect was not determined. Wiame *et al.*[170] exposed the surface of Cu(111) to a low dosage of oxygen (180 L) which resulted in a coverage of < 1%. The oxygen defects appears as FO with a dark centre and a period of 1.8 nm. The observed FO of a single O adatom was found to closely match that of Friedel's prediction[171] of screening impurities producing a long range oscillatory behaviour. Clusters of O atoms were also observed, their geometry reflected the 3-fold symmetry of the surface. The clusters were observed to diffuse through interactions with the STM tip during scanning.

A number of defects have been observed on Cu(111), however, their nature is rarely ever determined. Crommie *et al.*[167] observed FOs on Cu(111) and suggested that sulphur was the impurity but could not find definitive proof. Bartels *et al.*[168] exposed the Cu(111) surface to CO and observed FO with a depression in the centre, depicted in Fig.(A.1a), when using a CO molecule terminated STM tip, the contrast of the remaining CO molecules on the surface changed to be brightly contrasted in the centre (Fig.(A.1b)). Wahstrom *et al.*[169] observed FOs on Cu(111), some of the FO were ob-

served with protrusions (bright) centres and some with depressions (dark) centres, shown in Fig.(A.1c). The nature of the defects which caused these FOs was not determined. Cu atoms on Cu(111) are reported as having a protrusion in the centre of the FO [165], FOs with depressions in their centre were also observed but the corresponding defect was not determined. Defects which occur in a graphene layer grown on Cu(111) were investigated to determine the impact of the defects on the graphene layer[172]. Defects which produced bright FO were determined to correspond to C vacancies while dark FO defects are thought to be due to point defects in the Cu(111) substrate. While the point defects do not influence the structure of the graphene layer, the LDoS within a radius of ≈ 0.6 nm centred on the defect is enhanced. Large crystal defects in high temperature superconductors such as slip steps in cleaved crystals have been shown to have a severe effect on transport current[173]. Wahlstrom *et al.*[169] observed long range order between adatoms on the Cu(111) surface. The sample was initially annealed to 900 K enabling diffusion of adatoms before cooling, resulting in the sticking of the adatoms to the Cu(111) surface. The FO observed as a result of these adatoms have a period of $15\text{\AA}$. Inter-adatom distances were analysed for adatoms which were in isolated pairs. The adatoms were observed to be separated by distances of the Fermi wavelength ($15\text{\AA}$). The interaction is reported to be important up to distances of $80\text{\AA}$.

FOs generally do not offer a practical way of determining the nature of a defect, due to the relatively similar FO being produced by different types of defects. Carefully measuring the FO and comparing it to a model as done by Wiame[170] for oxygen adatoms, is only efficient when the defect is known. Unique impurities will produce a unique FO but the difference may be difficult to distinguish considering interference from nearby defects and experimental error such as piezo creep. A common issue with identifying residual atomic-like defects is their low density on the surface. Surface sensitive techniques, such as Micro-Raman spectroscopy and XPS, conventionally used to identify the composition of surface layers are not sensitive enough to characterise these defects/impurities (by several orders of magnitude). The sensitivity of XPS varies depending on the material, however coverage

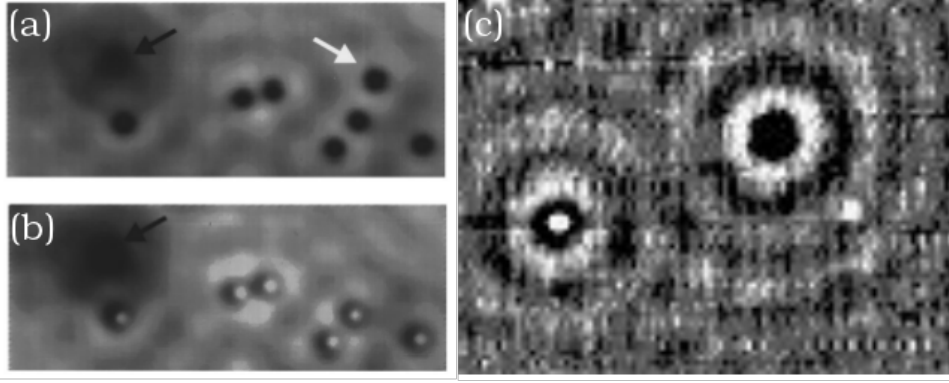


Figure A.1: **Experimental images of defect resulting in Friedel oscillations on the Cu(111) surface** (a) STM image of Cu(111) with $\approx 1\%$ of a ML of CO. CO molecules appear as depressions on the surface. (b) Following the tip picking up the CO molecule pointed to by the white arrow, the CO molecules appears as protrusions. Imaging conditions: 40 mV and $I = 0.8$ nA.[168] (c) Two adatoms on Cu(111) which appear with a protrusion and a depression in the centre of the respective FO. $V = 0.02$ V, $I = 0.131$ nA[169]

of less than 1% is typically difficult to detect. STM and STS provide a non-destructive way of measuring the electronic properties of impurities and defects on the atomic scale. Identifying impurities may be achieved by exposing the sample to a possible impurity source and monitoring the surface for an increase in the defect density however this can be a time and resource intensive process without prior knowledge of the defect.

The overall goal of oxidising Cu(111) was to investigate the barrier for the incorporation of oxygen into the lattice. In the process of preparing the surface a number of defects were observed on the surface. The nature of these defects was unclear and the possibility that they are related to the initial oxide structures which form on Cu(111) was considered. The defects were investigated experimentally. STM measurements revealed a number of distinct defects, some of which exhibited a complex and interesting structure. In order to understand these defects, density functional theory (DFT) simulations were conducted. Simulated STM images of different surface defects and impurities could be calculated and compared to the experimental images of the defects. A careful and thorough DFT study was conducted, during

which, it was realised that a standard of such calculations did not meet the satisfactory requirements for a simulation of this type. The convergence of system parameters to the total energy was found to be inadequate. A new method of convergence was developed, based on the DoS of the system. The DoS is a more significant quantity than the total energy for the purpose of simulating STM images. The DoS convergence method accurately and quantitatively generates the system and the corresponding simulated STM images. Over the course of this chapter experimental images of the defects will be depicted, convergence with respect to the total energy will be shown to be insufficient for the DFT calculations and the DoS method will be shown to be a more appropriate measure of accuracy. Finally, the simulated STM images yielded from the DFT calculations will be compared to the experimental STM results in order to gain some further knowledge regarding the various defects on the Cu(111) surface.

A.2 Experimental results

A.2.1 Introduction

Two Cu(111) single crystal samples (99.999% purity) were used over the course of this study. Both preparation procedures follow the steps outlined in 6.2, however the first crystal was annealed up to 1000 K while the second was annealed up to 1200 K. This change did not appear to have an impact on the surface structure and defect density, judged by STM and LEED measurements. Furthermore, annealing at 1100 K for 12 hours or more did not increase the amount of defects present on the surface.

A.2.2 Defects observed following cleaning procedure

The Cu(111) surface was prepared following the procedure outlined in section 6.2 in which a clean Cu(111) termination was achieved as judged by LEED measurements, depicted in Fig.(6.1a). A large scale atomic resolution STM image of the Cu(111) surface is presented in Fig.(A.2). The periodic hexag-

onal structure of Cu(111) is observed, and further indicated by the Fourier transform (FT) of the image, presented in the upper left inset. The observed Cu(111) period is ≈ 2.63 nm, comparable to the bulk period of 2.55 nm. The corrugation of Cu atoms on the surface is approximately 6 pm.

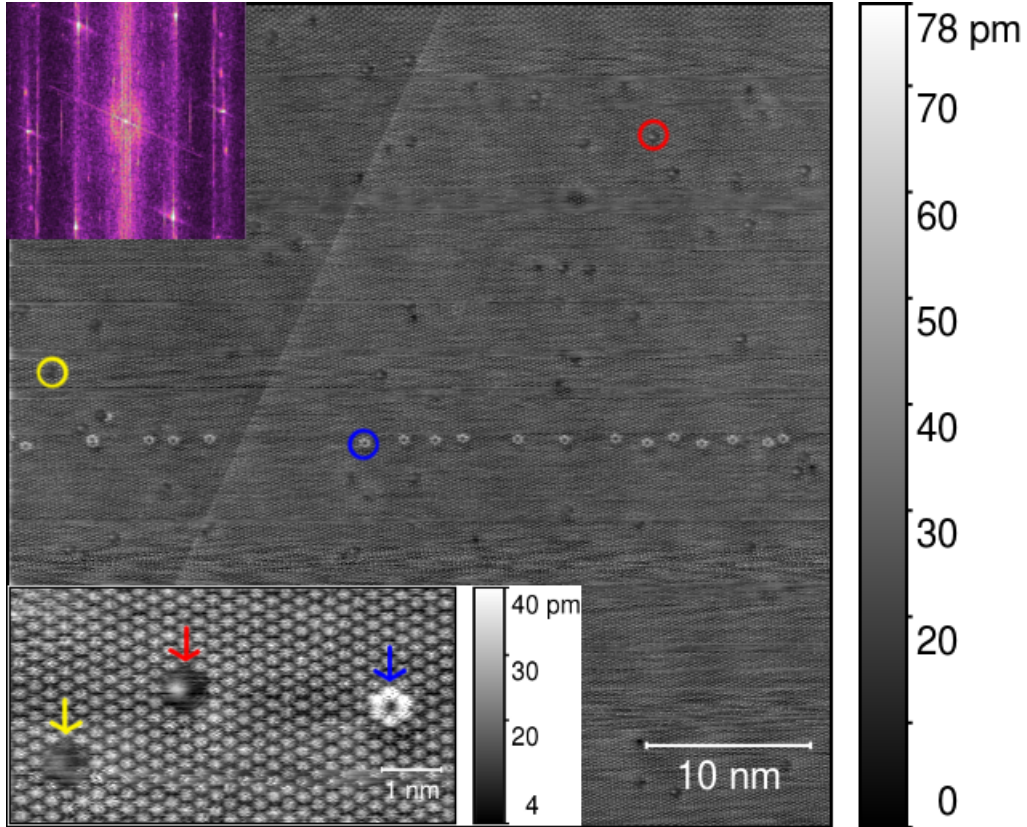


Figure A.2: **Atomic resolution image of Cu(111) with 3 highlighted defects.** 50 nm $\times$ 50 nm image of Cu(111). Numerous defects are present, 3 are indicated by coloured circles. High resolution image of the 3 defects are presented in the lower inset. Red & Yellow = “Asymmetric” defect. Blue = “Bright” defect. FT of image is presented in upper inset, indicating reciprocal periodicity.

A number of defects in the surface are evident as seen in the lower inset of Fig.A.2. 3 defects are indicated by coloured circles in the large scale image and arrows point to the corresponding defect in the inset high resolution image. The defect indicated by the blue markers is only observed within this particular experiment and is the result of a tip-surface interaction, this

defect is no longer discussed within this thesis. The defects indicated by the red and yellow markers are similar in nature and are discussed in the following section under the title of “asymmetric” defect. Atomic resolution of the defects gives an insight into their structure. However one must still consider tip effects playing a role in all STM images.

“Asymmetric” Defect

This “asymmetric” defect indicated by the red markers in Fig.A.2 is by far the most prevalent on the surface. Approximately 50 of the defects are present in the $50 \times 50 \text{ nm}^2$ image. This corresponds to 50 defects per 70,000 Cu atoms, a surface density of $< 0.1\%$, approximately equal to that observed by Burgi *et al.*[165].

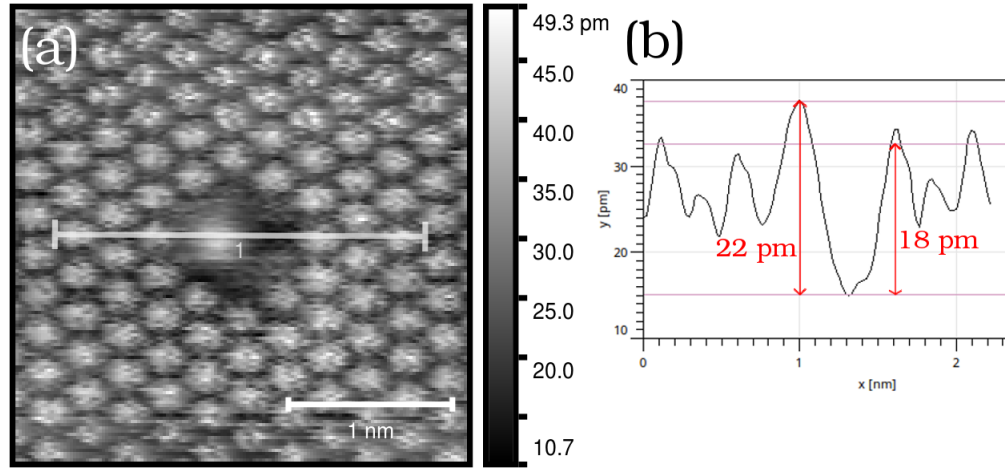


Figure A.3: **Atomic resolution STM image of “asymmetric” defect.** (a) The “asymmetric” defect is characterised by a hexagonal depression with a dipole-like feature within. The dipole-like feature is composed of a protrusion, which is always located to the same side of the defect, and a depression within the hexagonal depression, opposite the protrusion. $V = 0.3 \text{ V}$, $I = 75 \text{ pA}$. (b) Height profile of the defect. The protrusion and depression of the dipole-like feature are separated by 22 pm. The protrusion extends 4 pm above the surrounding Cu atoms.

The atomic resolution STM images of the defect in Fig.(A.3a) depicts a hexagonal shaped depression with containing a protrusion. The size of the

depressed region corresponds to the space occupied by a Cu atom and its six nearest neighbours (diameter ≈ 0.8 nm). The protrusion is located to the side of the hexagonal depression and sits approximately on a 3-fold hollow site. There is a further depression within the hexagonal region, localised on the opposite side to the protrusion and similar in size to the protrusion. Using this minimum in the hexagonal depression as a zero point, the height of the other features are calculated. A line profile is presented in Fig.(A.3b) which indicates the relative height of the tip across the defect. The distance between the minimum of the depressed region and the maximum of the protrusion is approximately 22 pm. The peak in corrugation of the nearby surface Cu atoms are a distance of 18 pm from this minima, indicating the protrusion is just 4 pm above the surrounding Cu atoms. The remaining part of the hexagonal depression is 6 pm above the minima. The protrusion and depression minimum resemble a dipole-like structure. These defects are stable on the surface and are not observed to diffuse. The defect is always on the same side of the hexagon across all of observed defects of this type, changing the tip scan direction did not influence this orientation. This observation is unexpected as Cu(111) demonstrates a 3-fold symmetry, indicating that 3 equivalent positions for this asymmetry should exist.

Two images of the same area of the surface, taken at the same time, are presented in Fig.(A.4a&b). Fig.(A.4a) depicts the image of the surface resulting from the forward (left to right) scan, while Fig.(A.4b) depicts the backward scan (right to left). Lines are scanned sequentially, with forward and backward scans being acquired before moving to the next line. The forward scan produces an atomic resolution image of the surface, while the backward scan produces an image of the FOs due to the defects. These images highlight the large difference in scale of the FO relative to the atomic structures upon which they are based. The “asymmetric” defect is indicated with red markers in both images. This defect produces a FO with a depression (dark) centre and a period of 1.4 nm, called a Fermi wavelength. The tip appears to be changing as the scan direction changes, resulting in the two different images being produced. In later STM images the tip appears to stabilise and consistently produces atomic resolution images for both the

forward and backwards scan directions. The defects do not differ in appearance with the stable tip. The characteristic protrusion of this defect can be seen in the upper middle part of the corresponding FO, indicating that the backward scan direction, which produces the FO may also be probing the surface with atomic resolution. The FO appears to be shifted from the defect location, a likely consequence of the unstable tip. The FT of Fig.(A.4b) is presented in the inset of Fig.(A.4b). Filtering the image to only include the components within the region indicated by the broken white line results in the surface presented in Fig.(A.4d). This filter emphasises the FO and the period is determined from the line profile presented in Fig.(A.4c).

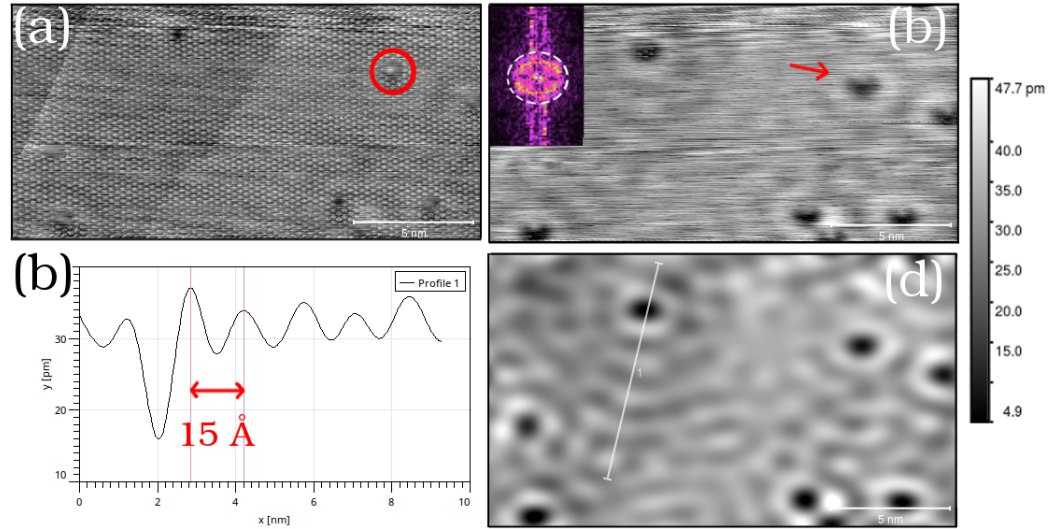


Figure A.4: **Atomic resolution and corresponding FO image of “asymmetric” defect.** Images are from the same scan. (a) Forward scan displaying surface in atomic resolution. (b) Backward scan displaying surface with FOs resolved. (c) height profile of line in (d) indicating the Fermi wavelength, 1.4 nm. (d) Filtered image (b) using the region of the FT of (b) indicated by white oval in inset of (b). (a)&(b): $V = 0.3 \text{ V}$, $I = 75 \text{ pA}$.

Atomic resolution of the defects is not always attained. The following images of the FOs due to the “asymmetric” defect were obtained on the same sample under similar experimental conditions. Fig.(A.12) indicates that the “asymmetric” defects have a preferred distance relative to one another, dictated by the Fermi wavelength (period of FO). This occurs with a separation

corresponding to a half integer multiple of the Fermi wavelength($15 \text{ \AA}$), in agreement with the observations of Wahlstrom *et al.*[169], detailed in section A.1. This results in the extrema of the respective FO overlapping constructively. Fig.(A.5) depicts a number of the FOs resulting from the “asymmetric” defects. Four half integer multiple distances of the Fermi wavelength are observed between nearest neighbour adatoms: 0.5 (blue), 1.5 (yellow), 3.5(red). The counting of wavelengths is conducted from the outer edge of the innermost FO peak for each defect Wahlstrom *et al.*. It should be noted that the defect which produces the irregular FO with depression in its centre (above yellow arrow) in Fig.(A.5) is not commonly observed on the surface and may be the a result of the “asymmetric” defect neighbouring and strongly interacting another defect.

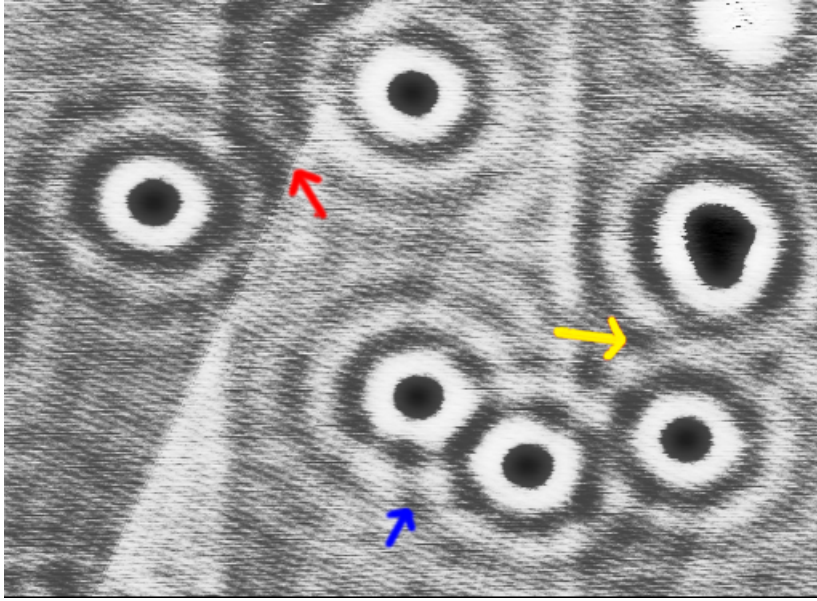


Figure A.5: **STM image depicting FOs of “asymmetric” defects.** The “asymmetric” defects produce a FO with a depression at the centre. The Fermi wavelength is $\approx 1.5 \text{ nm}$. Distances between defects is a half integer multiple, m , of the Fermi wavelength. m : Blue = 0.5, Yellow = 1.5, Red = 3.5.

The long range interaction between adatoms may be the reason behind the observed asymmetry in these defects. In conjunction with dictating the distances between the adatoms, the Fermi wavelength may also mediate the

location of the protrusion within the depressed hexagonal region. While 3 equivalent sites exist on Cu(111), it is likely energetically favourable for all of the defects to orientate in the same direction, ensuring that all extrema of their FOs overlap constructively. The “asymmetric” defect was not observed to be mobile on the surface, through pulsing or otherwise. Details regarding pulsing experiments can be found in section A.2.3.

Shifting attention to the “asymmetric” defect indicated by yellow markers in Fig.(A.2). This defect resembles the one marked in red, however, the relative height of the protrusion is smaller. A number of these defects can be seen in in Fig.(A.6) alongside the red “asymmetric” defect. The difference in appearance of these similar “asymmetric” defects does not appear to be the result of a tip effect, as the yellow “asymmetric” defects, which have smaller protrusions, consistently have smaller protrusions over many different images. Inspecting this defect closely, inset of Fig.(A.6) reveals what appears to be 6 Cu atoms within the darkly contrasted hexagonal region.

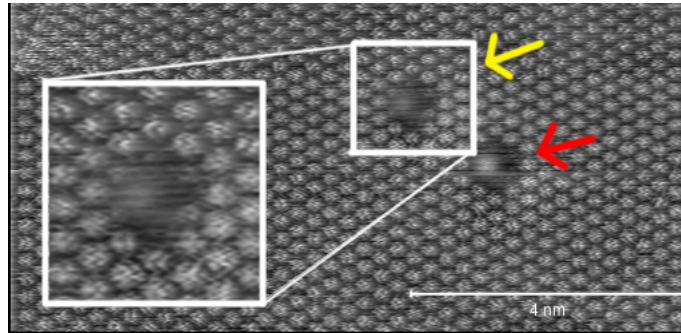


Figure A.6: **STM image exhibiting differences in “asymmetric” defects.** Protrusions are less evident in the “asymmetric” defect indicated in yellow. Faint Cu atoms are visible within the depressed hexagonal region. $V = 0.3 \text{ V}$, $I = 75 \text{ pA}$.

While many high resolution STM images of the asymmetric defects were acquired throughout that particular experiment: Fig.(A.2), Fig.(A.3), Fig.(A.4) & Fig.(A.6), a single bias voltage (0.3 V) was used to probe the surface. Many more images were taken over a range of bias voltages during other experiments however the resolution achieved is not always as great as presented in

these images. Despite this, additional information about the defects can be obtained.

Over the course of experiments, both “asymmetric” defects were regularly observed to produce FOs with a depression in the centre. A distinction between the two defects (“red” and “yellow”) could be observed when the tip condition improved and atomic resolution was obtained.

The images presented in Fig.(A.7) were all obtained with a tunneling current of 50 pA and the bias voltage decreases from a to d, 0.6 V, 0.4 V, 0.2 V, 0.15 V. Both “asymmetric” defects are present, two of the “red” type are in the upper part of the images, while the “yellow” type is towards the bottom of the image. At 600 mV, (a), both defects contain a protrusion with a darkly contrasted hexagonal region surrounding it. There is a slight distinction between the two defects, the protrusion of the “red” defect is larger than that of the “yellow”. The protrusion height matches that observed previously, approximately 5-6 pm higher than the surface Cu atoms. At 400 mV, (b), the protrusions from both defects become more brightly contrasted relative to the surface, with an apparent height of 20 pm. At 200 mV, (c), the clearest distinction between the defects is observed. Both defects display an asymmetry in the form of the protrusion appearing to the side of the hexagonal depression. The “yellow” protrusion which was fainter at 600 mV is much fainter at 400 mV, this property is generally reflected across all bias voltages. At 150 mV, (d), both defects return to being symmetric as the bright protrusion once again resides in the centre of the hexagon. The size of the protrusion is smaller than that at 600 mV or 400 mV and a more distinct hexagonal depression is observed.

The images presented in Fig.(A.7) probe the LDoS of the “asymmetric” defects over an energy range from 150 meV to 600 meV. Across this range it can be observed that the electronic structure of the defect changes from a symmetric to asymmetric configuration and back again. While the “asymmetric” defects are similar, clear differences in their electronic structure are present. A hypothesis to explain these differences, primarily the difference in the relative height and size of the protrusions is as follows. While the “asymmetric” defects have a preference to be separated by a multiple half

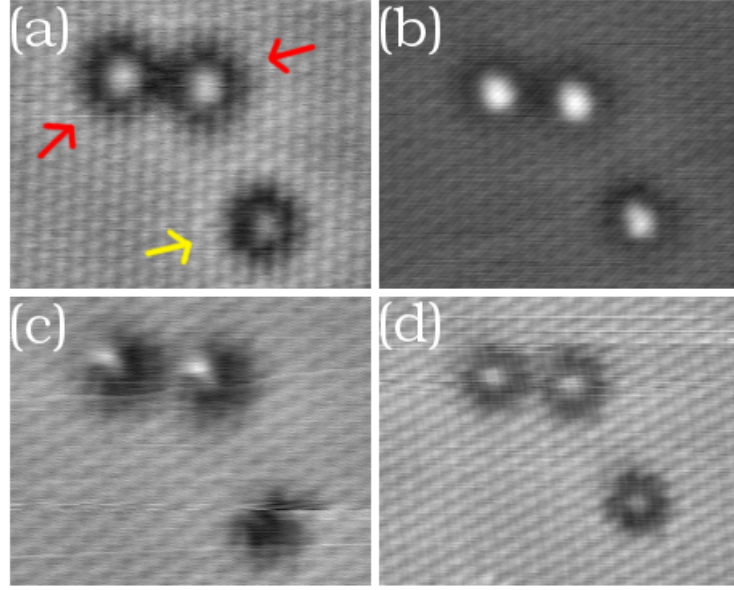


Figure A.7: **STM images of the “asymmetric” defects exhibiting differences in electronic structure.** Two red “asymmetric” defects are located in upper part of image, One yellow “asymmetric” defect is located to the bottom of the image. All images use a tunneling current of 50 pA. (a) 0.6 V (b) 0.4 V (c) 0.2 V (d) 0.15 V.

integer, some variance in the exact distance is expected. The relatively small size of the Cu(111) inter atomic spacing compared to the Fermi wavelength, means that a defect could bind to a neighbouring Cu site of the perfect half integer Fermi wavelength spacing, and pay a small energetic price to do so. While the defect orientates in the same direction as its neighbours, it will have a slightly different electronic structure, which could influence how the protrusion appears. In this way, defects which sit at perfect half integer spacing may appear as, say, the “asymmetric” defect indicated in red in Fig.(A.2), while defects which sit slightly off of the perfect spacing appear as the yellow “asymmetric” defect in Fig.(A.2). The defect which is not on the perfect spacing will of course negatively influence its neighbour defects, but assuming they are on the perfect spacing to other defects, the impact will be screened. Wahlstrom *et al.*[169] observed small variance from the half integer Fermi wavelength spacing for the distance between adatoms on Cu(111).

Images of the “asymmetric” defects from other experiments yield similar results, while the relative contrasts change, the basic asymmetric structure remains the same. The STM image presented in Fig.(A.8a) exhibits 6 protrusions in a hexagonal shape on the Cu lattice. While 5 of the protrusions share the same height contrast (15 pm), one of the protrusions has a relative height of 30 pm above the surface.

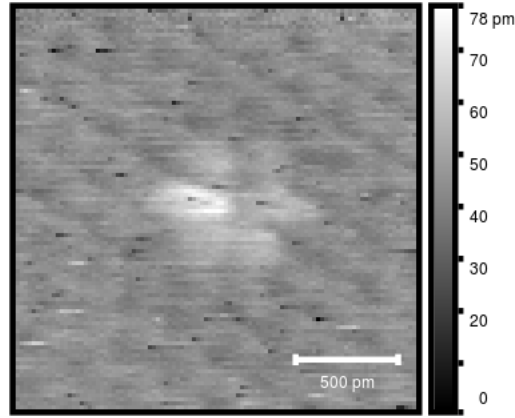


Figure A.8: **Additional STM image of “asymmetric” defect.** The contrast of the defect has changed, however the asymmetry is still present. $V = 0.05$ V, $I = 50$ pA.

The “asymmetric” defects are observed on both Cu(111) single crystals used in these experiments and persist on the surface after sputter annealing cycles. Annealing temperatures in excess of 1200 K was not sufficient to remove the defects, a temperature which Cu is noted to evaporate from the surface. The pressure in the preparation chamber is of the order of 1×10^{-9} mbar during the annealing process. The sample is then moved to the STM chamber within 1 hour, where the base pressure is 10^{-11} mbar. Given these relatively low partial pressures it is unlikely that contaminants from the chamber are the source of the defects.

The defects were not observed to diffuse on the surface and remained unchanged under pulsing up to the point of tip degradation (≈ 4 V), at which point it was not possible to discern between changes in the defect and changes due to the tip. This observation along with the high annealing temperatures are an indication that these structures are very stable on the surface. Impuri-

ties from the bulk of Cu may be the source of the defects, annealing can bring these impurities to the surface or near surface region. Sulphur is reported to segregate from the bulk Cu(111) at 900 K.[174, 175]. Rousset *et al.*[174] observed an ordered sulphur reconstruction at the step edges of Cu(111) using STM. A coverage of 0.25ML is reported and the sulphur structures are reported to have a corrugation of 0.9 Å. No such reconstruction or corrugation was observed over the course of this work. Hinch *et al.*[175] reports a segregation rate of 0.01 ML/hour at 820 K for sulphur atoms in Cu(111). The relatively low density of the defects on the surface make it impossible to use conventional surface identification techniques such as XPS to determine the defects. Analysing the structure of the defect as observed in STM imaging gives some indication of the type of defect present.

Beginning with the simplest case, a single adatom/molecule on the Cu(111) surface. Using symmetry as an argument: the defect appears cantered on the top site, a hexagonal depression surrounds a top site. Fig.(A.7a&d) depicts the protrusion occupying a region centered on the top site. The protrusion seen in Fig.(A.3) is approximately on the 3-fold hollow site, however there is a depression on the opposite side of the hexagon, resulting in this dipole-like structure being centred the top site. It is difficult to imagine a case where a single adatom could produce the asymmetry observed in experiments without involving some asymmetry in the tip structure. An adatom may diffuse from the top site to the 3-fold site, through interaction with the tip, but diffusing back to the top site is very unlikely, considering the trend in the top site being energetically unfavourable for a large number of atoms on FCC(111) terminated crystals such as Cu[176].

A molecule, initially orientated perpendicular to the surface on the top site, may overcome this symmetry issue. It may be energetically favourable for the molecule to tilt relative to the surface. This might occur in a number of ways. Firstly, as previously discussed, long range interactions between molecules such as those due to fluctuations in the electron surface states (FO) may influence the relative tilting of molecules on a surface and impose a preference for one orientation over another. Another possible explanation involves the electric field between the STM tip and the surface. The

electric field between the STM tip and the sample may cause the molecule to deflect to one side as the tip approaches. In this case, if the tip was perfectly symmetrical, one would expect the molecules tilted orientation (if they tilt) to depend on the scan direction, however an asymmetric tip would produce an asymmetric electric field and thus impose a preferred orientation on the tilted molecule. Furthermore, changing the scan direction does not change the relative tip-surface orientation, so an asymmetric tip will always produce the same asymmetric electric field relative to the surface, resulting in all molecules deflecting in the same direction. It is also possible that particular distinct molecular orbitals are imaged depending on the tunneling conditions, resulting in the observed asymmetry. The bright protrusion, along with the depression within the dark hexagonal region, seen in Fig.(A.3), may be the result of two distinct orbitals interacting with the tip orbital.

“Single Defect” - Tip interaction

While the “symmetric” defect was stable on the Cu(111) surface and was never observed to diffuse *via* an interact with the tip, another defect did. This defect, or at least this interaction, was only observed on one occasion.

Three STM images taken sequentially are presented in Fig.(A.9), the bias voltage in these images is 0.2 V and the tunneling current is 100 pA. The defect initially appears as a small bright protrusion (10 pm) surrounded by a depressed region, depicted in Fig.(A.9a). The defect appears to be in the top binding site of the Cu(111) lattice. This defect and the tip interact during scanning, evident from the spike in tip height at the defect location observed in Fig.(A.9b). The scan direction is from bottom to top, the protrusion is evident in the bottom of the image and vacant in the top of the image. Fig.(A.9c) depicts the defect following the interaction. While the protrusion is no longer present, the depressed region is still apparent, indicative of a defect/impurity near the surface. The tip may have induced diffusion of the defect, altering the binding site of the defect from the top site to potentially:

the 3-fold hollow, bridge site or a subsurface site. If this is the case, the defect in Fig.(A.9a) is an adatom.

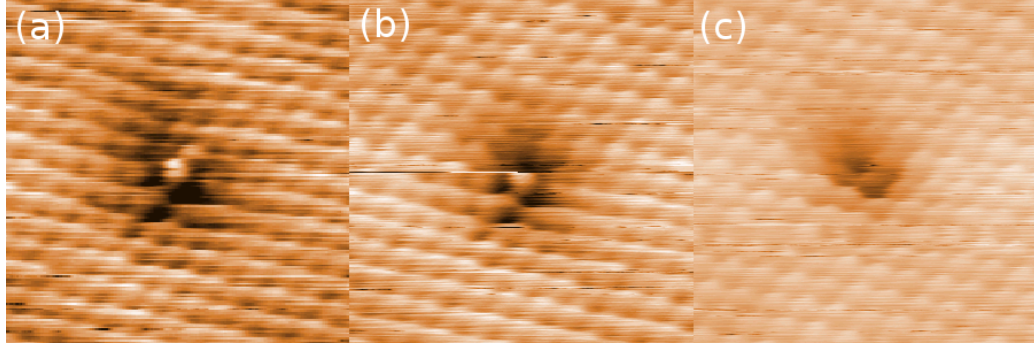


Figure A.9: **STM images of defect-tip interaction.** Three sequential images (a) Adatom sitting in top binding site of Cu(111). (b) The protrusion is observed in lower half of image. The tip interacts with adatom, producing a spike in the tip height, the protrusion is not observed in the remaining part of the image. (c) Following an interaction with the tip, the adatom is no longer visible on top of the Cu atom however a depressed region is evident indicating the presence of a defect.

The images presented here are in atomic resolution, however the FO of the defect are clearly present, evident from the depressed region surrounding the defect and a faint bright ring can be observed surrounding the depressed region, indicating the first peak of the FO.

A number of adatoms could be responsible for this defect, such as O, Cu, S or CO. However given the relatively small size of the protrusion H may also be a candidate atom. H_2 is present in UHV chambers due its small size making it difficult to pump out and the relative easy at which it can penetrate the walls of the chamber. The ion gauges within the chamber used to measure pressure offer a hot filament for H_2 molecules to dissociate, resulting in atomic hydrogen. While H_2 is largely non reactive with Cu at 78 K, atomic hydrogen has been observed to bind to the surface[177]. A H adatom may then adsorb to the surface. The relatively low probability of this occurring may account for the unique observation of this defect.

Nevertheless, these images provide a good incentive to further investigate adatoms and defects on the surface of Cu(111) through computational means.

A.2.3 Defects observed following oxidation at 78 K

Adatoms on surface - Pulsing

Following the oxidation procedure described in section 6.3, a small number of an additional defect was observed on the Cu(111) terraces. During these experiments, atomic resolution images of the defects were not attained, however, the Friedel oscillations (FOs) due to these defects are apparent. Two types of defects can be distinguished by STM, those which produce a depression in the centre of the FO and those which have a protrusion in the centre. The FO with a depression in the centre primarily correspond to the “asymmetric” defects detailed in section A.2.2. Their prevalence on the surface does not increase under any of the oxidation procedures in chapter 6. The defect observed as a result of oxidation at 78 K produces a FO with a protrusion, this protrusion extends from the centre of the FO to the first peak of the FO. STM images of both defects are depicted in Fig.A.10 alongside a height profile indicating the relative heights of the defects.

The defects which produce the FO with a protrusion in the centre are mobile on the surface at 78 K. This indicates that they are likely due to an adatom or small cluster of adatoms on the surface, possibly O or Cu. Evidence to support the small cluster hypothesis is the irregularity in the shapes and size of the central protrusion. The STM tip can induce diffusion of these adatoms, though it has not been determined whether these adatoms can diffuse without external influence. The adatoms can be observed on occasion to diffuse while the tip is in the process of resolving the feature, which can be seen in Fig.(A.10c). Furthermore, applying a small pulse (-0.8 V), in the tunneling regime, nearby this feature induced diffusion consistently, whereas diffusion was only seen occasionally during scanning at lower bias voltages.

While the protrusions observed in Fig.(A.10) are irregular in shape and size, other protrusions on the surface are smaller and symmetric, indicating that it may be due to a single adatom. Fig.(A.11a) depicts one such defect along with two of the “asymmetric” defects. Applying a bias voltage in excess of -0.8 V directly on the protrusion resulted in its removal from the surface. A FO with a depression in the centre, similar to the FO of the “asymmetric”

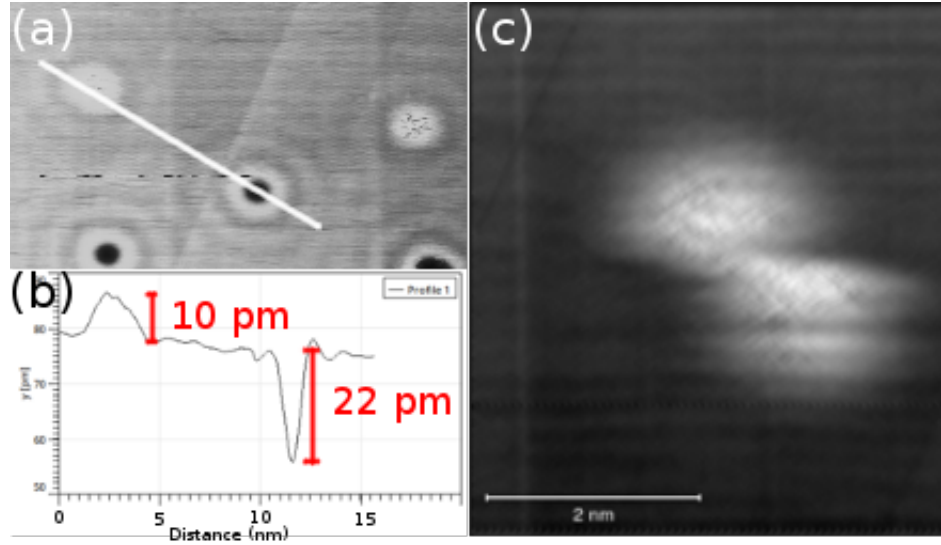


Figure A.10: *STM image of “asymmetric” defect and adatoms on Cu(111).* Following an exposure to a small dose of O_2 at 78 K. **(a)** A number of mobile defects which produce a FO with a protrusion in the centre are observed. The FO’s with the depression in the centre correspond to the “asymmetric” defects detailed in section A.2.2. **(b)** Height profile of both defects. **(c)** STM image of adatom exhibiting diffusion while scanning.

defects is observed in the position where the adatom was prior to the pulse being applied. Images of the surface before and after the pulse can be seen in Fig.(A.11a) and Fig.(A.11b), alongside the corresponding height profiles in Fig.(A.11c&d). Small scale STM images were produced between these images in order to accurately apply the pulse to the mobile protrusion, however there is no reference point in these images as the “asymmetric” defects are not in frame. This accounts for the small shift in the adatom and resulting defect position between the images presented in Fig.(A.11a) and Fig.(A.11b). Pulsing the Cu surface away from the defects in excess of ± 2 V did not result in any noticeable change in the surface as judged by STM images. The defect which results from pulsing the adatom, produces a FO with a depression in the centre. This may be due to a change in the adatom/cluster location or bonding state. O and Cu are the most likely adatoms to exist on the surface. If the protrusion observed in Fig.(A.11a) is an oxygen adatom, pulsing may have induced an oxide reaction. Nordlander *et al.* reports an

oxygen penetration barrier of 0.9 eV on Cu[54, 55]. The oxide which is formed may then produce a characteristically difference FO.

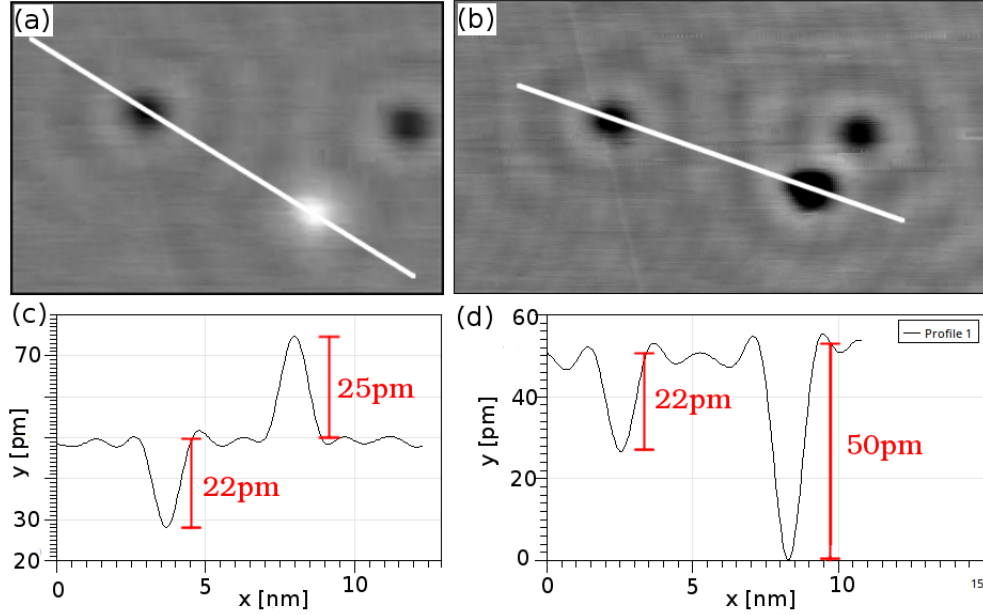


Figure A.11: **Pulsing experiment of adatom.** (a) STM image of 2 defects (depressions) and an adatom (protrusion) prior to a pulse being applied to the protrusion. (b) STM image of the same region of (a) following a voltage pulse. The protrusion is absent and a defect (depression) is in its stead. (c) height profile of the line in (a) (d) height profile of the line in (b)

The “asymmetric” defects, which produce a FO with a depression in the centre, are stable on the surface under pulsing up to ± 4 V in the tunnelling regime, at which point the tip would often degrade. Furthermore, they are not observed to be mobile on the surface and are separated by a quantised distance from one another, as discussed in section A.2.2. The interaction between the “asymmetric” defects the adatoms which produce a protrusion in the centre of their FOs and has been investigated. Pulsing the adatoms with the STM tip at the edge of the protrusion using a voltage of -0.8 V induced diffusion of the adatom across the surface. While not consistent, the adatom tended to diffuse in the direction radially away from the tip location when the pulse is applied. By carefully applying pulses with the STM tip the adatom could be encouraged to diffuse in a desirable direction.

Using this method two atoms were “pushed” towards the “asymmetric” defects. However there was a limit to how close the adatoms would approach, corresponding to the first peak of the adatom’s FO (outside of the protrusion centre) overlapping with the second FO peak (outside of the inner ring) of the “asymmetric” defect, observed in Fig.(A.12a). Pulsing the adatoms from this position towards the centre of the “asymmetric” defects results in the adatoms “bouncing” off of the “asymmetric” defect and being further displaced than initially. An animation of this effect can be seen at <https://github.com/KillianWalshe/Gifs/blob/master/FO1.gif>. These observations further support the presence of long range interactions of adatoms and defects on the Cu(111) surface. These interactions make it energetically favourable for the adatoms and defects to position such that the extrema of the FOs to overlap constructively, which coincides with distances half integer multiples of the Fermi wavelength.

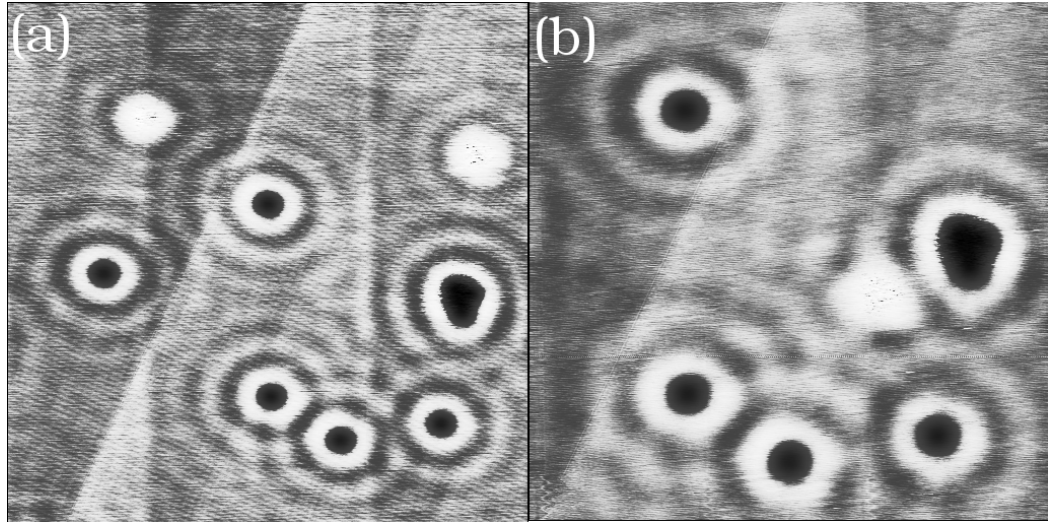


Figure A.12: **STM images of interaction between adatoms and “asymmetric” defects.** Pulsing adatoms (protrusions) induced diffusion, which can be directed towards defects (depressions). **(a)** Two adatoms at closest approach to defects, dictated by the Fermi wavelength. **(b)** Applying larger pulses to a confined adatom resulted in the adatom temporarily overcoming the conventional closest approach. **(a)&(b)** are filtered to emphasise the FOs.

When this region of the surface was initially scanned an adatom was present within the “corral” produced by the “asymmetric” defects. Given the close proximity of the “asymmetric” defects to one another, the adatom was “stuck” within this area, bounded by the FOs. With the adatom confined to this region, larger bias pulses (≈ -1 V) could be applied to the adatom without inducing diffusion away from the “asymmetric” defects. By applying pulses to the adatom, it was possible to “push” it so that it resides within the first FO peak (away from the inner ring) of the irregular shaped defect as depicted in (Fig.A.12b). The shape of the protrusion is now distorted, possibly an indication that the defect is due to a small cluster of adatoms. Further pulsing results in the protrusion residing in the inner ring of the defect. The animation can be seen at <https://github.com/KillianWalshe/Gifs/blob/master/FO2.gif>. After some time the protrusion is no longer evident in the scan frame, however, an identical protrusion appears nearby, outside of the “corral”. If this is in fact the same adatom, it further supports the strong interactions between adatoms and defects on the Cu(111) surface.

Unfortunately the nature of these defects is not yet determined and so the amount of information which can be yielded is limited. Pulsing experiments appear to be successful, however more experimentation is needed, preferably with atomic resolution, so that the structures before and after pulsing may be determined.

A.3 Density Functional Theory - Cu(111)

A.3.1 Introduction

The defects observed on Cu(111) are complex and interesting in nature. The amount of information which can be obtained from experimental methods alone is limited. Theoretical methods such as density functional theory (DFT)[178] has widely been used to model the electronic structure of materials such as metals, metal-oxides and molecules. DFT has been implemented successfully for a huge range of systems, however some problems still exists, primarily based in the approximations[179] such as LDA[180] and GGA[181].

DFT calculations use and the fact that DFT is only completely reliable for the ground state of a system (0 K). For this reason it is vital for DFT to be used in conjunction with experimental methods. DFT can relatively quickly produce a wealth of information regarding the electronic structure of a system under different conditions however without experimental observations, these results have limited impact.

Many codes exist which implement DFT methodology to compute *ab-initio* calculations, the most well known of which is the “Vienna Ab initio Simulation Package” (VASP)[182]. In this work, the Quantum Espresso (QE) package[26] is used, while very similar to VASP as a plane-wave code implementing pseudopotentials, it has the added bonus of being free to download and use under the GNU general public license. QE also provides post processing packages to calculate electronic properties such as the DoS and also allows for the simulation of STM images using the Tersoff-Hamann scheme[14, 183], both desirable products of this study.

In order to assist in identifying the defects observed in STM experiments on Cu(111) DFT calculations were performed. Comparing simulated STM images from a model system of various defects, adatoms and impurities to the experimental STM images can potentially contribute to the identification of the defects. Prior to adding a defect to the surface and simulating STM images, a Cu(111) “slab” must be produced. A slab cell comprises as a crystal system with a layer of vacuum, resulting in a surface termination of the crystal. The size of the slab and the run-time computational parameters need to be determined. A slab which is too small in size will yield inaccurate and often unphysical results, while a slab too large will require considerable computational resources to compute. The run-time parameters which typically determine the level of each approximation also need to be determined for similar reasons.

Convergence tests are conducted for the slab size and parameters, these tests are conventionally conducted with respect to the total energy of the system. Over the course of this study it was observed that converging the system parameters wrt the total energy was not suitable for a number of reasons. An alternative method of convergence was developed which relies

on converging the system wrt the DoS of the system. This method allows for the difference between the DoS of two systems to be quantitatively measured. Simulated STM images are generated from the LDoS of the system, which in turn is taken from the DoS. Thus, converging wrt the DoS not only ensures that the simulated STM images are converged but offers a measure of the level of convergence. The following sections detail a pragmatic approach to producing a converged system using a DFT plane-wave code.

A.3.2 Convergence tests

When deciding on the value of an approximation to use in a calculation, two factors need to be considered: accuracy and resources. The approximation should not cause the result to differ significantly from the case where the approximation is not used, however highly accurate simulations generally require a large amount of computational resources be it RAM or time. A compromise is desired, one where the simulation is accurate within some reasonable threshold and used the minimum amount of resources. Convergence tests allows one to do exactly this. The total energy of the system is conventionally used to determine the optimal values for parameters such as the slab size, number of points to sample the Brillouin zone(k-points) and the maximum energy of the plane-waves. These parameters are detailed in section 2.3.4.

Total energy convergence test

Assuming you have a bulk unit cell, a convergence test for a particular parameter, such as the plane-wave cut off energy, is conducted in the following way: Firstly, a range of values for the parameter is selected, these values should include at least one value which is significantly higher than the value which is expected to be required. This value is known as the “well-converged” value. A SCF calculation is then conducted for each value of the parameter and the resulting total energy is analysed. Plotting the difference between the total energy of each parameter value and the “well-converged” value yields a graph, the fit of which asymptotically approaches 0. The optimal value for

the parameter is one which uses the least computational resources while only deviating slightly from the “well-converged” value. A standard satisfactory threshold for the total energy is $<1 \text{ meV/atom}$ [184]. In practice the “well-converged” value can be determined by simply simulating the system with increasingly accurate parameter values. An example of a total convergence plot is shown in Fig.(A.13) for the total number of k-points. Here, the difference in the total energy between each k-point density and a density of 2250 is given on a per atom basis. While a number of k-point densities are within the 1 meV threshold, a k-point density of 1200 is the first point for which oscillations die out, making it more reliable than the lower k-point densities.

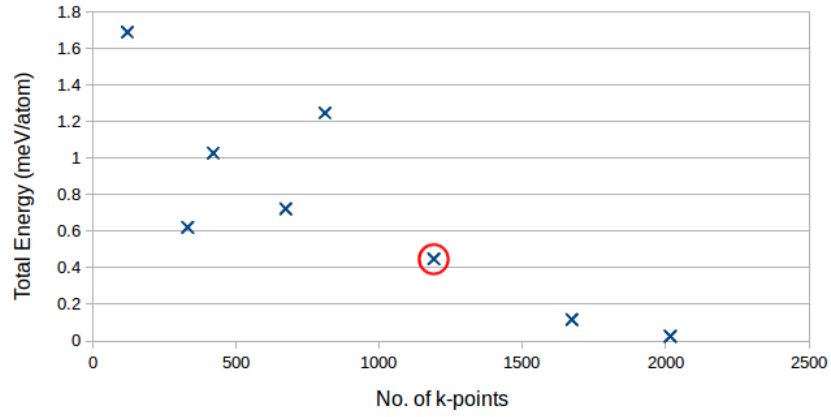


Figure A.13: **Sample total energy convergence test.** The difference in the total energy for each k-point density and a density of 2250 k-points is given on a per atom basis. The energy difference approaches 0 as the sampling density increases. The k-point density of 1200 is indicated.

DoS convergence test

It was discovered that a number of parameters did not converge with respect to the total energy. An alternative quantity to converge the system with respect to is the DoS. The DoS is selected as it is an indicator of the LDoS on the surface, a quantity used to generate the simulated STM images. Thus, if the DoS is well converged the simulated STM images would be also be con-

verged to satisfaction. Furthermore, we would have a quantitative measure of the accuracy of the DoS and by extension, the simulated STM images.

A quantitative measure of the DoS needs to be established so that convergence testing may be conducted in a similar fashion to that of the total energy. The DoS of a system covers a large energy range, however STM measurements typically probe only a fraction of this range. STM measurements conducted on Cu(111) yielded atomic resolution of the surface atoms and defect structures when the applied bias voltage is between -0.5 V and 0.5 V. It is therefore appropriate to use the same energy window of 1 V centered on the Fermi energy for the calculated DoS used in convergence testing. Provided the DoS is well converged within this energy window, one can expect the resulting simulated STM images to also be converged. The energy window value is denoted as E_w .

In order to quantify the DoS in this range, a method that represents the data accurately needs to be determined. The root mean square (RMS) is typically used to characterise waveforms such as voltage or current in electrical applications. Applying the RMS to the difference between two sets of data, i.e. the “well-converged” data set and the parameter values to be tested, is a meaningful measure of the error between the two data sets. This error can be normalised by division of the RMS of the “well-converged” value to give what is known as the “normalized root-mean-square deviation”. The normalized root-mean-square deviation can be turned into a percentage difference by multiplying by 100. For the purpose of this study a normalised integrated RMS is used to evaluate the difference between the well converged DoS (DoS_{wc}) and the test DoS (DoS_t) over the energy window, E_w , which is centred on the Fermi energy (E_f). The DoS is normalised per electron with the number of electrons for the “well-converged” and test DoS denoted n_{wc} and n_t respectively. The exact formula for this method is show in Eq.(A.1)

and is henceforth referred to as the *RMS Difference* or *RMSD* for short. The *RMSD* is a normalised measure of how far on average the error is from 0.

$$RMSD = 100 \cdot \frac{\sqrt{\frac{1}{E_w} \int_{-\frac{E_w}{2}}^{\frac{E_w}{2}} \left[\left(\frac{DoS_{wc}(x+E_f)}{n_{wc}} - \frac{DoS_t(x+E_f)}{n_t} \right)^2 \right] dx}}{\frac{1}{E_w} \int_{-\frac{E_w}{2}}^{\frac{E_w}{2}} \left[\frac{DoS_{wc}(x+E_f)}{n_{wc}} \right] dx} \quad (A.1)$$

Analysing the *RMSD* for a parameter in a similar way to that of the total energy allows for convergence testing to be conducted with the DoS of the system. An example is now demonstrated: Fig.(A.14) shows the DoS for two systems using solid blue and orange lines corresponding to a “well-converged” value (DoS_{wc}) and one which is to be tested (DoS_t). Their RMS values are indicated by the broken blue and orange lines respectively. The difference between the DoS of these systems is indicated by the red solid line and its RMS by the red broken line. Using Eq.(A.1), the *RMSD* is calculated to be 7.5%.

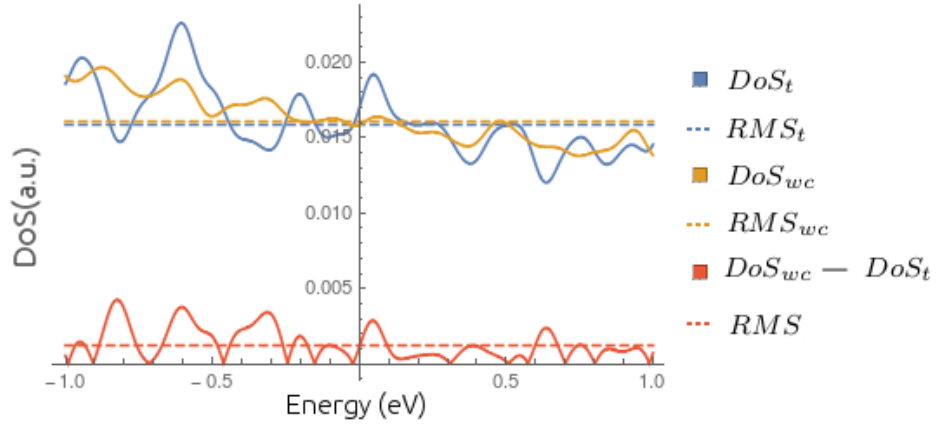


Figure A.14: ***RMSD* illustration.** DoS_t = DoS of parameter value to be tested, RMS_t = RMS of test parameter DoS, DoS_{wc} = “well-converged” DoS, RMS_{wc} = RMS of “well converged” DoS, $DoS_{wc} - DoS_t$ = Difference in DoS between well-converged and test values. RMS = RMS of $DoS_{wc} - DoS_t$. *RMSD* : 7.5%

While the RMS of each DOS is very close (broken blue and orange lines), the difference between them is large (red line) which results in a large *RMSD* value. A threshold difference needs to be selected for convergence test in order to choose an optimal parameter value. A threshold of 1% is judged to be a reasonable value and the goal of all convergence tests is to have an *RMSD* less than this value.

Convergence tests comparison - Electron smearing

The total energy convergence method is now compared to the *RMSD* method for different electron smearing values. This parameter is described in section 2.3.4, but to summarise, this parameter determines how “smooth” the DoS curve is by artificially changing the “temperature” of the system, allowing electrons to smear across bands. High smearing values may result in a loss of information in the DoS, however low smearing values are more computationally expensive. Fig.(A.15a) depicts the *RMSD* convergence test for different smearing values. Fig.(A.15b) depicts the total energy convergence test for the same values. In both tests the differences are relative to a smearing energy of 0.001 Ry. While both graphs appear similar some differences are noted. The total energy convergence test meets the threshold of 1 meV/atom at a smearing energy of 0.04 Ry, while the *RMSD* tests indicates a difference of 30% for this energy. This is a significant difference in the DOS which would directly impact the LDoS and therefore the simulated STM images. As the smearing parameter is reduced both convergence tests show a decrease in their measured differences, the total energy difference reducing to a value close to 0.02 meV however the corresponding *RMSD* value is approximately 8%. This comparison a clear indicator that the total energy convergence test is inadequate for the purpose of simulating the DoS or any quantity which relies on the DoS such as the LDoS and by extension simulated STM images. It is for this reason that the *RMSD* convergence method is used throughout this study.

The effect smearing has on the DoS can be seen in Fig.(A.15c) where smearing energies ranging from 0.005 Ry to 0.05 Ry are presented. For refer-

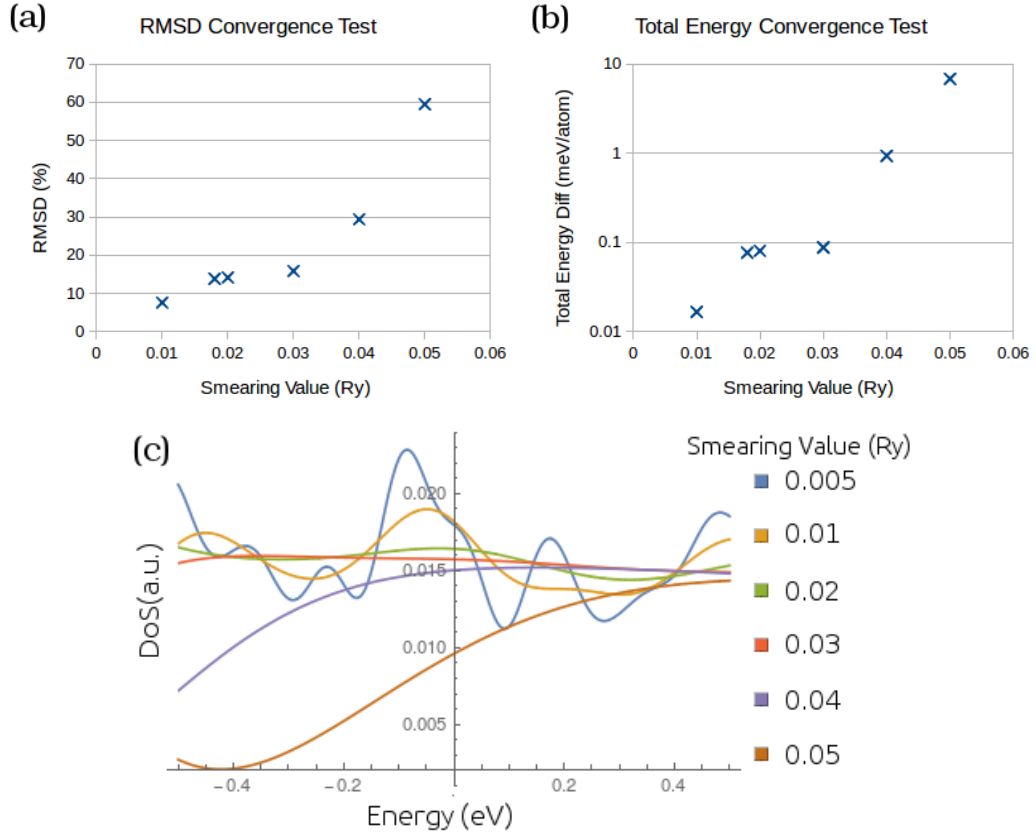


Figure A.15: **Comparison of *RMSD* and Energy convergence tests (Electron smearing).** (a) *RMSD* electron smearing convergence test. (b) Total energy electron smearing convergence test. “well-converged” value: 0.01 (Ry), plane-wave energy: 100 Ry. (c) DOS curves corresponding to different smearing parameters. Larger values indicate more smearing.

ence, 0.005 Ry corresponds to an artificial “temperature” 80 K, while 0.018 Ry is approximately 300 K.

Issues with the *RMSD* convergence method

A high smearing parameter may result in some of the important features of the DoS such as surface states being suppressed. However, a low smearing parameter presents issues when using the *RMSD* convergence method. Low smearing values result in more detail in the band structure and by extension the DoS. As detailed in section 2.3.4, a more detailed band structure requires

more k-points to be sampled accurately and therefore to converge with respect to the DoS. An issue this presents in metals is that an extremely large number of k-points are often required to accurately sample the bands[185]. This is evident from the *RMSD* convergence test for k-points sampling is shown in Fig.(A.16) for two smearing parameters, 0.005 Ry and 0.018 Ry. A high k-point density is computationally expensive, to combat this issue, electron smearing is used. Using electron smearing the small oscillations in the DoS can be removed and the DoS may converge more easily. An obvious concern when employing electron smearing in simulations is the risk of suppressing important electronic states, such as surface states for simulated STM images. While the *RMSD* is approximately the same for both electron smearing values tested here across the range of k-points, it will be shown that other parameters will converge for 0.018 Ry but not for 0.005 Ry. The optimisation of the parameters required to produce a Cu(111) system suitable for producing simulated STM images is now detailed, beginning with the bulk unit cell.

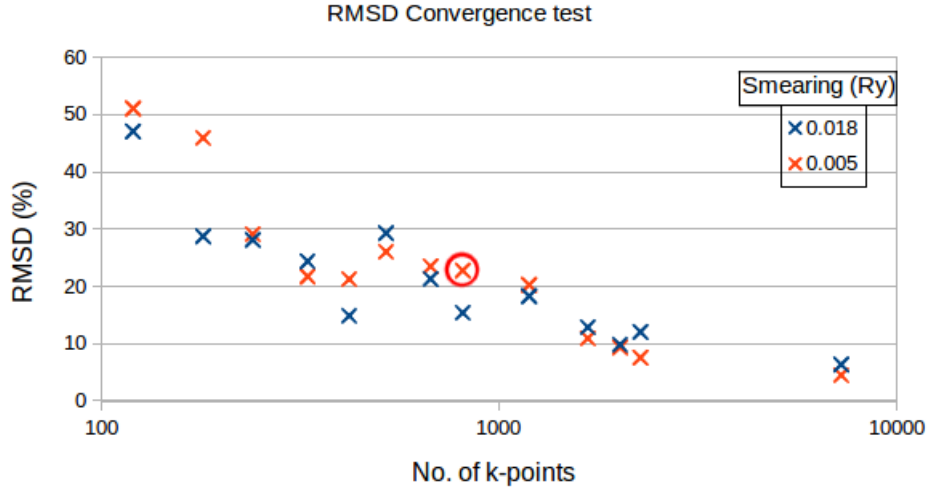


Figure A.16: ***RMSD* k-points convergence test.** The k-point convergence test is shown for the bulk cell using two smearing values: 0.018 Ry (blue) and 0.005 Ry (orange). “well-converged” value: 18900, optimised value: 810 (15-9-6), *RMSD*: 22%. Plane-wave energy: 60 Ry.

A.3.3 Bulk cell optimisation

The starting point of any set of calculations is the bulk unit cell. Along with verifying that the starting unit cell, which is the basic building block of the slab, is consistent with experimental measurements, the bulk cell offers a system in which a number of parameters can be optimised at a relatively cheap computational cost. Calculations on slabs can be resource demanding due to the relatively large cell size and number of atoms, and hence, obtaining a good estimate for the optimised value of each parameter is highly beneficial. These estimated optimal values can later be fine tuned for the final slab.

The Cu crystal termination in experiment is the (111) plane, hence, a unit cell with the (111) plane terminating the slab is required. The bulk unit cell for Cu is comprised of 3 atomic layers each consisting of 2 atoms. The layers follow the ABC stacking scheme for FCC(111) crystals.

The initial cell parameters and atomic positions are taken from the Crystallography Open Database[186] which stores experimental results on a wide range of crystals. An image of the Cu unit cell produced by XCrySDen[187], a crystalline and molecular structure visualisation program, is shown in Fig.(A.17)

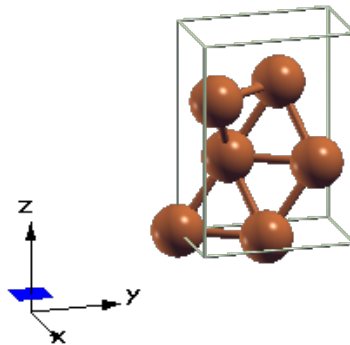


Figure A.17: **Bulk Cu(111) unit cell**

The pseudopotential chosen for this study is from the SG15 Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials[188]. Optimisation

calculations has been performed for the elements in this suite of pseudopotentials. A plane wave energy cut off of 60 Ry is recommended[189].

The default values for other parameters were used initially with the exception of the electron smearing parameter. A value of 0.005 Ry was initially used which approximately corresponds to a “temperature” of 78 K, approximately that of liquid nitrogen, which the STM experiments were performed at. The bulk k-point density and plane-wave cut off energy are converged using SCF calculations with a self consistency energy threshold of 10^{-8} .

Bulk K-point Sampling Optimisation

The number of points used to sample the Brillouin zone in each dimension: x, y, z needs to be specified. The notation used, in this study, to indicate the sampling density follows the format of k_x - k_y - k_z , where k_n is the number of k-points in the n direction. The total number of k-points which make up the 3d grid is calculated by multiplying these 3 values together. The ratio of the number of k-points should reflect that of the cell dimensions for a homogeneous system, ensuring the Brillouin zone is sampled evenly as specified in section 2.3.4.

The *RMSD* k-point convergence plot is presented in Fig.(A.16). The k-point sampling density does not converge within our predefined threshold of 1% for the reasons detailed in section A.3.2. A k-point sampling density of 810 points (15-9-6), indicted by the red circle, corresponding to a *RMSD* of $\approx 20\%$ is selected. The k-point sampling density will be converged again for a slab in section A.3.4.

Bulk Plane-wave Energy Optimisation

The *RMSD* convergence test is shown in Fig.(A.18a) alongside the total energy convergence test in Fig.(A.18b). The *RMSD* convergence test indicates that the plane-wave cut-off energy converges very well by 70 Ry ($< 0.2\%$). The total energy convergence test however indicates that the system is not converged within the threshold of 1 meV/atom, even for energies in excess

of 100 Ry. This is another reason why the total energy convergence test is inadequate for this system.

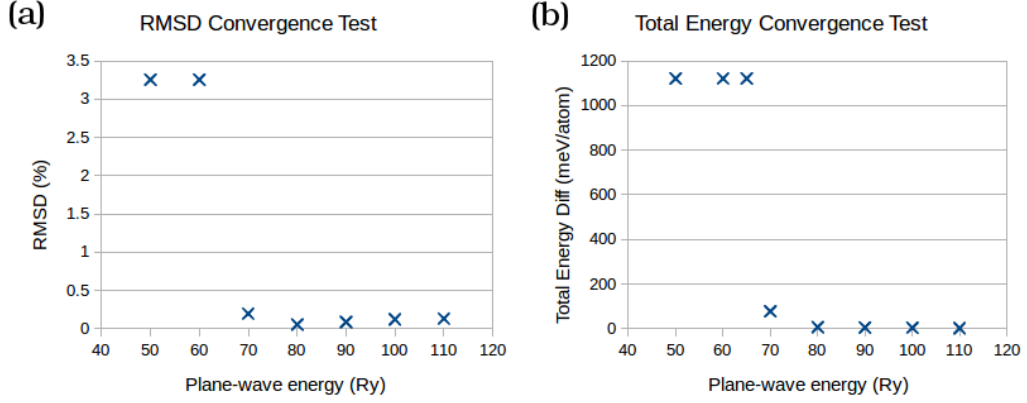


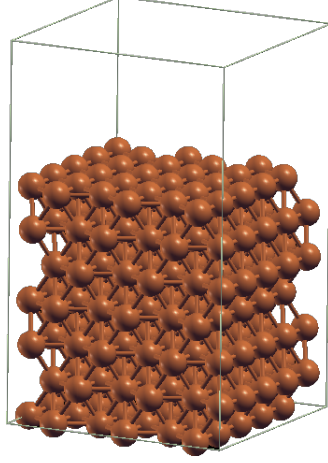
Figure A.18: **Comparison of Energy and *RMSD* convergence tests (Plane-wave energy).** (a) *RMSD* plane-wave energy convergence test indicating suitable convergence ($< 1\%$) at 70 Ry. (b) Total energy plane-wave energy convergence test indicates no value of energy is within the threshold (1 meV/atom). “well-converged” value: 120 Ry, optimised value: 70 Ry *RMSD*: 0.25%.

A variable cell relaxation calculation (vc-relax) with the optimised plane-wave cut off energy (70 Ry) and k-point sampling density (15-9-6) yields the optimised cell dimensions and atomic positions which will be used as the basis in the slab.

A.3.4 Slab cell optimisation

A “slab” refers to a crystal structure with a layer of vacuum in the unit cell, by introducing a vacuum layer the crystal is terminated by a surface on both sides. This enables simulated surface studies to be conducted. An image of a sample Cu slab cell is shown in Fig.(A.19).

The periodic repetition of the unit cell results in an infinite number of slabs each separated by a distance corresponding to the vacuum thickness of the unit cell. The size of this vacuum layer should be sufficiently large such that the surface of one slab does not interact with the surface of another. Increasing the vacuum increases the unit cell size and hence the time and

Figure A.19: **Cu(111) slab unit cell**

resources for computation. The vacuum thickness is thus a parameter which requires convergence testing.

The computational cost of adding more atoms, which in turn add more electrons to the system scales cubically[178]. Large slab in excess of 300 atoms or so are generally not feasible to simulate. This is a far cry from the thickness of crystal structures and thin films in reality. In practice, many systems begin to exhibit bulk-like properties in relatively thin slabs which can be computed using plane-wave codes. Given that the number of atoms in the slab contributes significantly to the computational requirements for a calculation, optimising the number of atomic layers is crucial. If the slab is too thin, the two surfaces of the slab interact with one another and yield an unphysical result inconsistent with that of a large crystal. The central layers of the slab should have bulk-like properties such as inter atomic spacing or LDoS, within a small tolerance. This is to ensure that the surface layers observe a bulk-like structure beneath them, as they would in a real crystal. This calculation may yield a result which requires the slab thickness to be infeasibly large. A way to remedy this, but not without its own problems, is to fix the atomic positions of the atoms in one surface layer (bottom) and some layers above it to the bulk positions. This method is commonly

employed but certainly reduces the accuracy of the calculation. Relaxing this system produces 1 relaxed surface and 1 surface terminated with the bulk positions. This ensures that the layers above the fixed ones see a bulk-like structure and thus can reduce the number of layers required in order to get a slab to converge. However in reality the fixed layer may not be bulk-like, this clearly depends on the system. The issue that may arise from this procedure comes from a potential charge separation across the 2 surface layers. Even with a small charge difference on each surface, a strong electric field could be produced due to the periodic repetition of slabs in the calculation. Fixing the atomic positions in some layers reduces the number of atoms in the slab which need to relax, therefore speeding up the relaxation calculations.

Convergence tests for the vacuum, slab thickness and in-plane slab dimensions are achieved using the relax calculation of the plane-wave code detailed in section 2.3.4. A force threshold of 1×10^{-3} (a.u.) is used for all relax calculations.

Vacuum thickness optimisation

A slab comprised of 4 atomic layers was used for the vacuum convergence test. This cell had a vacuum layers introduced by simply increasing the out of plane lattice parameter (z-direction). The *RMSD* convergence test is presented in Fig.(A.20).

The vacuum thickness converges very quickly, likely due to coppers metallic nature and therefore having localised electrons. This is seen in the total energy of the system and the DoS remaining relatively unchanged as the number of layers increases. 12Å of vacuum is determined to be sufficient.

Inplane Slab Dimensions Optimisation

The purpose of this study is to simulate defects on the Cu(111) surface, it is imperative that the defects do not interact strongly with one another. The in-plane slab dimensions need to be increased such that a test defect will not self interact strongly when the slab cell is repeated. In order to ensure that the slab converges for any defect we may like to simulate, we imagine the

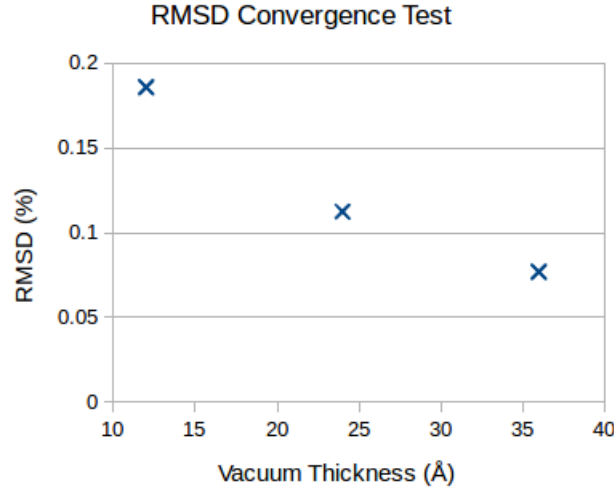


Figure A.20: ***RMSD* vacuum thickness convergence test.** “well-converged” value: 50 Å, optimised value: 12 Å, *RMSD*: 0.18%.

“worst-case scenario” defect. This defect is the largest, most disruptive one to the system. If this system is used for convergence testing, then it is safe to assume the other less disruptive systems will also be converged. For this work we tested the case of 7 missing Cu atoms from the surface layer with a H atom placed in a 3-fold hollow site. Convergence of specific systems may be done at a later date once a narrower band of systems has been identified. It is the intention at this point to produce a base system that will quickly give reasonable, accurate results, with minimum additional calculations on top of the basic relax calculations required when adding and removing atoms from the system. The x and y dimensions were selected such that the cell is as close to being square as possible, that is the x and y slab cell dimensions are equal. This is to ensure the distance between defects is the same in all directions. A slab thickness of 4 atomic layers was used for this convergence test. Increasing the in-plane slab dimensions, even by a small amount results in a considerable increase in the total number of atoms. For this reason only systems could be simulated. The first uses a cell with 30 atoms in each layer, the second with 56. The *RMSD* between these systems is 20% for an electron smearing value of 0.005 Ry and 0.7% for a value of 0.018 Ry.

Slab Thickness Optimisation

Using a slab with 30 in plane atoms and the test defect, the number of layers in the slab is varied. The optimised vacuum layer thickness is used in the slab thickness convergence tests. Atomic layers could be added to the cell by translating the corresponding layers beneath by the bulk inter-layer spacing, ensuring the ABC stacking criterion. The number of k-points used in the z-direction scaled as the slab thickness scaled, doubling the real space slab thickness corresponds to halving the number of k-points in the z-direction as described in 2.3.4. The RMSD convergence test is shown in Fig.(A.21) for two electron smearing values 0.018(Ry) and 0.005 Ry. 7 atomic layers is close to convergence ($\approx 1\%$) for the 0.018 Ry smearing energy. Using this value the Cu(111) slab is comprised of 210 atoms, a relatively large slab which will take considerable time to relax.

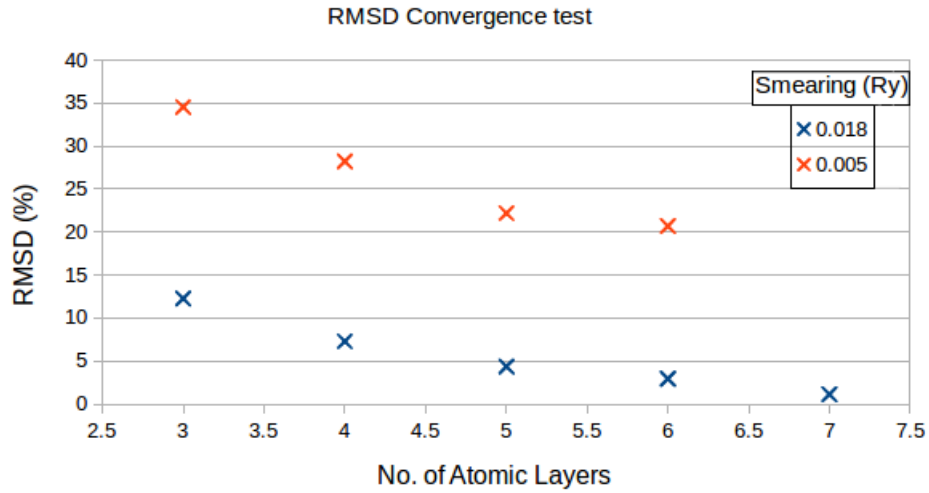


Figure A.21: **RMSD slab thickness convergence test.** The number of atomic layers of the slab is varied using two smearing values: 0.018 Ry (blue) and 0.005 Ry (orange). “well-converged” value: 8 atomic layers, optimised value: 7, *RMSD*: 2%. Plane-wave energy: 70 Ry, k-point density: 10-10-1

The convergence tests at 0.005 Ry reveal that the slab thickness and in-plane dimensions are not well converged. Using larger slabs to improve the convergence tests add immensely to the required computational resources.

A small increase in the in-plane dimension or the number of atomic layers exceeds the resources available to us. For this reason, the slab comprised of 210 atoms ($5 \times 6 \times 7$) is used for further calculations and the simulation of STM images. An advantage of using the *RMSD* convergence test is that a quantitative error in the DoS can be measured, which gives an error in the simulated STM images. With this in mind the validity of the simulated STM images can be considered. The plane-wave cut off energy and k-point sampling density are optimised for the slab. The optimal value for the plane-wave cut off energy remained at 70 Ry, with a *RMSD* $< 0.5\%$.

Slab k-point convergence

The in-plane and out of plane k-point sampling densities are converged using the *RMSD* method separately for the slab system. The slab cell is approximately square (ratio = 1:1.04) so an equal number of k-points are used in both in-plane directions. Typically only 1 k-point is used in the out of plane direction when simulating a slab. This is due to the way in which k-points scale with the cell dimension as outlined in section 2.3.4. However given the sensitivity of the DoS to the k-point sampling density observed in section A.3.2, a convergence test was conducted. For the purpose of the out of plane k-point sampling, 3 k-points were used for in-plane directions. The *RMSD* convergence test is presented in Fig.(A.22) for electron smearing values of 0.005 Ry and 0.018 Ry. The “well-converged” value is 10 out-of-plane k-points. The out-of-plane k-points are quick to converge for both electron smearing values, with an *RMSD* value of $\approx 0.05\%$ for 3 out-of-plane k-points. As expected, the single k-point sampling density produced a reasonable *RMSD* value of 2% and 0.25% for the 0.005 Ry and 0.018 Ry smearing energies respectively.

The *RMSD* convergence test for in-plane k-points using 3 out-of-plane k-points is shown in Fig.(A.23) for electron smearing values of 0.005 Ry and 0.018 Ry. The “well-converged” value is 10 in-plane k-points. A steady decrease in the *RMSD* value is observed for both smearing energies, with a single exception for 0.005 Ry at 7 in-plane points. At 8 out-of-plane k-points the slab is close to convergence (2%) for 0.018 Ry, however for 0.005 Ry the

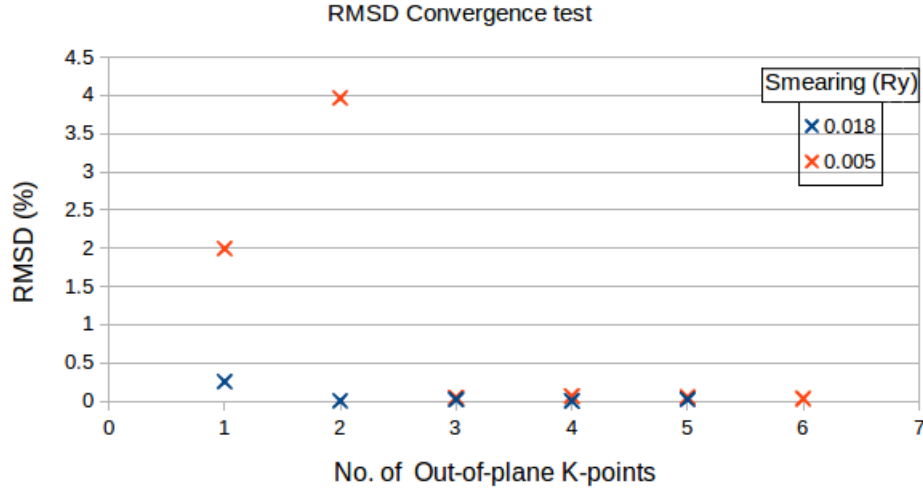


Figure A.22: ***RMSD* out-of-plane k-points convergence test.** “well-converged” value: 10 k-points, optimised value: 1, *RMSD*: 0.25%. In-plane k-points: 3.

RMSD value is 9%. The in-plane k-point sampling is chosen to be 10 for each direction, while this is not fully converged, it is close the limit of our computational resources. The in-plane k-point convergence test is repeated for the electron smearing energy of 0.018 Ry using 1 out of plane k-point. The *RMSD* values for 1 and 3 out-of-plane k-points differ from each other by approximately 0.5% (not shown). This minute difference indicates that 1 out-of-plane k-point is sufficient. This concludes the optimisation for the slab. A table of the final parameters and the corresponding *RMSD* to the “well-converged” value is given in table A.1. Defects which are smaller and therefore less disruptive to the periodicity and electronic structure of the slab, should, in principle, converge better than the test defect.

A.4 Simulated Adsorbates & Defects on Cu(111)

After the slab size is decided on (5371) a pristine slab of this size is allowed to fully relax. The relaxed slab has defects and impurities added as required, and the new system is allowed to relax. The bottom 4 layers are fixed in

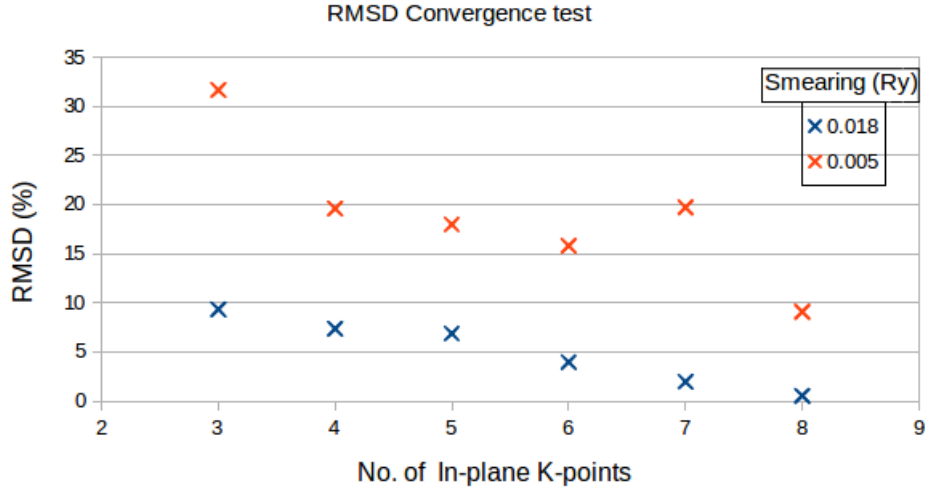


Figure A.23: ***RMSD* in-plane k-points convergence test.** “well-converged” value: 10 k-points, optimised value: 10, *RMSD*: -%. Out-of-plane k-points: 3.

	Optimised Value	Well-conv. Value	<i>RMSD</i> (0.005 Ry)	<i>RMSD</i> (0.018 Ry)
In-plane k-points	8–8 (10–10 used)	10–10	9%	2%
Out-of-plane k-points	1	10	2%	0.25%
Plane wave energy (Ry)	70	120	0.25%	-
Vacuum size (Å)	12	50	0.18%	-
In plane slab dimensions	30 atoms (5×6)	56 (8×7)	20%	0.7%
No. of atomic layers	7	8	≈ 20%	2%

Table A.1: **Summary of slab convergence tests.**

place in order to speed up calculations. The force on these fixed layers is monitored to ensure they do not exceed the threshold set for the other atoms.

A.4.1 Preferential binding sites of adsorbates

Four binding sites were analysed during the course of this study, the Top (T), Bridge (B), Hollow (H) and Subsurface sites (SS). The difference in binding energies for some select adatoms are presented in table A.2 alongside the

	Binding site	Energy Difference(eV)	Literature
H	T	0.59	0.54[190]
	H	lowest	
	B	0.13	0.14[176]
	SS	0.92	0.93[176]
O	T	1.51	1.26[176]
	H	lowest	

Table A.2: **Binding Energies of some atoms** T - Top, H - Hollow site, B - Bridge site, SS - Subsurface site (6 fold).

corresponding energies from the literature. Despite not converging with respect to the total energy, the errors appear to cancel and the relative energies remain accurate. Calculating the binding energies for O adatoms in the top and hollow sites with smearing parameter values of 0.005 Ry and 0.018 Ry resulted in a difference of binding energies for each site of less than 0.05%.

A.4.2 Simulated STM images

Simulated STM images are generated using the Tersoff-Hamann scheme[14] detailed in section 2.1.1. The following section comprises of simulated STM images of various atoms and molecules on Cu(111) alongside the atomic models for each new binding location presented. Some binding locations were not simulated due to their considerably unfavourable binding energies stated in the literature. The atoms which are simulated were chosen based on their relative likelihood of being the “asymmetric” defect observed in experiment in section A.2.2. Following the presentation of the simulated STM images a comparison of simulated images that are notably similar to the experimental images are compared and subsequently discussed. Simulated STM images using DFT is not an absolute method to determine surface structures. Simulated STM images do however support proposed models, such as the binding location of the atom presented in this section. A prominent example of this can be found in the literature and relates to the oxygen-induced $p(4 \times 4)$ reconstruction of Ag(111). Carlisle *et al.*[191] present a structural model of this reconstruction based on comparison between STM images and simulated

STM images resulting from DFT calculations, however using crystallographic techniques such as STM, x-ray diffraction and core level spectroscopy, Schmid *et al.*[192] produced a different model for this reconstruction which is now accepted as being correct. Furthermore, using DFT calculations Schmid *et al.* demonstrated that DFT methods yielded the incorrect model as being the lowest in energy.

The bias voltage which images were simulated range from 100 mV to 1 V and the isovalues chosen to encompass the range of reasonable STM images as outlined above. The most reasonable simulated image is presented for each surface structure. Examples are what are considered good and bad images are shown in in Fig.(A.24) for the case of a hydrogen atom in the top binding site at 300 mV. Fig.(A.24a&b) resolve the Cu surface atoms in a similarly to how they are resolved in experiment and so are considered “good” simulated images. Fig.(A.24c) does not display surface atoms and therefore is considered “bad”. It was not always possible to adjust the contrast such that the Cu surface atoms were visible as some adsorbates and defects produced a large height contrast making the relatively small contrast of the Cu atoms difficult to resolve.

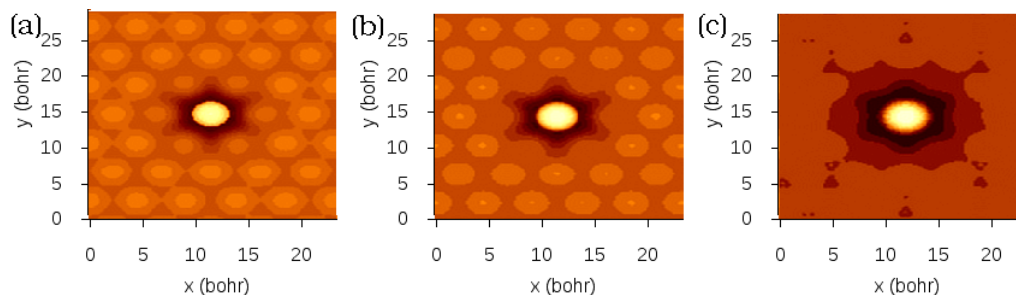


Figure A.24: **Examples of “good” and “bad” simulated STM images.** (a&b) The surface Cu atoms are resolved well and the image is deemed “good”. (c) The surface Cu atoms are not resolved and so the image is not considered suitable for comparison to experimtnal STM images.

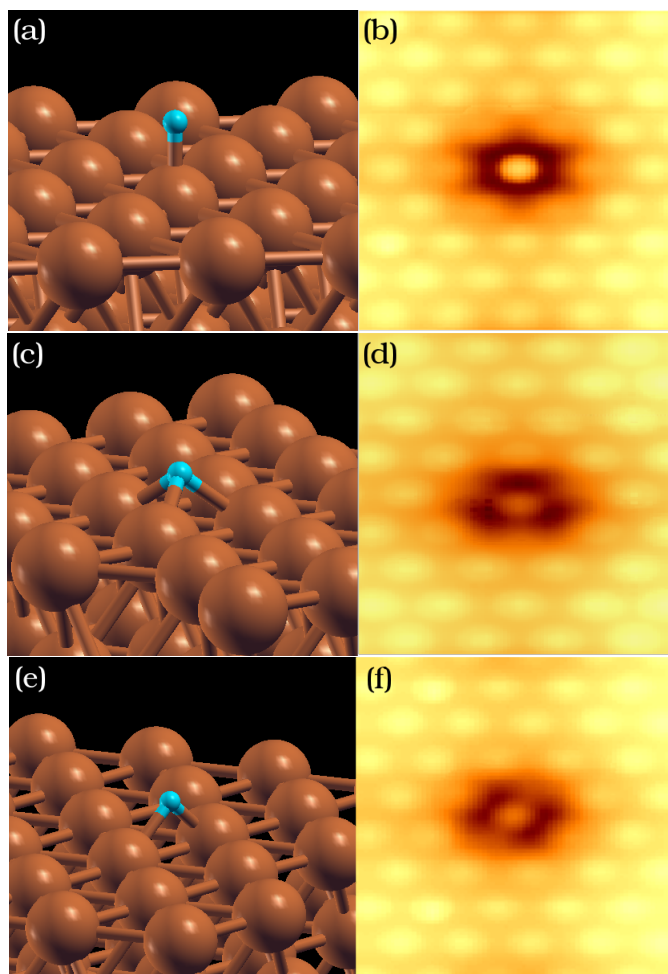


Figure A.25: **Hydrogen on Cu(111).**(a) Model of a H atom in the on top site. (b) STM simulated image of a H atom in the on top site. (c) Model of a H atom in the FFC hollow site. (d) STM simulated image of a H atom in the FFC hollow site. (e) Model of H atom on bridge site (f) STM simulated image of a H atom in the Bridge site.

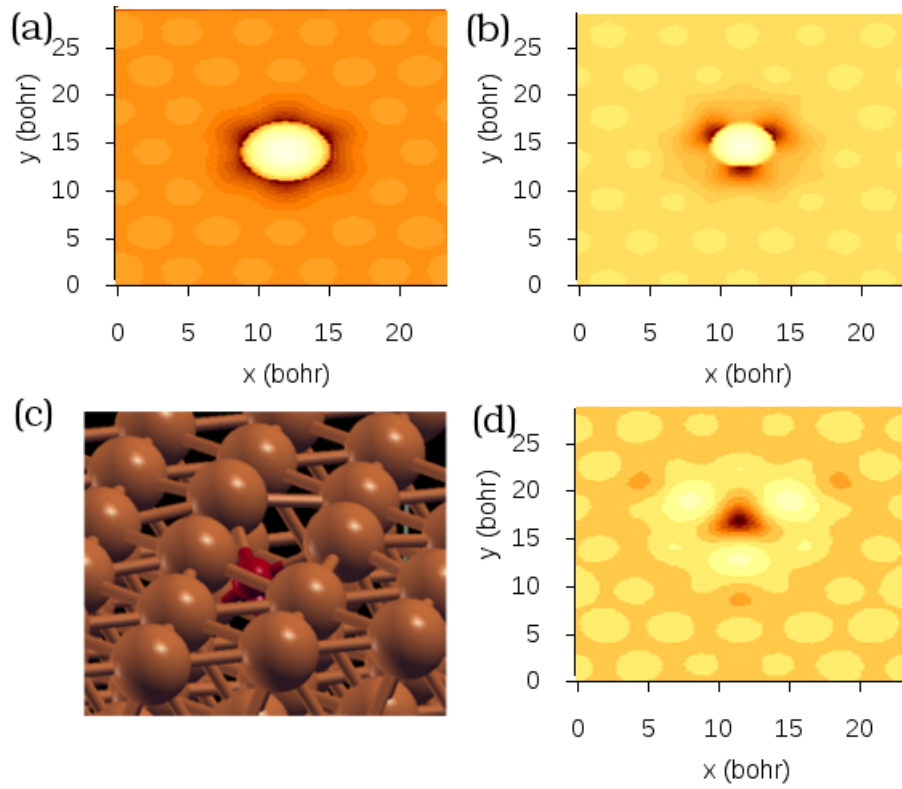


Figure A.26: **Oxygen on Cu(111).**(a) STM simulated image of an O atom in the on top site. (b) STM simulated image of a O atom in the FCC hollow site. (c) Subsurface interstitial O, 0.2Å displacement of Cu atoms.

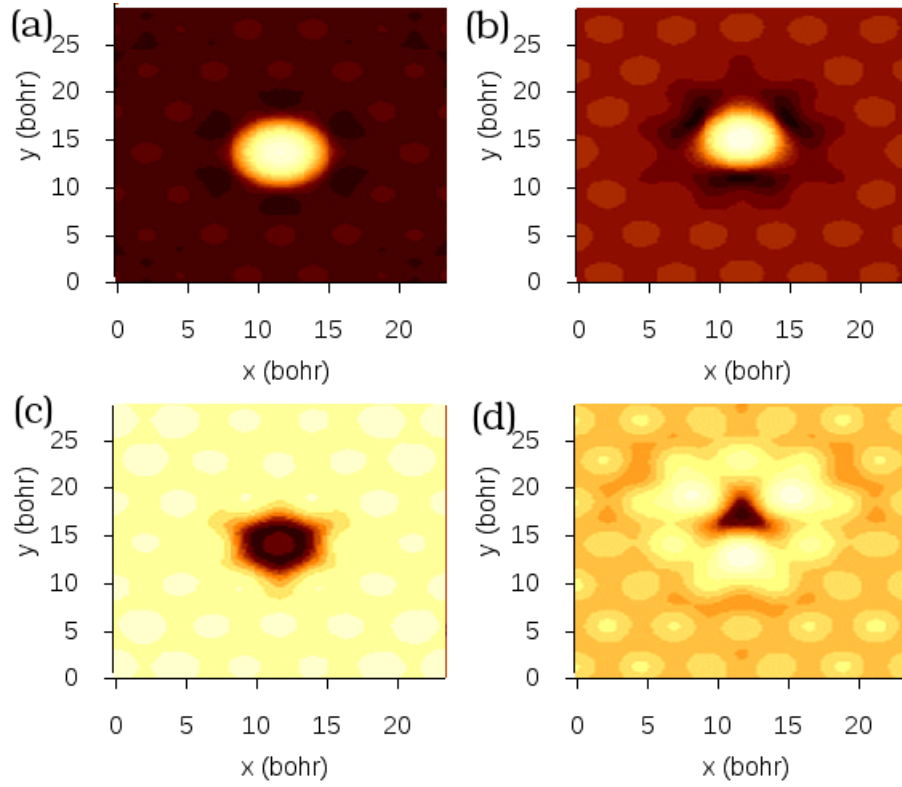


Figure A.27: **Carbon on Cu(111).**(a) STM simulated image of a C atom in the on top site. (b) STM simulated image of a C atom in the FFC hollow site. (c) Cu atom substituted for C (d) C atom in subsurface ffc site (6-fold hollow).

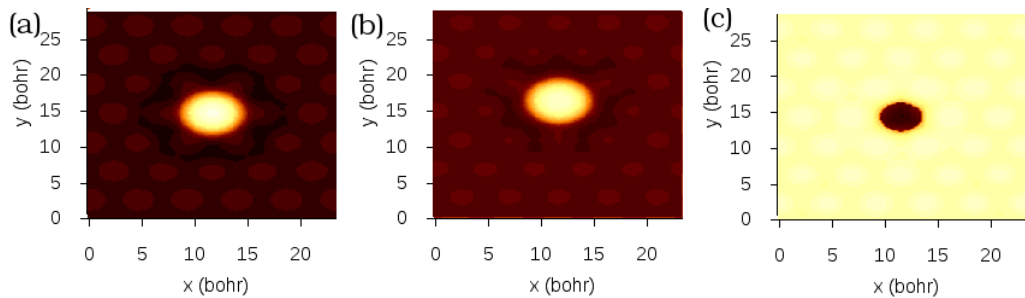


Figure A.28: **Copper on Cu(111).**(a)Cu atom on Top site (b) Cu atom on 3-fold hollow site (c) STM simulated image of a single Cu vacancy

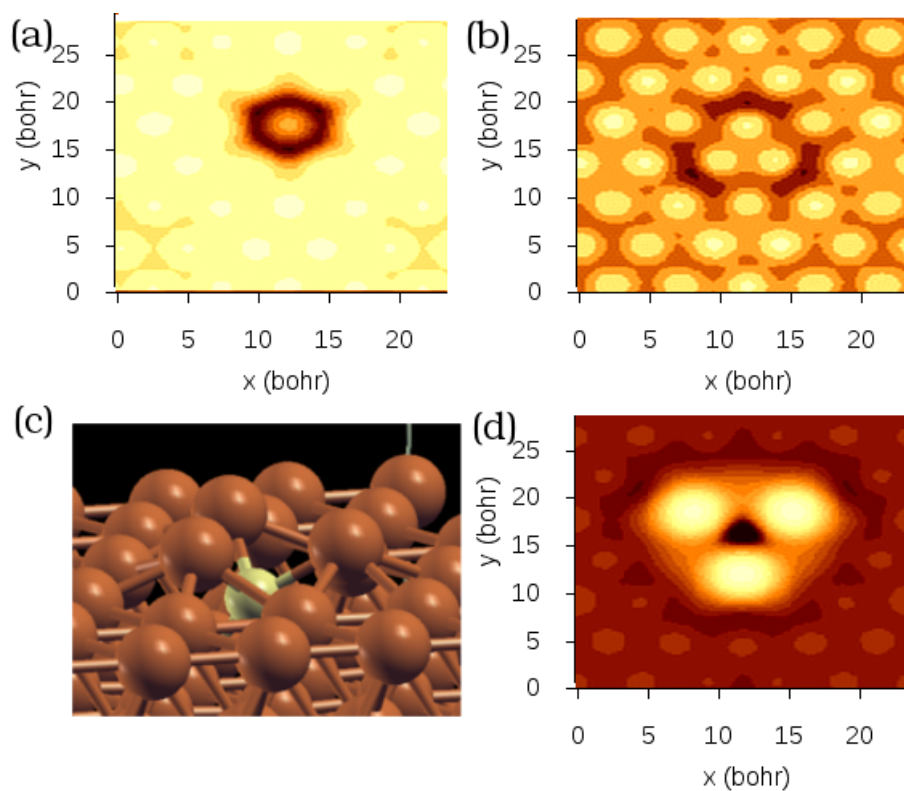


Figure A.29: **Sulfur on Cu(111).**(a) STM simulated image of S impurity substitute (b) S sublattice substitute. (c) Model of interstitial S impurity, result in Cu atoms displaced $1\text{\AA}$ from lattice. (d) Simulated STM image of interstitial S impurity

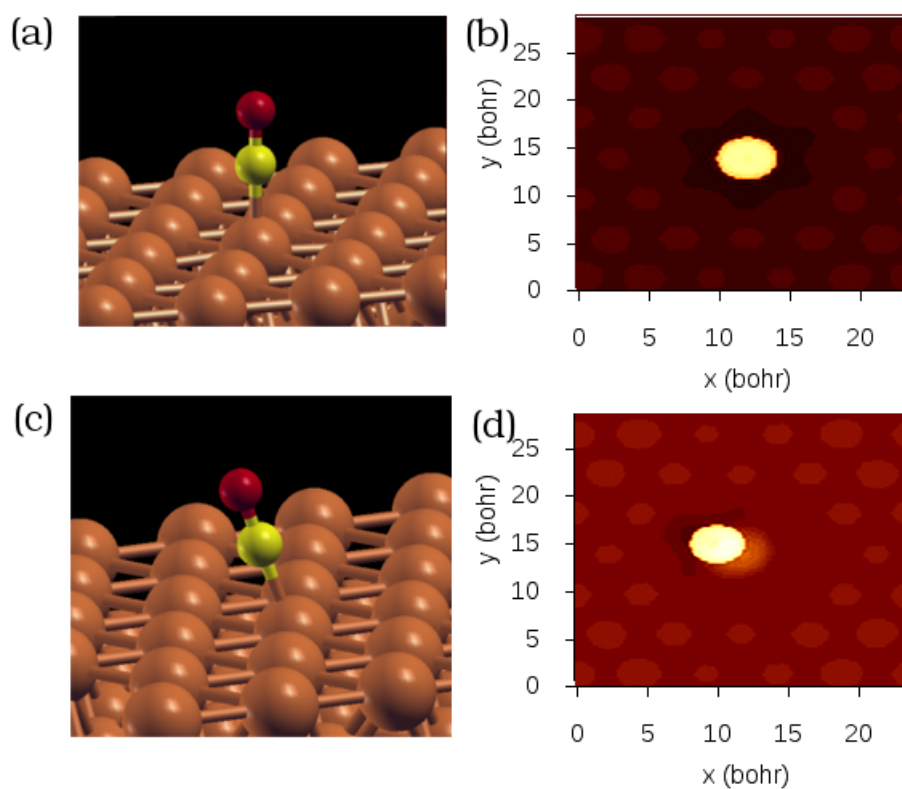


Figure A.30: **Carbon Monoxide on Cu(111).**(a)Model of CO molecule in top site (b)STM simulated image of CO in top site (c) Model of CO molecule in top site with artificial tilt (d) STM image of CO molecule in top site with artificial tilt

A.4.3 Comparison of experimental & simulated STM images

“Asymmetric” Defect

A large number of adsorbates and defects were simulated in order to identify the “asymmetric” defect observed in STM measurements. These particular adsorbates were chosen to be selected based on relative likelihood to be the source of the defects based on the structure of the defects observed in STM measurements and the probability of the particular impurity existing within the UHV chamber or bulk of the Cu(111) crystal. A large number of other defects, particularly complexes of point defects meet the basic requirements to warrant a simulation, however time and resources are a limiting factor and so best judgement at the time was used when deciding which systems are simulated. A number of other impurities and defects which are not presented here were simulated for one or two relaxation steps, as an indicator of their compatibility without committing to the full calculation, which can take a considerable amount of time. While they were not allowed to fully relax, care was taken to position the impurities close to the relaxed state based on previous DFT results from the literature.

Different adsorbates in the same binding site produced similar STM images, which reflected the symmetry of the binding location, as one would expect. The key difference between each adsorbate was the relative intensity of the protrusion relative to the surface Cu atoms. Placing a single atom or a molecule orientated perpendicular to the surface on the top site resulted in a bright protrusion at the site location independent of the bias polarity. Depending on the simulated tunneling current (constant current value) used, the 6 nearest neighbouring Cu atoms were either visible, partly visible or not visible. When the atoms are not visible the region in which they occupy appears darkly contrasted resulting in a dark hexagon surround the bright protrusion. Tilting the molecules artificially resulted in the protrusion shifting to one side of the darkly contrasted region.

Adsorbates in the 3-fold hollow site produced a bright feature at the binding location and three darkly contrasted regions in a triangular shape. While the bridge sites produced a small protrusion with two depressed regions on either side. The depressed region of the bridge sites resemble a hexagon elongated in one direction.

Substitutional impurities appeared as protrusions or depressions relative to the surround Cu atoms and did not produce an asymmetry as expected or cause the surround Cu atoms to change contrast significantly, so as to resemble the darkly contrasted hexagon seen in experiment. Single Cu atom vacancies appears as a small darkly contrasted region approximately the size of the Cu atom and located at the vacancy. These vacancies resemble those observed in experiment on occasion, seen to the upper right of Fig.(A.6) in section A.2.2.

Interstitial impurities located at the 6-fold hollow sites resulted in large changes in the surface structure and LDoS. For sulphur, the Cu atoms surround the impurity relaxed 1 Å out of the surface, while for oxygen they relaxed 0.2 Å. The result of these three protruding Cu atoms is three considerably large, brightly contrasted features in the simulated STM images. Subsurface substitutions resulted in little change to the LDoS however it is noted that the resulting features display a 3-fold symmetry.

From the simulated STM images, some insight is gained into the nature of the “asymmetric defect”. The hexagonal depression which surrounds the protrusion is characteristic of an atom or molecule in the top binding location and substitutional impurities such as C and S in the surface layer. These substitutional impurities do not produce a protrusion with a relative height in excess of the surrounding Cu atoms, whereas atoms and molecules in the top site are observed to. Substitutional impurities are locked into the lattice and are not easily moved, making it difficult to produce the asymmetry of the defects observed in experiment. An atom or molecule in the top site may then be the best candidate, however the defects are very stable under pulsing with the STM tip, unlike typical adatoms and molecules which are generally mobile on the surface under the influence of the tip. A comparison between the experimental images of the “asymmetric” defect and the defect

which produced the most similar STM images (CO molecule) is presented in Fig.(A.31).

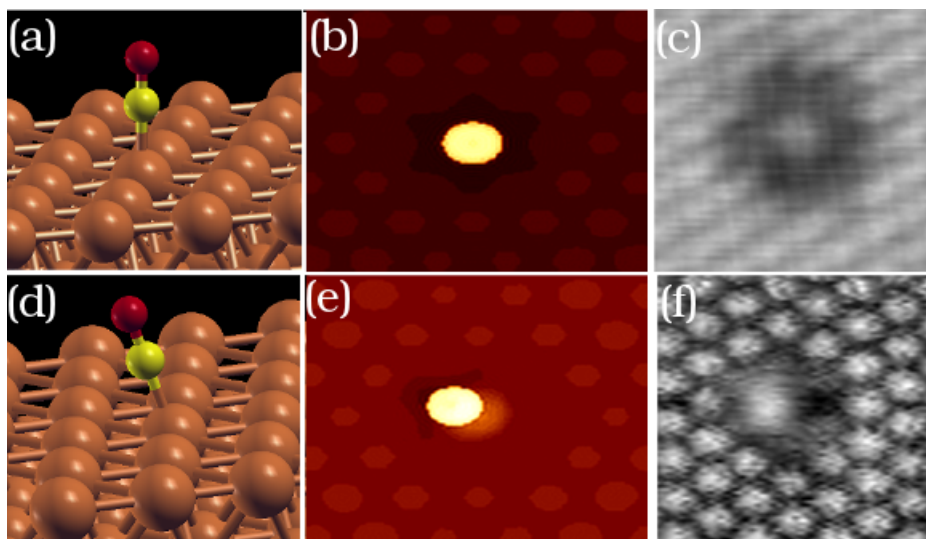


Figure A.31: **“Asymmetric” defect Comparison: Simulated & experimental STM images.** (a) Model of CO molecule in top site (b) STM simulated image of CO in top site (c) STM image of “asymmetric” defect. $V = 0.15$ V, $I = 50$ pA. (d) Model of CO molecule in top site with artificial tilt (e) STM image of CO molecule in top site with artificial tilt. (f) STM image of asymmetric defect. $V = 0.3$ V, $I = 75$ pA.

Fig.(A.31) depicts the model of a CO molecule in an upright and tilted position (a & d) relative to the surface, the corresponding simulated STM images (b & e) and two experimental images of the “asymmetric” defect (c & f). The experimental STM image in (c) bears resemblance to the CO molecule in the upright top binding location (b). The experimental STM image in (f) appears similar to the CO molecule in the tilted top binding location (e), however the depression adjacent to the protrusion in (f) is not apparent in (e).

“Single” Defect - Tip Interaction

The single defect described in section A.2.2 is presented again alongside atomic models and simulated STM images of a H atom in the top, hollow

and bridge sites in Fig.(A.32). The initial image of the defect, (c), resembles the simulated STM image of the H atom in the top site (b). Both produce a small protrusion surrounded by a darkly contrasted hexagonal region in the 6 nearest neighbour Cu surface atoms. The top site is unfavourable for adsorption as its binding energy is 0.59 eV higher than that of the most stable, hollow site. Following the interaction of the STM tip with the protrusion, the defect appears differently in STM images, (f&i) (same image). A depression is evident in STM images indicating that the defect which caused the protrusion and depression in (c) is still present, however it may have changed its binding site. Simulated STM images of a H atom in the hollow and bridge sites are presented in (e&h). Both the hollow site and the bridge site exhibit a similarly contrasted bright feature at the H atom location, relative to the surrounding Cu atoms. The 3-fold hollow site has 3 darkly contrasted regions surrounding it, while the bridge site has two, both reflecting their respective symmetries. The resolution of the experimental image is not to the standard to make a conclusion, however it would appear that the bridge site is the more likely candidate. The energy difference between the 3-fold site and the bridge site is 0.13 eV, which may be close enough for the H atom to be stable at either site. DFT calculations do not always get the relative binding energies correct, as was the case for CO on PT(111)[193].

H is relatively abundant in vacuum systems, its relatively small size allows it to penetrate the walls of UHV systems and it is difficult to pump out. Ion gauges with exposed heating filaments can split H_2 molecules resulting in atomic H in the chamber. This may be a source of the feature seen in experiment.

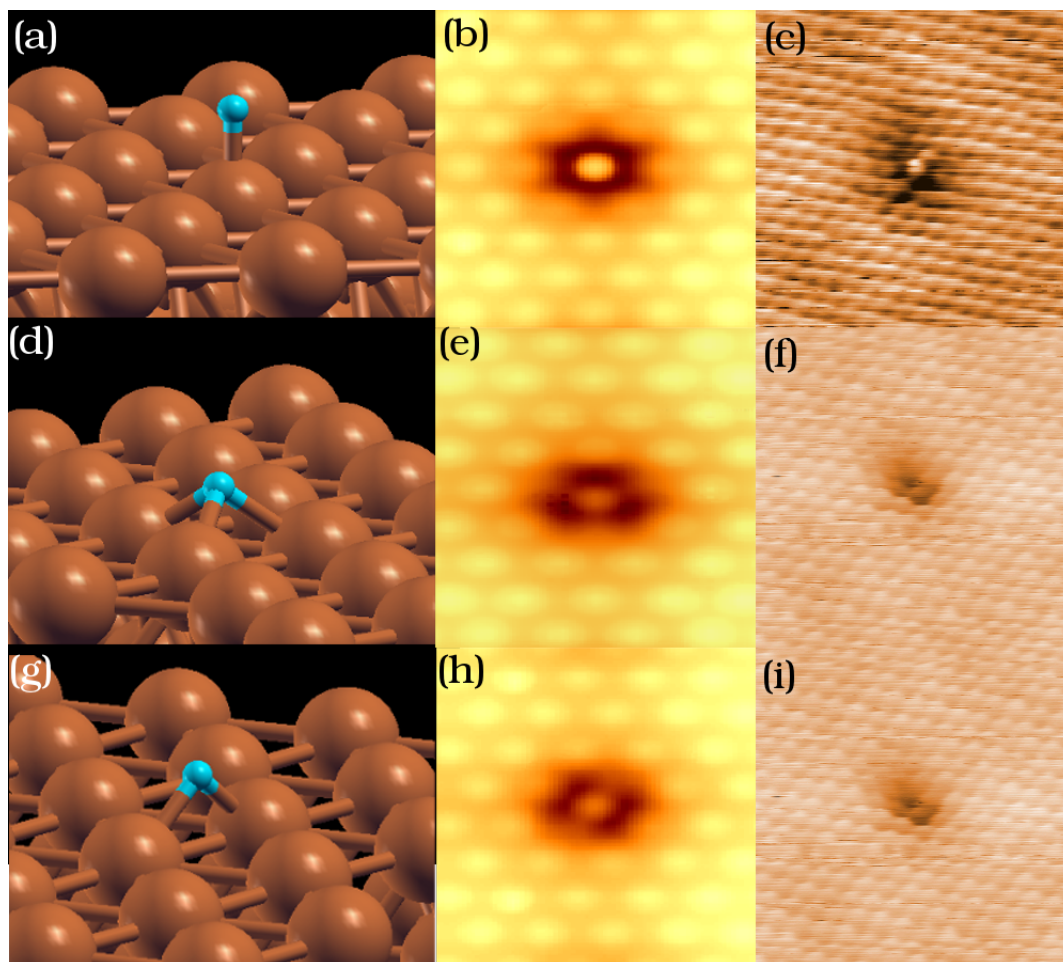


Figure A.32: **Comparison of simulated STM images of H on Cu(111) and experimental of the “single” defect.** (a) Atomic model of H in top site. (b) Simulated STM image of H in top site. (c) Experimental image of defect. (d) Atomic model of H in hollow site. (e) Simulated STM image of H in hollow site. (f) Experimental image of defect following interaction with STM tip. (g) Atomic model of H in bridge site. (h) Simulated STM image of H in bridge site. (i) Experimental image of defect following interaction with STM tip. (again)

A.5 Discussion & Conclusions

A number of defects were observed on the Cu(111) surface in STM images. The “asymmetric” defects are stable on the surface and exhibited a hexagonal depression, 7 Cu atoms in size, and a small protrusion within the depression. These defects are separated from one another by a distance dictated by the Fermi wavelength. The characteristic protrusion of this defect is observed to change appearance in STM imaging depending on the tunneling conditions. The defect exhibits an asymmetry, where the protrusion is located to one side of the depression. Across all defects of this type, the protrusion is always oriented in the same direction. The presented hypothesis suggests that the orientation of the protrusion within the defect is determined by the Fermi wavelength. Defects align to minimise their energy, both in position on the lattice and in orientation. Simulated STM images of various adatoms and impurities on the surface suggest the binding location for this defect is the top site. Another surface defect is observed to interact with the STM tip. STM images prior, during and after the interaction indicate that the tip induced diffusion of the feature. Simulated STM images of a H atom in the top site closely matches that of the initial experimental image before the interaction occurred. Simulated STM images of a H atom in the bridge site strongly resembles the experimental image of the defect following the interaction. The bridge binding site is calculated to be more energetically favourable than the top site.

A method of convergence testing for DFT simulations was developed based on the *RSMD* of the DoS of the system. This pragmatic approach to converging a system offers a quantitative measure of the accuracy of the DoS and by extension, the simulated STM images. The conventional total energy convergence tests are shown to be inadequate through comparison with the DoS method. A Cu(111) slab is converged with respect to its DoS following this method. While not all parameters converged to a desired threshold for this particular system, the DoS method offers a consistent and accurate approach to converging slabs for DFT simulations with a quantitative measure of the error.

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