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Functional nanostructures self-assembled on templated surfaces

A thesis submitted to
The University of Dublin
for the degree of
Doctor of Philosophy in Physics

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May 2013
Declaration

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Dublin, May 2013

Olaf Lübben
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Summary

This work consists of surface studies of three systems; firstly, the growth of Fe nanoclusters on the Ge(001) surface has been studied using low-temperature scanning tunneling microscopy (STM), X-ray magnetic circular dichroism (XMCD) and density functional theory (DFT) calculations. STM results indicate that Fe nucleates on the Ge(001) surface, forming well-ordered nanoclusters of uniform size. Depending on the preparation conditions, two types of nanoclusters were observed having either four or sixteen Fe atoms within a nanocluster. The results were confirmed by DFT calculations. Annealing the nanoclusters at 420 K leads to the formation of linear nanocluster arrays, which follow the Ge dimer rows of the substrate, due to cluster mobility at such temperature. The Fe nanoclusters and nanorow structures formed on the Ge(001) surface show a superparamagnetic behaviour as measured by X-ray magnetic circular dichroism.

Secondly, nanoscale writing using oxygen adatoms on the MoO₂/Mo(110) surface is demonstrated by STM. High-temperature oxidation of the Mo(110) surface results in a strained bulk-like MoO₂(010) ultra-thin film with an O-Mo-O tri-layer structure. Due to the lattice mismatch between the Mo(110) and the MoO₂(010), the latter consists of well-ordered molybdenum oxide nanorows separated by 2.5 nm. The MoO₂(010) structure observed by STM is confirmed by DFT calculations. Further oxidation results in perfectly-aligned double rows of oxygen adatoms, imaged by STM as bright protrusions. These adatoms can be controllably removed from the surface by the STM tip. Tip movement along the surface can be used for controlled lithography (or writing) at the nanoscale, with a minimum feature size of just 5 nm. By moving the STM tip in
a controlled fashion, information can be written, read and erased by applying specific biases between the surface and the tip.

Finally, the growth of Fe nanoclusters on the MoO$_2$/Mo(110) surface has been studied by STM and XMCD. STM results indicate that at low coverage Fe atoms self-assemble on the MoO$_2$/Mo(110) into well-separated nanoclusters, which nucleate at equivalent surface sites. Their size, shape, and the observed spatial separation are dictated by the substrate and depend on preparation conditions. Linear Fe nanocluster arrays are formed on the MoO$_2$/Mo(110) surface at room temperature at surfaces coverage greater than 0.5 ML. This is due to the pronounced oxide nanorow pattern present on the MoO$_2$/Mo(110) surface. These nanocluster arrays follow the direction of the oxide rows of the strained surface. The Fe nanoclusters formed on the MoO$_2$/Mo(110) surface show a superparamagnetic behaviour as measured by XMCD.
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1. Introduction

The self-assembly of atoms or molecules into ordered surface-supported nanostructures is one of the key topics in solid state physics, surface science and nanotechnology [1-10]. An understanding of the mechanisms of the controlled growth of such nanostructures is fundamental to progress in existing technologies [1]. One major reason for this attention is the prospect of controlling atomic scale structures on surfaces, which can lead to mass fabrication of usable systems and novel devices.

The applications of nanostructures are many-fold and include catalysis, magnetism, molecular electronics and nanoelectronics, biological applications, photonics and plasmonics, nanomechanics, energy applications, acoustics and lithography [1, 11]. In nanolithography atoms and molecules are manipulated e.g. by a scanning tunneling microscope tip. Atoms or molecules are placed in an ordered fashion on the surface, removed in a distinct way from the surface or added onto specific surface sites [12-15]. This technique can then be exploited to perform lithography on a scale that is difficult to achieve with common techniques like E-beam lithography. The investigation of nanocatalysts on substrates gives an insight into the chemical reactions taking place on an atomic level. Here, reactions of individual catalytically-active structures can be resolved [16-18]. This knowledge can then be used for the directed design of improved catalysts. Another application of nanostructures is in the realm of magnetism. Magnetic materials are deposited on surfaces in order to create magnetic nanoclusters of a specific size, manipulate single spins or to create heterogeneous structures with specific properties [19, 20]. The manipulation of single spins is a promising approach towards spin electronics (spintronics). A
possible application of magnetic nanostructures self-assembled in an ordered fashion on a surface would be the storage of information. The combination of such self-assembled magnetic nanostructures with semiconducting substrates is an interesting prospect for nanoelectronics.

A promising approach towards the control of self-assembly is the use of preformed surface templates onto which particular nanostructures can be arranged in a well-ordered fashion [9, 10, 21, 22]. Surfaces such as the Ge(001)-(2 x 1) reconstructed surface and the MoO₂/Mo(110) surface exhibit well-defined nanorows formed by Ge dimers and Mo oxide, respectively [23–25]. Such surfaces are suitable templates for the growth of well-ordered, uniformly sized metal nanoclusters [10, 25, 26]. The size, shape, and the spacing between clusters are dictated by the substrate and growth conditions, and in turn size and shape effects can dictate the electronic structure of the clusters.

One of the promising functionalities of nanoclusters relates to their magnetic properties. Perhaps the most fundamental aspect in the field of magnetism is the mechanism by which ions, atoms or minute clusters of atoms possessing spin interact with each other. This interaction defines whether the overall system is ferromagnetic, antiferromagnetic, spin glass-like or only weakly magnetic. There are quantum mechanical interactions called exchange interactions stemming e.g. from the Pauli exclusion principle and classical electrodynamics mechanisms e.g. dipole-dipole interaction. Which of the two interactions is more important depends on the size of the clusters, the separation between them and the material occupying the space in between the ions/clusters. While there is a large body of knowledge regarding the nature of magnetic interactions, the number of unanswered questions and controversies in the field is also immense.

Semiconductor surfaces such as the Ge(001)-(2 x 1) reconstructed surface are suitable templates for the growth of well-ordered, uniformly-sized metal nanoclusters [26, 27]. Their size, shape, and the spacing between clusters are dictated by the substrate. Such metal-nanocluster-semiconductor systems can be considered to be examples of low-dimensional dilute magnetic semiconductors (DMS), as the interaction between transi-
1. Introduction

The growth of metal clusters takes place via the semiconducting substrate \[28\]. Furthermore, the layout of clusters on the surface into a regular exposed system allows for good control of the separation between clusters, which cannot be achieved in most three-dimensional DMS systems. DMS are promising materials for use in many technological applications and their study is important for future developments in nanotechnology as well as from the fundamental point of view. Such systems have attracted much attention recently since they can be utilised as essential building blocks in the field of spin-dependent electronic (spintronic) devices, providing a link between magnetism and semiconductor technologies \[29-32\]. The incorporation of ferromagnetic elements into semiconductor devices may lead to data processing and magnetic storage on a single chip. One of the most suitable host semiconductor materials for developing DMS is the group IV semiconductor germanium (band gap = 0.62 eV at 300 K \[33\]), that can be readily doped with magnetic elements \[30, 34-37\]. It was shown that germanium crystals doped with Cr and Fe exhibit ferromagnetic behaviour at 126 K and 233 K, respectively \[36, 38\], provided the concentration of dopants is high enough. Furthermore, the possibility of using ferromagnetic metals as a source of spin polarised electrons for injection into semiconductors has led to strong interest in the growth of ferromagnetic layers on Ge \[39-43\].

The complexity of the issue may be illustrated by looking at two examples. The first example is that of dilute magnetic semiconductors (DMS). It is hoped that dilute magnetic semiconductors will become an essential building block in the field of spintronic devices and the link allowing integration of magnetism and semiconductor technologies. The field is somewhat controversial. There are high profile publications suggesting that the addition of a small proportion of magnetic atoms into some semiconductors turns them into ferromagnets with a high Curie temperature \[44\]. This is both surprising and counter-intuitive because the exchange interaction between distant ions should not be large. Such a strong exchange interaction is the common pre-requisite for a high Curie temperature.

There are counter arguments suggesting that the high Curie temperature is the result
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of the formation of clusters that precipitate in the lattice of the semiconductor material. For example some authors believe that it is likely that a fraction of the recent reports on high Curie temperature in DMS and dilute magnetic oxides (DMO) represent magnetic impurity clusters [45]. It was proposed that the high Curie temperatures observed in some DMS or oxides doped with magnetic impurities is not an artefact but rather the result of meta-stable phases [46]. In some other semiconductor materials it is accepted beyond doubt that additions of small concentrations of magnetic impurities lead to ferromagnetism with a considerable Curie temperature. Notable among them is Mn-doped GaAs [34]. Many other recent materials include Mn-doped GaN, Cr-doped ZnTe, Mn-doped ZnO, Mn-doped Ge, Co-doped SnO₂ and TiO₂, Mn-doped ZnGeP₂, Mn-doped InAs. The reported magnetic doping elements include virtually all the transition metals: Mn, Cr, V, Fe and Ni etc. The semiconductors from which DMS were formed also include Si and Ge. A topical review report on the experimental status in the field of DMS can be found in Prellier et al. [47]. It is well accepted that the key point defining the magnetic properties is not just the concentration of the magnetic doping atoms but also how they are located in the lattice (interstitially or replacing the host atoms, the degree of order in their location, etc.).

Nanostructured surfaces can be also used for the controlled lithography at nanoscale. Looking back a few hundred years, Johannes Gutenberg's system of movable type brought the written word to the masses in the 15th century and changed the world. It catalysed the Renaissance and the scientific revolution, and has led to many aspects of the modern world that are now taken for granted. Lithography techniques have undoubtedly come a long way since Gutenberg's time, but their importance to society is arguably no less monumental. Modern techniques, such as electron beam, ion beam and photo-lithography can produce feature sizes down to hundreds or tens of nanometers. This allows more complex and sophisticated integrated circuit architectures than ever before, however even these techniques have fundamental limits to their resolution. It is for this reason that the direct manipulation of atomic structures will likely be the next
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step in the evolution of lithography. Soon after the invention of the scanning tunneling microscope (STM) in 1981 [48], researchers began using the unprecedented precision of the STM tip to deform atomically-flat samples [49, 50]. These first attempts at nanoscale lithography were quite crude, involving mechanical and thermal deformation of the substrate, however they have inspired many more sophisticated approaches to this problem. Lithography on the nanoscale can be performed in one of three modes, modification of the substrate, for example by resist exposure or oxidation [51, 52]; material deposition [53, 54]; or material removal or etching [55, 56]. The oxidation of metal surfaces can produce a variety of ordered oxide nanostructures and two-dimensional surface oxides, which are of great significance for heterogeneous catalysis. In this work a novel lithography system is described, in which an STM tip is used to remove single oxygen adatoms from the oxidised molybdenum surface. The minimum feature size of this technique is 5 nm, which is a fundamental constraint due to the average distance between two adatoms, dictated by the substrate. Such fine resolution is an order of magnitude improvement over even the most cutting-edge electron beam techniques, and represents an interesting avenue for the development of new procedures for future technologies.

Another application for nanostructured surfaces is in the field of catalysis. Traditional catalytic systems make use of complex and heterogeneous materials; however, by control- lably growing functional nanoparticles and nanoclusters on single-crystalline substrates, the effect of size and shape on catalytic activity can be tested in a systematic manner. In addition, by using highly localised techniques, such as scanning tunneling microscopy (STM) and density functional theory calculations (DFT), the effects of edges, kinks, atomic vacancies and other defects known to be vital for catalysis can be probed.

Recently, STM and DFT have been combined to describe the model Co-Mo-S surface-supported nanoparticle system, which is important for the industrially-significant hy- drodesulphurisation process, and have shown that the size and shape of the nanoparticles very strongly affect their reactivity properties [57]. Iron-based catalysts are used in many catalytic systems such as the splitting of the N\textsubscript{2} triple bond utilised in the Haber process.
and the partial oxidation of methanol for the production of formaldehyde. The efficiency of such mixed-phase reactions depends on the surface area of the catalyst available for the adsorption of reagents, thus nanoclusters of functional materials evenly distributed over a surface represent some of the highest surface area-to-mass ratios possible.

Although such processes have been used industrially for decades, the exact catalytic mechanisms involved are largely unknown. With the advent of STM however, it has become possible to observe individual nanoclusters before and after the adsorption of gas-phase molecules and to explore the effect of edge states, nanoparticle size and defects on catalytic activity. It is therefore paramount to understand the growth behaviour of such nanoparticles and to be able to control the size, morphology and distribution of these active sites in order for large-scale optimisation to be performed.

In this thesis, the nucleation of Fe on the Ge(001) surface at room temperature was studied (Chapter 4). A brief introduction to the Ge(001) surface and its different terminations are presented in Sections 4.1 and 4.2, respectively. The types of Fe clusters formed on the surface and the influence of the clusters on the Ge substrate are discussed in Section 4.4. Density functional theory calculations of Fe nanoclusters on the Ge(001) surface have been performed in order to get a better understanding of the actual Fe nanocluster size and their nucleation site. The results of these calculations are laid out in Section 4.5. Magnetic measurements have been conducted to discern the magnetisation properties of the Fe nanoclusters. The results and difficulties which occurred during magnetic measurements are presented in Section 4.6.

Another surface which is suitable for self-assembly as well as for lithography is the oxidised Mo(110) surface (Chapter 5). In Section 5.1, a summary of molybdenum, the molybdenum (110) surface and an ultra-thin film of MoO$_2$ on the Mo(110) surface is given. In section 5.2 experimental results and a model for the MoO$_2$ surface oxide structure formed on Mo(110) are shown. Slightly changing the oxidation parameters leads to the formation of oxygen adatoms on the MoO$_2$/Mo(110) surface. Section 5.3 shows how the MoO$_{2+x}$/Mo(110) surface can be used for lithography. Here, an STM tip is used to
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remove single oxygen adatoms from the oxidised molybdenum surface. The nucleation of Fe on the oxidised Mo(110) surface and the MoO$_2$/Mo(110) exhibiting oxygen adatoms are discussed in Section 5.5.

The conclusion and future work are laid out in Chapter 6.
2. Experimental techniques

2.1. Auger electron spectroscopy

2.1.1. The Auger effect

The Auger effect, named after Pierre Auger [58–60], is a non-radiative transition of an electron in the electron shell of an atom. It is an alternative process to X-ray emission in filling a hole in a more strongly bound electron shell. This effect was already described by Lise Meitner in 1922 in a less publicised work [61]. Since both have described the effect independently, the effect is in some recent publications known as Auger-Meitner-effect.

A relatively tightly bound electron is removed from the atomic shell (ionisation) when it receives sufficient energy from a photon or electron. This vacancy is then, due to its low-energy position, filled by an electron from a higher energy level. The free energy does not necessarily need to be dissipated by emission of a photon (e.g. as a characteristic X-rays), but can also be transferred to another electron which then leaves the atom as a so called “Auger electron”.

The energy of the emitted Auger electron is dependent on the energy levels of the particular atom. It results from the energy level of the initially unoccupied state, the initial state of the electron that fills the unoccupied state, and the initial state of the Auger electron. For that reason, the possible transitions are named after the electrons involved. For example, an electron in the K-shell is removed, the vacant space is filled by an electron of the L-shell and an electron is emitted from the M-shell (see Fig. 2.1), then this electron is known as the $KLM$ Auger electron. This electron is emitted with
2. Experimental techniques

(a) Electron collision

(b) Auger electron emission

Figure 2.1.: Schematic of the Auger process.
2. Experimental techniques

a kinetic energy \( E_{KLM} \), equal to the energy difference between the three levels involved minus the sample work function \( \phi \), as indicated in equation 2.1.

\[
E_{KLM} = E_K - E_L - E_M - \phi
\]  
(2.1)

What actually happens within the atom can be imagined in such a way that although an X-ray photon is emitted, it is immediately absorbed again within the same atom, which then leads to the emission of Auger electron. However, this is only a conceptual model as the Auger effect is a non-radiative process, and therefore the selection rules in the transitions do not need to be considered.

The number of the emitted Auger electrons depends on the atomic number \( Z \) of the examined element. Auger electrons are mainly emitted from very light elements, and with increasing atomic number, mainly X-rays are emitted, so that the chemical analysis by Auger emission spectroscopy (AES) is limited to lighter elements. A special case of the Auger process is the so-called Coster-Kronig transition, e.g., \( L_1L_2M \). Here, the hole created in a higher subshell will be filled by an electron in the same shell. If the emitted Auger electron is also from the same shell, then this process is called a super-Coster-Kronig transition, e.g., \( L_1L_2L_3 \). The Coster-Kronig process was named after the two physicists Dirk Coster and Ralph Kronig [62].

2.1.2. Auger electron spectroscopy

The Auger electron spectroscopy is a very surface sensitive analytical technique due to the short mean free path of electrons in the relevant energy range (about 50 eV to 3 keV). It is used to measure the chemical composition of the surface of a conducting or semi-conducting sample [63, 64]. The measured surface thickness typically comprises only the top ten atomic layers. The Auger process can therefore be very efficiently used to detect contaminants with a high spatial resolution (0.01 µm to 100 µm). If, however, the contaminate free material is to be measured and not impurities inadvertently added during
sample preparation, these impurities need to be removed by, for example, sputtering with argon ions.

An Auger electron spectroscope can also measure images of a type similar to images recorded by a scanning electron microscope (SEM). Here, a secondary electron detector is necessary to convert the secondary electrons into an SEM image. In this way a resolution similar to the one of an "ordinary" SEM can be achieved. This function can be extended by also using the AES detector for imaging. In this way images can be recorded that exhibit element specific information. The process is called scanning Auger electron microscopy (SAM). The detection limit of this method is approximately 0.01 at% to 0.1 at%. It is only possible to evaluate AES peaks starting from this limit. In photoelectron spectroscopy Auger electrons occur as well. The peaks caused by the Auger effect differ from the "photopeaks" in that their energy is independent of the incident ultraviolet- or X-ray light.

A special case of the Auger process occurs in low energy ion scattering. Here, the Auger transition does not take place within the same atom. Instead an unoccupied atomic level caused by the external excitation is filled by an electron from the conduction band of the sample and the Auger electron is then also emitted from the conduction band [65].

2.1.3. Auger electron spectroscopy set-up

The Auger analyser is a cylindrical mirror analyser (CMA, model 10-155A Physical Electronics [66]). A schematic of the Auger analyser is presented in Fig. 2.2. The primary electron beam is generated from a hot filament source, and accelerated through a potential $V_2$. The beam current can be varied by changing the extraction potential $V_1$. The electron gun is within two concentric cylinders. The inner cylinder is grounded, while a deflecting potential is applied to the outer cylinder. The deflecting potential is chosen such that only electrons of a particular energy will pass through the exit aperture. The analyser current is given by the number of electrons that pass through this aperture.
2. **Experimental techniques**

**Figure 2.2.** Schematic of the cylindrical mirror Auger analyser.

Between the exit aperture and the collector, an electron multiplier is used to amplify the analyser current. Primary electrons of known energy, which are reflected from the sample surface, are used to optimise the signal intensity to find the analysed spot and calibrate the analyser. A full description of the operation of the Auger analyser can be found in [67]. A beam of energy of 3 keV was used for all measurements. The filament and emission currents were 3.2 A and 0.4 mA respectively, giving a target current of \( \sim 8 \mu A \). A SR 850 DSP lock-in amplifier from Stanford Research Systems [68] was used to output a \( 0.5 V_{rms} \) sinusoidal signal of frequency 12 kHz to modulate the deflecting voltage applied to the outer cylinder. A lock-in sensitivity of 100 \( \mu V \) was then used to detect the Auger signal. The scan was always set to 1 eV s\(^{-1}\). There is little information about the chemical bonding of the species, since the electrons being characterised are related to the core electrons and not the valence electrons. For instance, the chemical shifts involved with the Mo M\(_{4.5}\)V V Auger transition at 221 eV shift the peak ((2–3) eV) to a slightly higher energy with the formation of Mo\(^{4+}\) and Mo\(^{6+}\) oxidation states [69].
2. Experimental techniques

Shifts of this amount are undetectable with the experimental set-up being used.

2.2. Low energy electron diffraction

Low energy electron diffraction (LEED) is a method for the study of atoms on surfaces. It is one of the principal techniques for the determination of the surface structure of solids [70]. Here, the interference of waves which leads to the formation of a diffraction pattern is being exploited. This diffraction pattern is then made visible on a screen. In detail, a conducting sample with a well-ordered crystalline surface structure is exposed to a monochromatic beam of low energy electrons ((\(\approx 20-200\)) eV) normal to the surface. According to the de Broglie relation

\[
\lambda = \frac{h}{\sqrt{2m_eE}}
\]

where \(\lambda\) is the de Broglie wavelength, \(E\) the energy of the electron and \(m_e\) its mass, this corresponds to wavelengths in the range of 0.5 Å to 5 Å. This range is of the same order of magnitude as the lattice spacing of atoms in a crystal. The surface sensitivity of the measurement methods is due to the low penetration depth of the low energy electrons, which lies in the range of 0.5 nm to 1 nm. UHV conditions are crucial for the investigation of surfaces by LEED so that the sample surface remains free from impurities during the measurement. Furthermore, inelastic interactions of the diffracted electrons with gas molecules are avoided in a UHV environment.

A schematic view of the LEED set-up is shown in Fig. 2.3. Electrons are being emitted from a hot filament and accelerated by an anode in the direction of sample. Here, the electron beam is focused by an electrostatic lens system. For certain energies, the impinging electrons are then back-scattered by the Bragg planes of the crystal. Since the electrons are charged particles, they will be scattered by regions of high localised electron density, i.e. the surface atoms, by electrostatic Coulomb forces. Therefore, the surface
2. Experimental techniques

Figure 2.3.: Left: Schematic view of the LEED set-up. Emitted electrons are being accelerated and focused. After being diffracted from the sample surface, the electrons are filtered and then accelerated towards a fluorescent screen. Right: Schematic of the Ewald sphere construction of a diffraction pattern. A sphere with radius $1/\lambda$ is drawn through the origin of the reciprocal lattice. For each reciprocal lattice point that is located on the Ewald sphere of reflection, the Bragg condition is satisfied and diffraction occurs.
2. Experimental techniques

Atoms can be considered to act as point scatterers. By the principle of wave-particle duality, the beam of electrons may be equally regarded as a succession of electron waves incident normal to the sample. After the dispersion of the electrons in the sample, these are once more accelerated in the direction of the fluorescent screen. Before the electrons hit the screen they pass through a number of energy-filtering grids on which an opposing field is applied. This serves to filter out any inelastically scattered electrons. The screen is illuminated at the positions of the incoming electrons, making the diffraction pattern visible. Ideally this pattern consists of bright spots of light which are arranged symmetrically. From this symmetry, the symmetry of the crystal surface can be calculated. In relation to scanning tunneling microscopy it is pointed out that LEED shows the reciprocal lattice. This information can also be obtained from Fourier transformed STM images. Thus, STM and LEED measurements can compliment each other and help to confirm the measured results.

In the simplest kinematic example, a diffraction pattern is formed analogous to that of a diffraction grating. Only single scattering from the surface is considered in this example. This allows us to describe the shape and size of the surface unit cell, but it does not give information about the atomic arrangement inside the unit cell. Considering the atoms as point particles, the incident plane wave will be scattered in all directions. For an ordered crystal surface, interference will restrict the net flux to those directions where the scattered waves are in phase. This condition is met only when the scattered waves from neighbouring unit cells differ by an integral number of wavelengths \( \lambda \). For the simple case of a 1D lattice, this in-phase condition for constructive interference is illustrated in Fig. 2.4, where the incoming beam is normal to the sample. Therefore, the positions at which diffraction spots occur is defined by the Bragg equation.

\[
n\lambda = d\sin \theta \quad (2.3)
\]

The LEED pattern consists of spots, in agreement with Bragg’s law, that appear on
2. Experimental techniques

Figure 2.1.: Schematic of the Bragg condition for a 1D lattice. Only in the case of constructive interference between the scattered rays is it possible to detect a diffracted beam.

the screen giving an image of the reciprocal lattice of the surface. The real space lattice parameter $\vec{a}$ is related to the reciprocal space lattice parameter $\vec{a}^*$ by $\vec{a}^* = \frac{1}{\vec{a}}$.

For surface diffraction to occur in a 2D system, with translational vectors $\vec{h}$ and $\vec{l}$, the incoming electron beam must conserve both its energy and the component of its momentum parallel to the surface:

$$\vec{k}_\parallel^2 + k_\perp^2 = k'^2 + k'^2 \quad , \quad k'^\parallel = k_\parallel + \vec{g}_{hl}$$

(2.4)

where $\vec{k}_\parallel$ and $k_\perp$ are the parallel and perpendicular momentum components of the incident beam, respectively; while $k'^\parallel$ and $k'^\perp$ are those of the diffracted beam. The reciprocal lattice vector, now labelled $\vec{g}_{hl}$, is related to the beam energy $E_{eV}$, the electron mass $m_e$, and the diffraction angle $\theta$ by:

$$|\vec{g}_{hl}| = |h\vec{a}^* + l\vec{b}^*| = |\vec{k}'| \cdot \sin \theta = \frac{\sqrt{2m_eE_{eV}}}{h} \cdot \sin \theta$$

(2.5)

where $\vec{a}^*$ and $\vec{b}^*$ are the reciprocal lattice primitive net vectors. In three dimensions these
are related to the real space vector $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ by

$$\mathbf{a}^* = \frac{2\pi}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \mathbf{b} \times \mathbf{c} = \frac{2\pi}{\mathbf{c} \cdot \mathbf{a} \times \mathbf{b}} \mathbf{c} \times \mathbf{a} = \frac{2\pi}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \mathbf{a} \times \mathbf{b} = 2\pi \mathbf{a}^* \mathbf{b}^* \mathbf{c}^* (2.6)$$

Using column vector representation of (reciprocal) primitive vectors, the formulae above can be rewritten using matrix inversion:

$$\begin{bmatrix} \mathbf{a}^* & \mathbf{b}^* & \mathbf{c}^* \end{bmatrix}^T = 2\pi \begin{bmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{bmatrix}^{-1} (2.7)$$

In two dimensions, these relations become [70]

$$\mathbf{a}^* \cdot \mathbf{a}^* = \mathbf{b}^* \cdot \mathbf{b}^* = 2\pi \mathbf{a} \cdot \mathbf{b} = \mathbf{b} \cdot \mathbf{a} = 0 (2.8)$$

This shows the direct correspondence between the observed diffraction pattern and the reciprocal lattice of the surface. The reciprocal lattice vector $g_{hkl}$ lies in a direction that is orthogonal to the plane of the real space lattice which is denoted by the Miller indices $h$ and $l$. The Miller indices of the diffracting planes are used to index the diffraction spots of the LEED pattern.

The diffraction pattern can easily be described graphically in reciprocal space by the construction of the Ewald sphere (Fig. 2.3). A sphere with radius $1/\lambda$ is drawn through the origin of the reciprocal lattice. For each reciprocal lattice point that is located on the Ewald sphere of reflection, the Bragg condition is satisfied and diffraction occurs.

In general for LEED experiments, the incoming beam is normal to the sample. This means that $\mathbf{k}_0 = 0$ for the incident electrons. Therefore, the observed diffraction pattern will be an image of the reciprocal lattice of the surface. LEED patterns of surfaces are taken at the energy range between (20-200) eV. In this energy range, the de Broglie wavelength of the incident electrons is of the same order of magnitude as the inter-atomic distances of the crystal. The electron mean free path is ($\sim$ 5-10) Å, resulting in a technique that is sensitive only to the surface layers.
2. Experimental techniques

The observation of a LEED pattern does not guarantee that the whole surface is ordered. There is an instrumental limit to the diameter of the coherently scattering area on the surface called the coherence length. The significance is that interference will be strong within a coherent length of the source, but not beyond it. The coherence of an e-beam is limited by $\delta E$ and the beam divergence. The spatial coherent length of a standard LEED optics is only (10–20) nm. Therefore, features and domains larger than the coherence length of the LEED optics will not result in a diffraction pattern.

Further information regarding crystal lattice structure may be obtained by both the position and the intensity of the spots. The position of the spots yields information on the size, symmetry and rotational alignment of the surface layers with respect to the symmetry of the bulk crystal. The intensities of the various diffracted beams, which can be recorded as a function of the incident electron beam energy, generate so-called $I-V$ curves. By comparison with theoretical curves, the $I-V$ curves may provide accurate information on atomic positions. While this is an extremely powerful technique, unfortunately we do not have the experimental set-up to perform such measurements. Therefore, all of the LEED descriptions in this thesis are restricted to the simple kinematic approach.

2.3. Scanning tunneling microscopy

The scanning tunneling microscope (STM) invented by Binning and Rohrer in 1981 [48], is without doubt, the most important instrument developed in surface science in recent years. The possibility to image the atomic structure of conducting and semiconducting materials has revolutionised the field, enabling the study of the properties of material surfaces in direct space. In reality, the technique probes the electronic structure of the atoms at the surface and topographic information is derived from that. STMs are based on the principle of quantum mechanical tunneling.
2. Experimental techniques

2.3.1. Theory of the tunneling effect

The principle behind the operation of a STM is the quantum tunneling effect. To understand this effect, consider an electron with energy \( E \) moving in a potential \( U(z) \). In classical mechanics, it is described by the equation [71, 72]:

\[
\frac{p_z^2}{2m} + U(z) = E
\]  (2.9)

where \( m \) is the mass of the electron and \( p \) its momentum. In quantum mechanics, the state of the same electron is described by the equation:

\[
\frac{-\hbar^2}{2m} \frac{d^2}{dz^2} \psi(z) + U(z)\psi(z) = E\psi(z)
\]  (2.10)

In the classical case, it is possible to distinguish 2 situations: (i) The allowed region, where \( E > U(z) \) and the electron has a nonzero momentum \( p_z \) and (ii) the forbidden region, with \( E < U(z) \) which the electron cannot penetrate. In the quantum mechanics case in the region where \( E > U(z) \), equation 2.10 has solutions:

\[
\psi(z) = \psi(0)e^{\pm ikz}
\]  (2.11)

where \( k \) is the wave vector and is equal to \( k = \sqrt{2m(E-U)}/\hbar \). In the region where \( E < U(z) \), i.e. the tunneling region, the equation 2.10 has the solution:

\[
\psi(z) = \psi(0)e^{-\kappa z}
\]  (2.12)

where \( \kappa \) is a decay constant and is equal to: \( \kappa = \sqrt{2m(U-E)}/\hbar \).

The probability density of finding an electron near a point \(+z\) is proportional to \( |\psi(0)|^2e^{-2\kappa z} \), which has a nonzero value in the barrier region and thus a nonzero probability to penetrate the barrier. An analogous solution describes an electron state in the \(-z\) direction \( \psi(z) = \psi(0)e^{\kappa z} \).
2. Experimental techniques

This simple model explains some basic features of the one-dimensional metal-vacuum-metal tunneling effect (a more detailed treatment can be found in [73]), shown in Fig. 2.5. Now consider a metal surface and a sharp metal tip placed within a few angstroms of it.

(a) Sample  
(b) Tip


Figure 2.5.: a) Tip ($\rho_T$) and sample ($\rho_S$) density of states with an applied bias voltage ($eV$). A bias voltage is necessary to have a net tunneling current $I_t$. Instead of solving the Schrödinger equation for the coupled tip-sample system, Bardeen used the approach of perturbation theory. By using two subsystems, b) and c), $I_t$ is calculated through the overlap of $\psi$ and $\chi$ of the free systems using Fermi’s golden rule. [71]

The work function $\phi$ of the metal surface is the minimum energy required to remove an electron from the sample/tip to the vacuum level and the Fermi level $E_F$ is the upper limit of the occupied states in the metal if thermal excitation is neglected. If the vacuum level is considered as the reference point of energy, then $E_F = -\phi$. Considering the simple case in which the work functions of the sample and tip are equal, an electron can tunnel between them. Nevertheless, a bias voltage $V_b$ is necessary to have a net tunneling current $I_t$. Applying $V_b$ to the tip, a sample state $\psi_n$ with energy $E_n$ lying between $E_F - eV_b$ and $E_F$, has a probability to tunnel into the tip. Assuming that $eV_b \ll \phi$ the energy level of all the sample states of interest are very close to the Fermi
level, $E_n \approx -\phi$. The probability $w$ to find an electron at the tip surface $z = W$, is given by:

$$w \propto |\psi_n(0)|^2 e^{-2\kappa W}$$  \hspace{1cm} (2.13)

where the decay constant $\kappa$ is now given by $\kappa = \sqrt{2m\phi}/h$. The states on the sample surface within the energy interval given by $\epsilon V_b$ are responsible for the tunnel current $I_t$ and determine $I_t$ as follows:

$$I_t \propto \sum_{E_n=E_F-\epsilon V_b}^{E_F} |\psi_n(0)|^2 e^{-2\kappa W}$$  \hspace{1cm} (2.14)

For small $V_b$, the sum in equation 2.14 can be written using the local density of states (LDOS) at the Fermi level. At a location $z$, the LDOS $\rho_S(z, E)$ of the sample is defined as $\rho_S(z, E) \equiv \frac{1}{\epsilon} \sum_{E_F-\epsilon}^{E_F} |\psi_n(z)|^2$ for a sufficiently small $\epsilon$. The value of the LDOS near the Fermi level is an indicator of whether the surface is metallic or not. The $I_t$ can be conveniently written in terms of the LDOS of the sample:

$$I_t \propto V_b \rho_S(0, E_F) e^{-2\kappa W}$$  \hspace{1cm} (2.15)

The dependence of the logarithm of $I_t$ with respect to distance $W$ is a measure of the work function $\phi$, or the tunneling barrier height. It is also clear that the $I_t$ is very sensitive to small variations in the distance between tip and sample.

2.3.2. The scanning tunneling microscope

An atomically sharp metal tip is brought to within 1 nm of the surface of a conducting or semiconducting sample. A voltage is applied across the two electrodes, tunneling is established and a tunneling current is detected. As demonstrated above, the tunneling current $I_t$ can be expressed by Eq. 2.15. In reality, the tunneling current is also dependent on the LDOS of the tunneling tip. The significance of the tip contribution can be accounted for through a time-dependent perturbation model of metal-insulator-metal.
2. Experimental techniques

tunneling, proposed by Bardeen [74]. In this approach a transfer Hamiltonian $H_T$ is used to describe the tunneling of an electron, from a sample state $\psi$, to a tip state $\chi$ (see also Fig. 2.5. The tunnel current is a convolution of the sample LDOS $\rho_S$ and the tip LDOS $\rho_T$.

$$I_t = \frac{4\pi e}{h} \int _0 ^{eV} \rho_S(E_F - eV + E)\rho_T(E_F - E)|M|^2dE$$

(2.16)

The tunneling current $I_t$ also includes a tunneling matrix element $M$, which describes the amplitude of electron transfer across the tunneling barrier, as a function of the overlap between sample states ($\psi$) and tip states ($\chi$).

$$M = \frac{\hbar}{2m} \int (\chi \frac{\partial \psi}{\partial z} - \psi \frac{\partial \chi^*}{\partial z})dS$$

(2.17)

It is determined by a surface integral over the medium separating the two electrodes. If $M$ is constant over the voltage range probed, the tunnel current is determined by a convolution of the LDOS of the two electrodes, the tip and the sample.

Once tunneling is established, the tip is scanned mechanically across the surface. There are two basic modes for the scanning process, namely, constant current or constant height. The most commonly used mode is the constant current mode. In this case, the tunneling current is kept constant in the range from a few pA to (1-2) nA, by a feedback control unit that changes the tip-sample separation in response to a change in the tunneling current. However, in the constant height mode, the barrier height is kept constant and the tunneling current recorded as a function of the tip position. In this thesis, the STM was operated in the constant current mode for all the measurements performed.

2.4. STM tips

Atomically sharp and stable tips are crucial to achieve an STM image resolution at the atomic scale. Tungsten is an ideal material for this and is the most widely used material
for tip preparation. Tungsten is relatively hard, making it a stable probe material and it can be electrochemically etched, allowing the preparation of atomically sharp tips [72].

STM images in this thesis were obtained with W tips, which were prepared using a chemical etching procedure described in detail elsewhere [75].

W tips are prepared from 0.25 mm thick wire. The wire is cut into small rods and a small insulating PTFE tube is placed on the end of the rod. The rod is then clamped into a modified micrometer screw, which allows precise positioning of the rod in a beaker of 2.0 mol NaOH solution. The W wire acts as the anode while a submerged metal foil acts as the cathode. Under an applied 4 V DC bias, chemical etching occurs at the air/electrolyte interface. The W oxidises to form soluble WO$_3^{2-}$, which flows away from
the active etching region. This leads to a stretching of the wire at the interface region and eventually the submerged section of the wire falls off under its own weight.

During the etching process, the PTFE acts to physically restrict the active region [76] and also protects the tip that falls into the beaker. This tip etching set-up is shown in Fig. 2.6. The tips are then rinsed with propan-2-ol, placed in tip holders and inserted into UHV. The tips are then etched with Ar\(^+\) ions to remove the WO\(^4^-\) present from the chemical etching process. This process produces stable, atomically sharp tips.

In appendix A the advantages of single crystalline W[001] tips will be presented. Single crystalline W[001] tips have mainly been used for STM measurements of the MoO\(_2\)/Mo(110) surface.
2. Experimental techniques

2.5. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is an umbrella term for several widely-used X-ray spectroscopic measurement techniques: The near edge XAS (often abbreviated as XANES for X-ray absorption near edge structure or NEXAFS for near edge X-ray absorption fine structure) provides information on unoccupied electron states (orbitals) for the chemical element under study and thus the chemical composition of the sample to be tested. A sub-group is the near edge XAS with circularly polarised X-rays. This technique uses X-ray dichroism and is used to study the magnetisation of a sample.

If an X-ray photon enters a solid it can be absorbed and in this absorption process a core electron is excited to an empty state. If the energy of the X-ray photon is much larger than the binding energy of the core state the excited electron behaves like a “free” electron in the solid. However, if the X-ray energy is just enough to excite a core electron it will occupy the lowest available empty state. If the X-ray energy is too small to reach an empty state no excitation can occur.

Figure 2.7.: Schematic view of X-ray absorption (left) and X-ray absorption coefficient as a function of incident photon energy (right).

XAS [77–79] measures the absorption of X-rays as a function of X-ray energy $E = h\nu$. The ratio of the X-ray intensity before and after interacting with the sample is measured and the absorption determined. This transmission measurement is the simplest method, however, it requires that the sample is thin enough so that X-rays can pass through it. At low X-ray energies (e.g. absorption edges of carbon, nitrogen or oxygen), the sam-
2. Experimental techniques

Samples would have to be extremely thin (in the range of a micrometer). For transmission measurements both the bulk of the sample as well as its surface contribute to the absorption; however, the contribution of the surface is much weaker than that of the bulk, and therefore can not be determined separately. Fig. 2.7 (left) represents the schematic view of X-ray absorption in transmission. After the X-ray has traversed a distance $x$ into the slab of absorbing material, the intensity of the incoming X-ray beam $I_0$ has been reduced to

$$I = I_0 \exp(-\mu x),$$

(2.18)

where $\mu$ is the definition of the absorption coefficient. More specifically, the X-ray absorption coefficient $\mu(E) = -d\ln I/dx$ is determined from the decay in the X-ray beam intensity $I$ with distance $x$. If the absorption coefficient is plotted as a function of $E$ (Fig. 2.7, right), the experimental data show three general features: (i) an overall decrease in X-ray absorption with increasing energy; (ii) the presence of a sharp rise at certain energies called edges, which roughly resembles step-function increases in the absorption; and (iii) above the edges, a series of oscillatory structure that modulate the absorption, typically by a few percent of the overall absorption cross section. The first feature is illustrative of the well-understood quantum-mechanical phenomenon of X-ray absorption by atoms, as described, for example, by Fermi's Golden Rule (e.g., [80]). The energy position of the second feature is unique to a given absorption atom and reflects the excitation energy of inner-shell electrons. The energy region close to the absorption edge (about 30 eV extension) is called XANES. Fig. 2.8 shows the transitions that contribute to the XAS edges and an example Fe 2p X-ray absorption spectrum.

Another way of measuring X-ray absorption spectra is to detect the total electron yield. The excitation of an electron leaves behind a vacant state which is filled again within an extremely short period of time (few femtoseconds or less) by an electron of higher energy. The gain in potential energy is typically associated with the excitation of another electron (see Auger process). The number of Auger electrons, the Auger electron
2. Experimental techniques

Transitions that contribute to XAS edges

Example Fe 2p absorption spectrum

Figure 2.8.: Transitions that contribute to XAS edges (left). Example Fe 2p X-ray absorption spectrum (right) [81].
2. Experimental techniques

yield, is therefore proportional to the number of electrons initially excited by the X-rays, the total electron yield, and therefore a measure of the absorption coefficient. In this work only the total electron yield was measured.

Another possible process for the filling of an unoccupied state is the emission of an X-ray photon (fluorescence photon). This process has in the soft X-ray regime a much lower probability (typically in the tenth of a percent), as the Auger process. However, since electrons are limited by their mean free path within a sample, fluorescence X-rays can pass through a thicker layer than electrons. This way a larger part of the sample is detected and the disadvantage of lower intensity partially compensated. The proportion of the immediate surface of the measuring signal is thus reduced, which is advantageous if one is interested in the spectroscopy of the bulk of the sample and the contributions of interfering surface impurities are to be reduced.
2. Experimental techniques

2.6. X-ray magnetic circular dichroism

X-ray magnetic circular dichroism (XMCD) is an umbrella term for a number of X-ray spectroscopic effects based on the coupling of (X-ray) photons with specific electron orbitals. The concepts of XMCD spectroscopy are presented in Fig. 2.9. In XMCD the absorption of X-rays by an atom with a magnetic moment is dependent on whether the X-ray radiation is left or right circularly polarised. Relevant is the difference spectrum of two XAS spectra taken in a magnetic field, one taken with left circularly polarised light, and one with right circularly polarised light. When recording a polarised absorption spectrum the direction of magnetisation and the helicity of the X-ray photons is to be aligned parallel and anti-parallel. The resulting absorption spectra are subtracted from each other. From the difference, by applying the so-called “sum rules”, direct information about the element-specific spin moment and the spin-orbital moment of the valence band can be obtained. Typically XMCD studies magnetic transition metals such as iron, cobalt, and nickel and their alloys or compounds. Recently, also metal complexes are being studied by XMCD. In XMCD, XAS spectra are measured at the $2p$ absorption edge. Hereby transitions into the $3d$ shell occur, which may be strongly magnetic, hence dependent on the magnetic field.
2. Experimental techniques

Figure 2.9.: Electronic transitions in conventional L-edge X-ray absorption (a), and X-ray magnetic circular dichroism (b, c), illustrated in a one-electron model. The transitions occur from the spin-orbit split 2p core shell to empty conduction band states. In conventional X-ray absorption the total transition intensity of the two peaks is proportional to the number of $d$ holes. By use of circularly polarised X-rays the spin moment (b) and orbital moment (c) can be determined from linear combinations of the dichroic difference intensities $A$ and $B$ [82].
3. Density functional theory

In this thesis, density functional theory (DFT) calculations are employed to aid the interpretation of experimental results. This chapter gives a short introduction to the theoretical background of density functional and pseudopotential theory, as well as describing details specific to the Vienna Ab-initio Simulation Package (VASP) used to generate the results in this thesis [83]. For a more in-depth derivation and historical background the reader is referred to the vast amount of literature which exists on these topics. VASP is an ab-initio quantum-mechanical molecular dynamics (MD) software package that uses pseudopotentials and a plane wave basis set to calculate an electronic ground state. Although the description in this chapter is based on VASP, the concepts are in general universal to all DFT codes [83, 84]. First the Born-Oppenheimer approximation and Bloch’s theorem are introduced. Then the basics of density functional theory leading to the Kohn-Sham (KS) equations are described. The approximations for the exchange-correlation (XC) energy that must be made in order to solve the KS equations are discussed next. Pseudopotential theory is used as a way to minimise the number of wavefunctions necessary to describe all the features of a valence electron moving through a solid. In the final section, an introduction to molecular dynamics based on the calculation of the Hellman-Feynman forces is given. Here, equations of motion are derived, which determine the relaxation of the ions in the supercell towards a minimum energy configuration.
3. Density functional theory

3.1. Born-Oppenheimer approximation and Bloch’s theorem

It is necessary to know the particle density in order to study a system of interacting electrons and nuclei. For this reason the construction of a suitable many-body wavefunction for the particular system is required. In principle, this wavefunction is a function of time and all nuclear and electronic coordinates. However, a certain approximation can be made to simplify the system.

Since nuclei are typically about 2000 times heavier than electrons, the electronic and nuclear motion can be decoupled by approximating that the electrons respond instantaneously to any change in nuclear coordinates. This approximation then allows one to rewrite the full many-body wavefunction as the product of a nuclear and an electronic wavefunction. The electronic wavefunction can be described with the time-independent Schrödinger equation. This can be done since it only depends on the instantaneous nuclear configuration, and not on time. The nuclei are also massive enough to be treated as classical particles. For that reason they respond to the electronic forces according to Newton’s laws. This semi-classical approximation, coupled with an adiabatic separation of variables is called the Born-Oppenheimer approximation.

A further simplification can be made if studies are limited to periodic systems. Bloch’s theorem states that any wavefunction, $\psi_{i, \vec{k}}$, of a periodic system must be the product of a cell-periodic part $u_j(\vec{r})$ and a phase factor. This is in order to preserve the translational symmetry of the density. The phase factor takes the form of a plane wave, $e^{i\vec{G} \cdot \vec{r}}$, whose wavevector is a linear combination of reciprocal lattice vectors, and $u_j(\vec{r})$ is written as:

$$u_j(\vec{r}) = \sum_{\vec{G}} c_{j, \sigma} e^{i\vec{G} \cdot \vec{r}}$$  \hspace{1cm} (3.1)

with $\vec{G} \cdot \vec{r} = 2\pi m$, $m$ is an integer, $\vec{r}$ are the crystal lattice vectors, $c_{j, \sigma}$ are the plane-wave coefficients, the subscript $j$ indicates the band index and $\vec{k}$ is a continuous wavevector confined to the first Brillouin zone of the reciprocal lattice. $u_j(\vec{r})$ has the
3. Density functional theory

same periodicity as the direct lattice so that the electron wavefunctions can be expanded in terms of a linear combination of plane-waves:

$$\psi_{j, \tilde{k}}(\tilde{r}) = \sum_{\sigma} c_{j, \tilde{k} + \tilde{\sigma}} e^{i(\tilde{k} + \tilde{\sigma}) \cdot \tilde{r}}$$ (3.2)

Plane-waves are a simple way of representing electron wavefunctions and offer a complete basis set. The basis set is independent of the type of crystal and treats all areas of space equally. This has the additional advantage that the basis functions are orthogonal, and that operations on them are computationally efficient. In particular it is straightforward to Fourier transform the wavefunction from real space to reciprocal space or vice versa.

Many of the systems under study, such as e.g. surfaces, are not periodic, and need the construction of a supercell. This is essentially just a unit cell, repeated periodically in space, but containing a “spacer” region to separate the region of interest from its periodic images.

Typically the “spacer” is a vacuum. The advantage of Bloch’s theorem can be used even for non-periodic systems by using supercells to represent the system. Obviously, it must be ensured that this supercell is a good approximation of the original, aperiodic system. This is done by checking that the results are invariant with respect to small changes in the size of the supercell.

3.2. Hohenberg-Kohn theorem

The Hohenberg-Kohn theorems are the foundations of DFT. They relate to any system that consists of electrons moving under the influence of an external potential $v_{\text{ext}}(\tilde{r})$. This functional is minimised for the correct ground-state electron density. The ground-state energy functional is written as:

$$E[n] = \int v_{\text{ext}}(\tilde{r}) n(\tilde{r}) d\tilde{r} + F[n]$$ (3.3)
3. Density functional theory

where $v_{\text{ext}}$ is the external potential, i.e. the potential related to the positions of the nuclei.

The main idea of the Hohenberg-Kohn theorem is that there is a one-to-one correspondence between the electron density $n(\vec{r})$ and the external potential. The functional $F[n]$ includes all electron-electron interaction and kinetic energy terms. It is convenient to separately identify the energy due to the Coulomb interaction, also called the Hartree energy from $F[n]$

$$F[n] = \frac{e^2}{8\pi\epsilon_0} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + G[n]$$

where $e$ is the charge of the electron and $\epsilon_0$ is the electric permittivity of vacuum. Since the exact form of $G[n]$ is unknown, the ground state of the system can be obtained by minimising $E[n]$ with respect to the density while conserving $N$:

$$\int n(\vec{r})d\vec{r} = N$$

This leads to the variational equation:

$$\delta\{E[n] - \mu \int n(\vec{r})d\vec{r}\} = 0$$

A Lagrange multiplier, $\mu$, is introduced due to the constraints of equation 3.5. By applying Eq. 3.3, Eq. 3.4 and Eq. 3.6 the ground state can be determined by:

$$v_{\text{ext}}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \int \frac{n(\vec{r}')}{|r - r'|} d\vec{r}' + \frac{\delta G[n]}{\delta n(\vec{r})} = \mu$$

where $\frac{\delta G[n]}{\delta n(\vec{r})}$ is the functional derivative of $G[n]$ with respect to $n(\vec{r})$. Even if the functional form of $G[n]$ was known, Eq. 3.7 cannot be solved for $n(\vec{r})$. 

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3. Density functional theory

3.3. Kohn-Sham (KS) equations

Kohn and Sham developed a method resulting in one-particle equations, called the Kohn-Sham (KS) equations, which may be solved [85]. The KS equations consider a system of \( N \) non-interacting electrons in an external potential \( v_{\text{ext},s}(\vec{r}) \). The ground-state density of this system is \( n(\vec{r}) \). The functional \( F[n] \) in Eq. 3.4 then reduces to \( T_s[n] \), which is the kinetic energy functional of non-interacting electrons. The equation determining \( n(\vec{r}) \) is then given by:

\[
v_{\text{ext},s}(\vec{r}) + \frac{\delta T_s[n]}{\delta n(\vec{r})} = \mu_s \tag{3.8}
\]

In this case, the general form of \( T_s[n] \) is again unknown. However, there is a way to solve it for \( n(\vec{r}) \). For the case of non-interacting electrons, the many particle ground state wavefunction is simply a product of single electron wavefunctions \( \phi_i(\vec{r}) \) that obey the time-independent Schrödinger equation:

\[
\left\{ \frac{-\hbar^2}{2m} \nabla^2 + v_{\text{ext},s}(\vec{r}) \right\} \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}), \quad i = 1...N, \tag{3.9}
\]

where \( m \) denotes the electron mass. The density for this system of electrons is then given by:

\[
n(\vec{r}) = \sum_{i=1}^{N} |\phi_i(\vec{r})|^2 \tag{3.10}
\]

The ground state is found by selecting the \( N \) states, \( \phi_i(\vec{r}) \), that have the lowest energy \( \epsilon_i \). Moreover, there is a way of finding the solution to Eq. 3.8 for this particular system of non-interacting electrons. This method is also valid for interacting electrons [85]. In this case the functional \( G[n] \) may be split into two terms:

\[
G[n] = T_s[n] + E_{\text{xc}}[n] \tag{3.11}
\]

Here, the first term is still the kinetic energy of a system of non-interacting electrons with a density \( n(\vec{r}) \), and \( E_{\text{xc}}[n] \) is called the exchange correlation (XC) energy, which
3. Density functional theory

contains the information of the interacting system with density \( n(\vec{r}) \). Equation 3.7 now becomes:

\[
v_{\text{ext}}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \frac{\delta T_s[n]}{\delta n(\vec{r})} = \mu
\]  

(3.12)

This equation has the form of Eq. 3.8 except \( v_{\text{ext}, s}(\vec{r}) \) is replaced by an effective potential \( v_{\text{eff}}[n] \):

\[
v_{\text{eff}}[n] = v_{\text{ext}}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}
\]  

(3.13)

As with the non-interacting case, the correct ground-state density of the interacting system is found by the self-consistent solution \( v_{\text{eff}}[n] \) dependent on \( n(\vec{r}) \) of the single-particle KS equations:

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\vec{r}) \right\} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad i = 1...N
\]  

(3.14)

\[
n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2
\]  

(3.15)

Therefore, the total ground-state energy of the electron system is:

\[
E[n] = T_s[n] + \int v_{\text{ext}}(\vec{r}) n(\vec{r}) \, d\vec{r} + \frac{e^2}{8\pi\epsilon_0} \int \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}' + E_{xc}[n]
\]  

(3.16)

Where:

\[
T_s[n] = \sum_{i=1}^{N} \int \psi_i^*(\vec{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi_i(\vec{r}) \, d\vec{r}
\]  

(3.17)

Some explicit form for \( E_{xc}[n] \) must be adopted in order to find the self-consistent solution to Eq. 3.15 and to calculate \( E[n] \).
3. Density functional theory

3.3. Local density approximation

The local density approximation (LDA) is the simplest approximation of the XC energy functional which was first used by Kohn and Sham [85]. With the LDA, in regions of space where the charge density is slowly varying, the XC energy can be considered as a locally-uniform electron gas of the same charge density. The LDA functional assumes that the per-electron XC energy at every point in space is equal to that of the per-electron XC energy of a homogeneous electron gas. This can be written as

$$E_{xc} = \int d^3r \ n(\vec{r}) \left( \frac{-3e^2}{4\pi} \right) \left( 3\pi^2 n(\vec{r}) \right)^{\frac{1}{3}} \tag{3.18}$$

A schematic diagram showing the principle of the LDA is presented in Fig. 3.1.

The LDA works very well despite its simplicity. It even works reasonably well in systems where the charge density is rapidly varying. However, it tends to under-predict atomic ground state energies and ionisation energies, while over-predicting binding energies. It is also known to greatly favour high spin state structures. For these reasons there have been attempts to move beyond the LDA, notably through the addition of
3. Density functional theory

gradient corrections to incorporate longer range gradient effects [86]. However in practice, although these improvements appear to result in better total energies, the resultant structure is often worse, and at a greatly increased computational cost. In general, the LDA is worse for small molecules and improves with system size.

3.3.2. Exchange-correlation

The only remaining problem is to find an approximate solution for the homogeneous electron gas exchange correlation (XC) term, $\varepsilon_{xc}(n)$. There are several parametrised methods for this and the one used in VASP is based on the work by Ceperley and Alder [87].

The correlation energy for a homogeneous electron gas comes from a set of quantum Monte Carlo calculations performed by Ceperley and Alder [87]. These were later parametrised by Perdew and Zunger [88].

The results of Ceperley and Alder apply to low density electron gases, and can be combined with results from perturbation theory for high density gases to cover a wide density range. The method defines the correlation energy per electron, $\varepsilon_c$, polarisation $\xi$ and Wigner-Seitz radius of each electron, $r_s$ as:

$$E_c = \Omega n \varepsilon_c(n, \xi) = \frac{(n_\uparrow - n_\downarrow)}{n}, r_s = \left(\frac{4\pi n}{3}\right)^{\frac{1}{3}},$$

(3.19)

where $n$ is the electron density. For the non-polarised ($\xi = 0$) and fully-polarised ($\xi = 1$) cases, $\varepsilon_c$ is given by [88]:

$$\varepsilon_c = \begin{cases} 
\gamma 1 + \beta_1\sqrt{r_s} + \beta_2 r_s^{-1} & r_s \geq 1 \\
B + (A + Cr_s) \ln(r_s) + Dr_s & r_s < 1 
\end{cases}$$

(3.20)

Parameters for $\beta_1$, $\beta_2$, $\gamma$, $A$, $B$, $C$, and $D$ can be found in, e.g., [88].
3.4. Pseudopotential theory

Given the fermionic nature of electrons, every electronic state of the system has to be orthogonal to every other state. As higher and higher states are being filled, this means the wavefunctions of these states have increasing numbers of nodes. This dramatically increases the width of the Fourier spectrum, and hence the number of plane waves that are needed to adequately represent the wavefunction.

Typically, the chemical properties of a molecule depend mainly on the valence electrons as opposed to the core electrons. Since core electrons occupy the inner, inert, shells of atoms, their main function is to shield the outer valence electrons from the nuclei. In the pseudopotential approximation, the electrons whose wavefunctions are localised in the core region are removed. Their effective potential is combined with the nuclear Coulomb potential and the resulting effective potential is called the pseudopotential. Therefore, the remaining valence electrons’ wavefunctions only have to be orthogonal to each other, so the number of nodes is reduced. The pseudopotential is constructed such that the wavefunctions outside the core region are unchanged. The use of pseudopotentials dramatically reduces the number of plane waves required to represent the wavefunctions without much effect on the results.

3.4.1. Projector Augmented-Wave Method

The electron wavefunctions of real materials have very different signatures in different regions of space. In the bonding region, the wavefunction is fairly smooth, whereas close to the nucleus, due to the large attractive potential of the nucleus, it oscillates rapidly. It is difficult for electronic structure methods to accurately describe the bonding region while accounting for the large variations in the atom center. The augmented-wave methods divide the wavefunction into parts, namely a partial-wave expansion within the atom centered sphere and an envelope function outside the sphere. The envelope function can be expanded into plane waves. The envelope function and partial-wave expansions
3. Density functional theory

are then matched by value and derivative at the sphere radius. The projector augmented-wave (PAW) method which is used by VASP was developed by Blöchl [89]. The PAW uses a transformation that maps the valence wavefunctions onto pseudo wavefunctions that are to be identified as the envelope functions. This linear transformation gives pseudo wavefunctions that are computationally cheap to calculate.

There are several benefits of the PAW method over pseudopotential methods. Firstly, all errors can be systematically controlled so that there are no transferability errors. This means that a traditional pseudopotential constructed from an isolated atom is not guaranteed to be accurate for a molecule. However, the converged results of the PAW method do not depend on a reference system such as an isolated atom, because it uses the full density and potential. The PAW method provides access to the full charge and spin density, which is relevant for hyperfine parameters. Hyperfine parameters are sensitive probes of the electron density near the nucleus. In many situations, they are the only information available that allows us to deduce atomic structure and chemical environment of an atom.

3.5. Relaxation of the ionic system

Thus far, the determination of the electronic ground state has been considered in a system with fixed ionic positions. The positions of the ions and the size and shape of the unit cell can be included as dynamic variables in a Lagrangian, usually referred to as a Car-Parrinello Lagrangian. This, along with the Euler equations of motion give the necessary equations for the relaxation of the system. In the Car-Parinello scheme, the Kohn-Sham energy functional $E[c_{n\mathbf{k}}]$ is a set of coefficients of the plane-wave basis set $n\mathbf{k}$. Each coefficient $n\mathbf{k}$ is essentially the coordinate of a classical particle. To minimise the KS energy functional, these particles are given an initial kinetic energy and the system is gradually cooled until the set of coordinates reaches the values $n\mathbf{k}_0$ that minimise the
3. Density functional theory

functional. The Car-Parrinello Lagrangian has the form [90]:

$$L = \sum_i \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_j \frac{1}{2} M_j \dot{R}_j^2 + \sum_v \frac{1}{2} \beta \dot{\alpha}_v^2 - E[\{\psi_i\}, \{R_j\}, \{\alpha_v\}]$$

(3.21)

where $\mu$ and $\beta$ are artificial masses associated with the electronic wavefunctions ($|\psi_i\rangle$) and coordinates defining the unit cell ($\alpha_v$), $E$ is the KS energy functional, and $R_j$ is the position of ion $j$ with mass $M_j$. The kinetic term is due to the fictitious dynamics of the electronic degrees of freedom, and the dynamics of the ions bound by the cell size and shape. The KS energy functional replaces the potential energy in a conventional Lagrangian formulation.

The equations of motion for the positions of the ions and the coordinates of the unit cell are given by:

$$M_j \ddot{R}_j = -\frac{\delta E}{\delta R_j} \beta \dot{\alpha}_v = -\frac{\delta E}{\delta \alpha_v}$$

(3.22)

The equations of motion for the degrees of freedom associated with the dynamics of the ions and of the unit cell can be integrated at the same time as the equations of motion for the electronic states and, as will be shown below, provide a method for performing ab-initio dynamical simulations of the ionic system. A relaxation of the ionic system can be performed using these equations simply by removing kinetic energy from the electronic system, the ionic system, and the motion of the unit cell. In this case, the system will evolve until the total energy of the system is minimised with respect to all of these degrees of freedom and the ionic configuration will have reached a local energy minimum. However, integration of the equations of motion for the ions and for the unit cell is not as straightforward as it first appears. This is because physical ground-state forces on the ions and integrated stresses on the unit cell cannot be calculated for arbitrary electronic configurations, as shown in the following section.
3. Density functional theory

3.5.1. The Hellmann-Feynman theorem

When an ion moves, the wavefunctions must change to the self-consistent KS eigenstates corresponding to the new position, in order for the KS energy functional to remain physically meaningful. These changes contribute to the force on the ion:

$$ f_j = -\frac{dE}{dR_j} = \frac{\delta E}{\delta R_j} - \sum_i \frac{\delta E}{\delta \psi_i} \frac{d\psi_i}{R_j} - \sum_i \frac{\delta E}{\delta \psi_i^*} \frac{d\psi_i^*}{R_j} $$

Eq. 3.22 shows that the force in the Lagrangian equation of motion is the partial derivative of the KS energy functional with respect to the ion position. This is not the physical force on the ion, but the force on the ion due to the particular electronic configuration. However, according to the Hellmann-Feynman theorem, when each electronic wavefunction is an eigenstate of the Hamiltonian, the two final terms in Eq. 3.23 sum to zero. Then the partial derivative of the KS energy with respect to the ion position gives the physical force on the ion [91, 92]. Therefore, once the electrons are brought close to the ground state the forces and stresses on an ionic configuration can be calculated. These calculated forces can then be used to calculate a new ion trajectory to update the ionic positions. This process is repeated until the required accuracy for the ground state is met.
4. Fe nanostructures on the Ge(001) surface

4.1. Introduction

The most fundamental aspect of the field of magnetism is that of the mechanism by which ions, atoms or minute clusters of atoms possessing spin interact with each other [93, 94]. This exchange interaction defines the overall magnetic properties of a system [93–97]. While there is a large body of knowledge regarding the nature of magnetic interactions, the number of unanswered questions and controversies in this field is also immense [93–97]. By controlling the separation between the nanoclusters, and the material composition of the overlayer, substrate and the clusters, it is possible to vary and control the exchange mechanisms [27, 93, 94]. To study exchange interactions, model dilute magnetic semiconductor (DMS) systems can be developed by depositing a thin semiconductor overlayer on top of a well ordered quasi two-dimensional array of magnetic nanoclusters (Fe, Ni, Co) formed by self-assembly on semiconductor surfaces (Ge, Si) [27]. In this case the semiconductor overlayer and the substrate provide media through which the exchange interaction between magnetic nanoclusters can propagate. The engineering of such nanostructured magnetic systems represents an important challenge in the area of nanotechnology, because magnetic semiconductors are essential building blocks in the field of spintronic devices allowing an integration of magnetism and semiconductor technologies. This, of course, requires well-defined control over the production
of nanoclusters including knowledge about their structural behaviour on surfaces, which is directly related to their magnetic properties.

Current semiconductor technology makes use of electron charge for information processing. On the other hand, magnetic recording devices, which make use of the spin of the electron, are generally used for mass storage of information. The possibility of making devices which allow the use of both the charge and spin of the electron is the focus of much current research [30, 98]. For example, the growth and characterisation of proposed half metals [99], the fabrication and measurement of new ferromagnetic semiconductors [34, 35, 37], and the growth of ferromagnetic layers on semiconductors with a view to injection of spin polarised carriers [43, 100] are all highly active areas of research.

Fe/semiconductor systems have attracted much interest due to the possibility of injecting spin polarised carriers from the ferromagnetic layer into the semiconductor. This avenue towards integrating charge and spin electronics is perhaps the most suited to current processing technologies [100]. Such spin injection has already been successfully demonstrated [101].

One of the most promising substrates to grow metal nanoclusters is the Ge(001) surface, since it exhibits a dimer row pattern, which can promote the growth of ordered, uniformly-sized nanoclusters.
4.2. Germanium(001)

Germanium is a group IV intrinsic semiconductor. Bulk Ge has a cubic diamond lattice structure with a lattice constant of 5.6575 Å [102]. Ge was the first semiconductor commercially used. However, silicon is now more widely used than Ge in the semiconductor industry. Reasons for this are the lower cost of Si, the higher temperature tolerance of Si-based devices, and the fact that, unlike Ge oxide, its oxide is not water soluble, which is an advantage in producing devices. However, Ge is still used in low operating voltage devices and in power rectifiers. Recently the interest in Ge has intensified significantly due to the use of epitaxial Ge thin films grown on Si for bipolar transistors. The advantage of bipolar transistors is that they have proven to be faster and more efficient than existing Si transistors [103].

Ge also has been studied in terms of the possibility of achieving a dilute magnetic semiconductor (DMS). Through doping Ge with magnetic elements, it may be possible to combine magnetic and electronic devices on a single chip [30, 34, 35, 37]. Also, the possibility of using ferromagnetic metals as a source of spin polarised electrons for injection into semiconductors has led to interest in the growth of ferromagnetic layers on Ge [39–43, 100]. As a DMS model system, Fe has been deposited on the Ge(001) surface. This chapter provides an introduction to the Ge(001) surface, and an overview of related work.

The work presented in this chapter concentrates on the nucleation of Fe on the Ge(001) substrate at room temperature. The surface and its different terminations are presented in section 4.2. The types of Fe clusters formed on the surface are discussed in section 4.4. Magnetic measurements have been conducted to acquire the magnetisation properties of the Fe nanoclusters. The results of the magnetic measurements are presented in section 4.6.
Figure 4.1.: The Germanium unit cell. Ge crystallises in the diamond structure, which can be thought of as two interpenetrating fcc lattices. The lattice constant of Ge is 5.6575 Å [102].

Figure 4.2.: Calculated electronic density of states of germanium. (a) From $-12 \text{eV}$ to $12 \text{eV}$. (b) Zoom in on the area around $E_f$. A band gap of $\approx 0.7 \text{eV}$ is calculated [104].
4. Fe nanostructures on the Ge(001) surface

Figure 4.3.: Band structure of germanium calculated by the $\vec{k} \cdot \vec{p}$ method in the [111] and [100] direction of the $\vec{k}$ space [105].
4. Fe nanostructures on the Ge(001) surface

4.2.1. Surface terminations of Ge(001)

Ge crystallises in the diamond structure (Fig. 4.1). A calculated density of states (DOS) for bulk germanium is shown in Fig. 4.2. Around $E_f$ a band gap $\approx 0.7\,\text{eV}$ is present, with a broad band centred at $\approx -1.1\,\text{eV}$ on the occupied side and one centred at $\approx 0.75\,\text{eV}$ on the unoccupied side. Fig. 4.3 shows the band structure of Ge in the [111] and [100] directions of $\vec{k}$ space [105].

The Ge(001) surface has two dangling bond $sp^3$ hybrid orbitals per surface atom due to a broken symmetry at the interface. As with the Si(001) surface, the Ge(001) surface reconstructs through the pairing of nearest neighbour surface atoms, forming dimer rows oriented along the $<1\bar{1}0>$ crystallographic directions [23]. This gives rise to the $(2 \times 1)$ surface reconstruction, which is the primary LEED pattern observed at room temperature [106].

$(2 \times 1)$ surface reconstruction

The original models for the $(2 \times 1)$ reconstructed surface were based on two schemes. The first was a symmetrical surface dimerisation, along the [110] direction, which would lead to an odd number of unpaired electrons per surface atom and result in a half filled metallic surface state. The second was an asymmetrical surface dimerisation model, introduced by Chadi [107], essentially consisting of an energy saving buckling of the surface dimers, which would result in a semiconducting type surface state band. A schematic of these dimerisation schemes, and how it gives rise to the $(2 \times 1)$ reconstruction, is shown in Fig. 4.4.

It is now accepted that the reconstruction is best explained by the asymmetrical surface dimerisation model, with the formation of asymmetrically buckled dimer pairs along the $<1\bar{1}0>$ crystallographic directions. These buckled dimers flip-flop rapidly at room temperature between their two equivalent positions. The calculations by Chadi imposed no symmetry constraints on the dimers and found that the buckled dimer [Fig.
4. Fe nanostructures on the Ge(001) surface

Figure 4.4.: (a): Side view of the bulk terminated Ge(001) surface. Each surface atom has two dangling bonds. (b): The dimerisation that gives rise to the (2 × 1) surface reconstruction. The dimers shown here are symmetric. (c): Schematic of the asymmetric, or buckled dimer, found to be the lowest energy configuration by Chadi [107].

4.4(c) forms spontaneously, and that the symmetric dimer is in fact unstable [107]. Later total energy calculations also favoured this model [108, 109]. The buckling results in a charge transfer between the two atoms of the dimer, with the buckled up atom being electron rich and the buckled down atom electron poor. First principle calculations by Krüger et al. [110] have determined the Ge(001) surface states for the asymmetric dimer model from the bulk states. A semiconducting gap of \( \approx 0.8 \) V was calculated. They found 4 salient surface bands; the dimer bond band \( D_1 \), the dangling bond band \( D_{up} \), the dangling bond band \( D_{down} \), and the anti-bondering dimer bond band \( D'_1 \). In addition there were found to be back-bond states of mainly \( sp \) character \( (B_i) \) and \( s \) character \( (S_i) \). These were found to be localised between the first and second layer, perpendicular to the surface. The \( D_{up} \) band was found to have a very broad peak from the edge of the gap region to \(-1.5 \) V. The \( D_{down} \) band was broad, from the unoccupied edge of the gap to 1 V. A back-bond state was found at \( \approx -1 \) V.

\textbf{c}(4 \times 2) Surface reconstruction

The \textbf{c}(4 \times 2) reconstruction is also observed on the Ge(001) surface. At room temperature, weak quarter order LEED spots have occasionally been observed on the surface, consistent with some localised \( 4 \times 2 \) reconstruction [106]. The intensity of these quarter order spots has been shown to increase with decreasing temperature, until at \( \approx 200 \) K only
the $c(4 \times 2)$ pattern is observed, showing the $(2 \times 1) \leftrightarrow (4 \times 2)$ two-dimensional phase transition to be of second order [106]. The buckled dimer again forms the basis of the $c(4 \times 2)$ reconstruction. Unlike the $(2 \times 1)$ reconstruction, the dimers are buckled out-of-phase (or anti-correlated) along the [110] oriented rows. They do not flip-flop between the two possible configurations of the dimer, as occurs for the $(2 \times 1)$ reconstruction, but are frozen in one buckled configuration. The model for the $c(4 \times 2)$ reconstruction was proposed by Chadi [107]. This configuration was found to be true, using surface sensitive X-ray diffraction (XRD), by Ferrer et al. [111]. The different buckling arrangement of the dimers in the $(2 \times 1)$ and the $c(4 \times 2)$ reconstructions is shown schematically in Fig. 4.5.

Kevan and Stoffel [112] studied the $(2 \times 1) \leftrightarrow c(4 \times 2)$ transition using photoemission spectroscopy (PES), and found the transition to be an order-disorder, metal-insulator transition. A metallic surface state was present for the room temperature $(2 \times 1)$ phase. This state gradually disappeared as the sample was cooled, and was absent for the low temperature $c(4 \times 2)$ phase. They suggested that the metallicity of the $(2 \times 1)$ phase is due to the flip-flopping of the dimers between their two equivalent buckled positions. Between these two buckled states they pass through a symmetric state, giving rise to a conduction band, which was not present for the frozen buckled dimers of the $c(4 \times 2)$ reconstructed surface.

$p(2 \times 2)$ surface reconstruction

Finally, a $p(2 \times 2)$ reconstruction can also occur on the surface. However, this reconstruction is strongly suppressed in comparison to the $(2 \times 1)$ and $c(4 \times 2)$ reconstructions. Like the $c(4 \times 2)$ reconstruction it arises due to frozen buckled dimers. However, contrary to the $c(4 \times 2)$ reconstruction, the buckling orientation of neighbouring dimers is in phase (correlated) along the [110] direction (see bottom of Fig. 4.5). Needels et al. [113] calculated the $p(2 \times 2)$ and the $c(4 \times 2)$ reconstruction to be almost degenerate. Experimentally this reconstruction has not been widely observed for the Ge(001) surface,
4. Fe nanostructures on the Ge(001) surface

however it has been imaged using STM, for $T \leq 80$K, where it was found to co-exist
with the c(4 x 2) reconstruction [114, 115].

4.3. Previous STM characterisation of the Ge(001) surface

4.3.1. The clean Ge(001) surface

STM images of the Ge(001) surface show rows oriented along the (110) direction, sepa­
rated by 8 Å along the (110) direction. The periodicity along the rows was 4 Å, corre­
sponding to the (2 x 1) surface termination, confirming the LEED pattern observed at
RT by Kevan [106]. The orientation of the dimer rows were found to rotate through 90°
on terraces separated in height by 1.4 Å. This is due to the 90° rotation of the tetra­
hedral dangling bonds between these terraces. This domain structure on alternating
terraces gives rise to the observed two domain (2 x 1) LEED pattern. Areas exhibiting
the c(4 x 2) reconstruction were also imaged, generally in the vicinity of defects and
steps. The STM images of the surface show a large polarity dependence. As there is a
higher $D_{up}$ electron density of the dimer pair, when tunnelling from the tip into the
sample, one would expect to emphasise the states of the $D_{down}$ band, whereas when tun­
nelling from sample to tip, one would expect to emphasise the states of the $D_{up}$ band.
This was found to be true, and was evident by a phase shift of the frozen dimers of the
c(4 x 2) reconstructed areas due to the change in junction polarity. Surprisingly, even
for the symmetric (2 x 1) surface, asymmetric behaviour can be imaged with STM. This
was most easily seen through a clear phase shift along the dimer rows for positive and
negative polarity images [116].

STS of the (2 x 1) surface was carried out in the study by Kubby et al., measuring
an insulating gap of 0.9 eV. Surface states were resolved, with two filled state features at
$-1$ eV and $-2.6$ eV, and one empty state feature at 0.9 eV. In line with the calculations
by Krüger [110] the $-1$ eV band was labelled as the $D_{up}$ band, and the 0.9 eV feature
as the $D_{down}$ band. Both peaks have widths of $\approx 1$ eV. The feature at $-2.6$ eV was
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Figure 4.5.: Top view of the surface reconstructions of the Ge(001) surface. The (2 × 1) reconstruction consists of rows of dimer pairs, oriented along the [110] direction. The dimers are buckled asymmetrically out of the plane of the surface, as shown. The c(4 × 2) reconstruction again consists of dimer pairs, however they are frozen out-of-phase, as viewed along the [110] direction. Finally the p(2 × 2) reconstruction involves dimers frozen in phase along the [110] direction. It differs from the (2 × 1) reconstruction in that the direction of the dimer buckling alternates along the [110] rows.
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labelled as the $D_i$ band. These results were in general agreement with the angle resolved photoemission spectroscopy (ARPES) results of Kevan and Stoffel [112], which found peaks at $-0.6$ V and $-1.3$ V. The difference in the energies of the resolved peaks between the two techniques was explained in terms of the increased sensitivity of STS to the $p_z$ states of germanium, compared to PES.

Later STM studies have consistently shown that the $(2 \times 1)$ reconstruction dominates at room temperature, with areas of the $c(4 \times 2)$ reconstruction also present [21]. The presence of missing dimer defects and missing dimer complexes (such as twin missing dimers) on the terraces has also been consistently noted. It has been shown that such defects lead to a local freezing of the flip-flop motion of the $(2 \times 1)$ dimers in the vicinity of the defect at RT, resulting in the presence of localised areas of the $c(4 \times 2)$ reconstruction around defects [117].

The formation of a striped domain pattern of $(2 \times 1)$ and $c(4 \times 2)$ domains at room temperature on extremely defect free surfaces has been imaged with STM [118]. Whereas the defect induced domains decay over a length scale of ($\approx 4-40)$ Å, these domains can be up to $80$ Å wide and form a well ordered striped domain structure over the entire surface. The presence of even a low concentration of surface defects destroys this domain structure. The authors suggest that this domain formation at room temperature is driven by a strain relief mechanism. This property of the surface was recently used to examine the contrasting electronic properties of the $(2 \times 1)$ and $c(4 \times 2)$ reconstructions by STS [119]. It was found that the $(2 \times 1)$ domains have states near $E_f$ that are not resolved for the neighbouring $c(4 \times 2)$ domains. The presence of states in the semiconducting gap of the tunneling spectra was explained using the mechanism proposed by Kevan and Stoffel [112]: The flip-flopping dimers of the $(2 \times 1)$ reconstruction pass through a symmetric state resulting in a conductivity band for the $(2 \times 1)$ domains that is not present for the $c(4 \times 2)$ domains.
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4.3.2. Growth of ultrathin metal films on the Ge(001) surface

There has been much recent work focused on the use of Ge(001) as a substrate for the deposition of metals. The Ag/Ge(001) system has been extensively studied using STM, due to its superconducting characteristics below 2 K [120–122]. This research has focused on finding the most favourable adsorption sites for the metal adatoms, and whether the nucleation occurs normal or orthogonal to the dimer rows. The Pt/Ge(001) system has also been studied, to identify the initial nucleation sites of the deposited Pt atoms, and to explore the temperature dependence of the growth [123, 124]. This system has been shown to form 1-D Pt nanowires with metallic conductivity on the surface following high temperature (>1200 K) annealing in ultra high vacuum (UHV) [125].

The growth of magnetic materials on the Ge(001) surface was of particular interest, driven by the possibility of integrating magnetic devices and electronic devices on a single chip [30, 34, 35, 37]. One avenue explored with respect to this integration was dilute magnetic semiconductors (DMS). It was predicted by Dietl et al. [29] that ferromagnetic order can be stabilised in the group IV semiconductors. Some of the most promising results were found by studying Mn substituted Ge, which has yielded a Curie temperature ($T_c$) of 116 K for MBE grown films [35], and 285 K for a single crystal [39]. This in turn has led to interest in the UHV growth of epitaxial Mn on both the (100) and (111) surfaces of Ge [41]. Investigating the formation of Ge based DMS, Choi et al. have shown that Cr and Fe doped crystals exhibit ferromagnetic behaviour at 126 K and 233 K respectively [36, 38]. In these studies they found an increase in the lattice constant of the Fe doped Ge lattice, arguing that this shows the Fe is incorporated into the host lattice. However, despite the intensive research, the actual use of DMS in working devices languishes, due to the very low values of $T_c$ and problems with integration into existing device technologies [100].

Alongside DMS research, the deposition of ferromagnetic metal films onto semiconductor substrates is also being actively studied. There are many advantages of using
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ferromagnetic metals as a source of spin polarised carriers [100]. Firstly, they are easily integrated into existing processing technology. Secondly, they are a source of spin polarised electrons, whereas for many of the DMS discovered the spin polarised carriers are holes. This is advantageous because electrons have been shown to have long spin scattering lengths in semiconductors [126]. Thirdly, the $s$ electrons provided by ferromagnetic metals are highly spin polarised, which is due to coupling between the $s$ and $d$ electrons of the ferromagnet. Finally, unlike DMS, the ferromagnetic metals have high Curie temperatures, allowing their use in devices at practical temperatures.

Indeed, Fe has already been shown to be a suitable candidate for spin injection into semiconductors at room temperature by Zhu et al. [101]. The injection of spin polarised electrons into GaAs was demonstrated for a GaAs(001)/(In,Ga)As light emitting diode covered with Fe. The degree of the emitted circularly polarised light was calculated to be consistent with a spin injection efficiency of 2%. The process was explained in terms of the formation of a Schottky barrier at the interface. This allows the tunneling of electrons through a depletion layer into the active region of the diode. This spin injection mechanism is not affected by the resistance mismatch of the metal and substrate [127].

The benefit of the Fe/GaAs(001) interface lies in the fact that Fe can be grown epitaxially on GaAs, because of the low lattice mismatch between the two. This is also true for Ge and ZnSe substrates. Some previous studies of the deposition of Fe thin films onto the Ge(001) surface have been performed [42, 128, 129]. Much of the work was focused on the growth mode of the films, the degree of intermixing, and the extent of magnetic dead layers at the interface. It was initially reported that Fe films grown on Ge at 150 °C can have magnetically dead layers of up to 100 Å [130]. However, more recent work proposes that the extent of magnetic dead layers is not as large as originally suggested. Ma and Norton [128] have performed a combined LEED, AES, angle resolved Auger electron spectroscopy (ARAES) and longitudinal magneto-optic Kerr effect (MOKE) study on this system. They found the initial nucleation to be disordered, with local order (as seen through LEED) commencing at seven monolayers of Fe. Room temperature longitudinal
MOKE loops have shown hysteresis for films with thickness $\geq 4$ ML. This suggested that the intermixing problem is less than previously thought, but still shows that the first (3–4) ML are either magnetically dead, or have an easy axis perpendicular to the film plane. Analysing the temperature dependence of the AES concentration of Fe it was suggested that severe intermixing of the Fe with the Ge substrate commences at 160 °C and rapid diffusion of Fe into the bulk occurs at 400 °C, with the Fe signal disappearing at this temperature, consistent with complete diffusion of Fe into the bulk. It was also found that the Fe thin films lack the four-fold magnetic symmetry of bulk $\alpha$-Fe. There is a uniaxial magnetic anisotropy, with the [110] direction behaving as a hard axis, and the [110] direction as a soft axis. Whilst Ma et al. do not offer an explanation for this anisotropy, Kneedler et al. have shown that for the similar Fe/GaAs(001) system the effect is less pronounced for thicker films, pointing to the interface as the origin of the effect [131].

Schleberger et al. have performed an X-ray photoemission spectroscopy (XPS) study on amorphous Fe-Ge nanostructures [132]. The formation of a sharp Fe/Ge interface was excluded on the basis of chemical shifts of the core levels. Nominal thicknesses of $> 10 \, \text{Å}$ Fe had to be achieved for the formation of a pure Fe top layer above the intermixed region. In contrast, the deposition of Ge onto an Fe substrate led to no significant shift, suggesting the formation of a sharp interface. However, a recent XPS study by Cantoni et al. shows that the intermixing of Ge in the Fe top layer for room temperature grown films is less that 3% [42]. Furthermore, using MOKE, they have detected the onset of room temperature ferromagnetism at 3 ML, indicating that there is virtually no magnetic dead layer, consistent with the formation of an abrupt interface.

Finally, in relation to the Fe/Ge interface, it is worth noting that Freeland et al. have found direct evidence of an induced magnetic moment in Ge at the Fe/Ge interface using XMCD [40]. Spin polarised s states at $E_f$, and a d-component at higher energy were found to be present at the Ge interface layer, both oriented anti-parallel to the moment of the Fe layer, with a magnitude of $0.1 \mu_b$. 

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4.4. Nucleation of iron on Ge(001)

4.4.1. Introduction

In this chapter, results of the nucleation of Fe on the Ge(001) surface are presented. First low temperature scanning tunneling microscopy (LTSTM) measurements ($T = 78$ K) were carried out on the clean surface. The initial nucleation of Fe on this surface was studied using LTSTM. Small clusters are found to form on the Ge(001) substrate during RT deposition. The arrangement of these clusters is discussed in detail. Following this, Fe films of increasing thickness will be presented and discussed. The bias dependence of the acquired STM images will be evaluated in section 4.4.6.

4.4.2. Clean Ge(001) surface

The STM experiments were performed at liquid nitrogen temperature (78 K), using a commercial instrument from Createc, in an ultra-high-vacuum (UHV) system consisting of an analysis chamber (with a base pressure of $2 \times 10^{-11}$ mbar) and a preparation chamber ($5 \times 10^{-11}$ mbar). An electrochemically-etched monocrystalline W(100) tip [133] was used to record STM images in constant current mode. The voltage $V_h$ corresponds to the sample bias with respect to the tip. No drift corrections have been applied to any of the STM images presented here.

The Ge samples were cleaved from a 3 inch n-type (Sb doped, $25 \Omega^{-1} \text{cm}^{-1}$ (001)-oriented wafer (MaTeck). The samples were mounted onto a molybdenum sample holder and inserted into the UHV system. The Ge(001) surface was cleaned according to a published procedure [134] by repeated cycles of either Ar$^+$ or Ne$^+$ ion sputtering at an energy of 0.6 keV and annealing at 925 K for 40 min. Sample temperature was measured using an optical pyrometer (Ircon UX20P). After the final anneal the sample was cooled down to 675 K at a rate of $10 \text{K min}^{-1}$ to acquire the $(2 \times 1)$ surface reconstruction present at room temperature [23]. The substrate cleanliness was verified by AES, LEED and STM. This preparation procedure results in the formation of the well ordered Ge(001) surface.
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Figure 4.6.: AES spectrum of the clean Ge(001) surface. The graph on the left shows the low energy peaks, and on the right the high energy peaks. After repeated bombardment and anneal cycles, contamination is negligible.

One problem associated with this preparation technique is the presence of very large protrusions on the surface. The number of these defects are found to be greatly reduced as the number of bombardment and anneal cycles is increased. These large defects have been explained in terms of the diffusion of carbon contaminants from the bulk crystal to the surface [134, 135].

The AES spectrum of the clean Ge(001) surface is shown in Fig. 4.6. Contamination of the surface was below the detection limit of the analyser. The only Auger peaks present are those associated with Ge. Low energy peaks at (23, 47, 53, 89 and 108) eV, as well as the higher energy peaks, specifically the one at 1147 eV, are characteristic of the Ge surface. The LEED pattern shows that the surface exhibits the well known (2 × 1) reconstruction (see Fig. 4.7), as expected for the Ge(001) surface at RT [106].

4.4.3. STM of the clean Ge(001) surface

STM images of the clean Ge(001) surface are shown in Figs. 4.8 (left) and 4.8 (right). The Ge dimer rows, oriented along the [110] direction, are clearly seen. These rows are separated by 8 Å in the [110] direction. In Fig. 4.8 (left) a 90° rotation of the dimer
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Figure 4.7.: LEED pattern taken from the clean (2 x 1) reconstructed Ge(001) surface ($E = 110$ eV). The unreconstructed (1 x 1) unit cell is outlined with a red square, and the (2 x 1) superlattice is outlined by the yellow rectangle.

row direction from one terrace to the next is visible. In agreement with previous STM studies [21], the Ge(001) surface exhibits a long range c(4 x 2) reconstruction, and a (4 x 2) unit cell is outlined in Fig. 4.8 (right) with a black rhombus. Some examples of missing Ge vacancy defects were present on the surface. These are marked in Fig. 4.8 (right) by blue circles.

4.4.4. Nucleation of Fe clusters on the Ge(001) surface

Initial nucleation of Fe on the Ge(001) surface at RT

After the clean Ge(001) surface was obtained, ultrathin films of Fe were deposited onto the substrate in UHV at RT. A thoroughly de-gassed crucible source containing ultrapure Fe was used for deposition. 30 min of evaporation were necessary to stabilise the flux rate, then Fe was deposited at a deposition rate of $\approx 0.05 \text{ Å min}^{-1}$. The film thickness was measured using a quartz crystal balance. The preparation chamber pressure was below $1 \times 10^{-9}$ mbar during Fe deposition. After Fe deposition at RT the sample was placed
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Figure 4.8.: STM images of the clean Ge(001) surface. The c(4 × 2) reconstruction forms over the entire imaged area (78 K, 1.5 V, 1.0 nA). Left: 35 nm × 35 nm. Terraces show the c(4 × 2) reconstruction. A 90° rotation of the dimer row direction in going from one terrace to the next is observed. Right: 10 nm × 10 nm. The c(4 × 2) unit cell is marked with a black rhombus. Ge vacancies are marked with blue circles.

into the STM to cool down to liquid nitrogen temperature. To avoid drift, measurements were performed at least several hours after placing the sample into the LTSTM. The pressure in the STM chamber was $3 \times 10^{-11}$ mbar during measurements.

If deposited at RT and immediately cooled down to 78 K, Fe forms small nanoclusters on the Ge(001) surface at low coverage ((0.05 - 0.2) ML). A typical low temperature STM image of 0.05 ML of Fe on the Ge(001) surface is presented in Fig. 4.9, where bright protrusions correspond to Fe nanoclusters. All nanoclusters have a square shape and the uniform size of (4.5 ± 0.5) Å, which corresponds to four Fe atoms per cluster. These nanoclusters have an apparent corrugation height of (1.1 ± 0.1) Å with respect to the underlying substrate, which does not depend on the bias voltage.

It is clear that these two-dimensional nanoclusters follow the substrate dimer rows, although the separation between the clusters varies throughout the image. During the initial nucleation of the Fe nanoclusters, the interaction between Fe and the Ge(001) sur-
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Figure 4.9.: Low-temperature STM image of 0.05 ML of Fe on the Ge(001) surface: $V_t = -1.7$ V, $I_t = 0.60$ nA, size 17.0 nm $\times$ 17.0 nm, 78 K. The unit cell of the underlying Ge(001)-c(4 $\times$ 2) reconstructed surface is shown in white.

The Fe surface is strong enough to provide well-defined nucleation sites. Following this, additional Fe atoms diffuse on the surface to form nanoclusters around the initial nucleation sites. This indicates quite a strong Fe–Fe interaction. The underlying Ge(001)-c(4 $\times$ 2) reconstructed surface is clearly visible (Fig. 4.9). It exhibits large terraces with the Ge dimers forming zig-zag rows oriented along the [110] direction, in agreement with previous studies [21, 116]. These are indicated by white dashed lines in Fig. 4.9. The separation of two adjacent dimers is 8 Å and 4 Å along the [110] and [110] directions, respectively.

If the sample is left at room temperature under UHV conditions for more than one hour after Fe deposition, larger clusters are observed on the Ge(001) surface, similar to results obtained by Jordan et al. [27]. Typical low temperature STM images of 0.2 ML of Fe on the Ge(001) surface are shown in Fig. 4.10. Under such preparation conditions Fe atoms form nanoclusters of a square shape with sides $(9.0 \pm 0.5)$ Å. Figs. 4.10a and 4.10b show occupied and unoccupied states of the Fe/Ge(001) system, respectively. The Ge(001)-c(4$x$2) reconstructed surface exhibits charge distribution consistent with published reports for both occupied and unoccupied states [116]. In turn, the occupied and
Figure 4.10.: Low-temperature STM images of 0.2 ML of Fe on the Ge(001) surface. The sample was left at RT under UHV conditions for more than one hour after Fe deposition. After this time, Fe nanoclusters of 9.0 Å × 9.0 Å are mainly visible. However, a few smaller 4 Å × 4 Å Fe nanoclusters are still present on this surface. (a) STM image of occupied states: $V_b = -1.5$ V, $I_t = 0.50$ nA, size 30.0 nm × 30.0 nm, 78 K. (b) STM image of unoccupied states: $V_b = 1.5$ V, $I_t = 1.60$ nA, size 24.0 nm × 24.0 nm, 78 K.
unoccupied states of Fe nanoclusters do not show a significant difference, which is typical for metals.

It is clearly seen from Fig. 4.10 that the Fe nanoclusters exhibit an inner structure consisting of four smaller clusters, similar to those observed in Fig. 4.9. Furthermore, they have a size \((9.0 \text{ Å} \times 9.0 \text{ Å})\), which is four times the size of smaller clusters \((4.5 \text{ Å} \times 4.5 \text{ Å})\). These findings suggest that the large Fe nanoclusters are formed due to the migration of the smaller clusters or single Fe atoms at RT. The larger nanoclusters consist of sixteen Fe atoms. However, the apparent height of these nanoclusters is \((1.1 \pm 0.1) \text{ Å}\), indicating that they are also a single monolayer in height. The observation of these larger clusters after allowing the Fe/Ge(001) system to relax suggests that a cluster size of \(9.0 \text{ Å} \times 9.0 \text{ Å}\) is the energetically most favourable at room temperature. However, even after this relaxation there are still some of the smaller \(4 \text{ Å} \times 4 \text{ Å}\) Fe nanoclusters present on the Ge(001) surface. Furthermore, the self-assembly of Fe atoms into nanoclusters of a limited size at RT indicates that the strength of the Fe–Fe interaction depends significantly on the size of the Fe nanocluster.

In turn, the Fe nanoclusters are spaced by whole multiples of \(4 \text{ Å}\) along the \([1\bar{1}0]\) direction, due to restrictions of nucleation sites.

4.4.5. Fe/Ge(001) Interface

A very important point to be addressed is the degree of intermixing within the Fe/Ge(001) interface. The intermixing greatly influences the properties of spin transport across the interface \([100]\). Previous surface studies have suggested varying degrees of reactivity of the interface at RT, from severe \([130, 132]\), to low level \([42, 128]\). While the quality of the actual Fe/Ge(001) interface cannot be addressed using STM, some properties of the system under study can be used as an indication of the degree of reactivity. For example, as was pointed out earlier, the observed corrugation height of the nanoclusters was \(1.1 \text{ Å}\) as expected for a monolayer of Fe on the Ge(001) surface. For
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Figure 4.11.: STM image of 0.4 ML of Fe on Ge(001). The size distribution is similar to that of 0.1 ML (see Fig. 4.9 on page 61). 40 nm x 40 nm, 78 K, -0.7 V, 2.60 nA.

intermixing of the nanoclusters with the Ge(001) substrate one would expect a reduced corrugation height. Secondly, the Ge substrate maintains its general structure in the areas surrounding the clusters confirming that no intermixing occurs at the Fe/Ge(001) interface. Previous STM studies of metal clusters on Si(111) have shown the formation of very large voids when intermixing occurs [136].

In summary the STM images show that the Ge(001) substrate maintains its structure in the areas surrounding the 9 Å x 9 Å Fe clusters. No large voids are imaged and the clusters have apparent heights consistent with a single monolayer of Fe.

4.4.6. Different Fe coverages on the Ge(001) surface

It was shown that the initial stages of Fe nucleation on Ge(001) at RT results in the formation of well ordered, uniformly sized clusters with a definite registry with respect to the Ge(001) substrate. This nucleation is seen for very low surface coverage. STM images of the Ge(001) surface with higher Fe coverage (0.4 ML and 0.6 ML) are shown in Figs. 4.11 and 4.12. For both coverages Fe nanoclusters are formed on the Ge(001) surface,
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Figure 4.12.: STM image of 0.6 ML of Fe on the Ge(001) surface. The average cluster size is increased. 75 nm × 75 nm, 78 K, 0.9 V, 0.11 nA.

and they do not merge into islands. For 0.4 ML (Fig. 4.11) the size of the clusters is still quite uniform. For 0.6 ML a quantitative analysis of the cluster size is presented in Fig. 4.13. On the left hand side of this figure the clusters are marked in red. The histogram on the right shows the equivalent square side distribution of the Fe nanoclusters. This distribution strongly suggests that a cluster size of 9.0 Å × 9.0 Å is the most common one at a Fe coverage of 0.6 ML.

4.4.7. Effect of annealing on the Fe/Ge(001) interface

In order to study Fe nanocluster dynamics on the Ge(001) surface the samples were annealed at two different temperatures. Annealing the Fe nanoclusters on the Ge(001) surface at 420 K for 30 min leads to the formation of nanorow structures (or linear nanocluster arrays) elongated along the [110] direction of the Ge dimer rows (Figs. 4.14 and 4.15a). These were measured to be up to 15 nm in length (Fig. 4.15b). The temperature of 420 K has been chosen due to the observation that, for temperatures higher than 430 K interdiffusion of Fe and Ge seems to take place [128]. The Fe nanorow struc-
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Figure 4.13.: Left: STM image of 0.6 ML of Fe on the Ge(001) surface. The Fe nanoclusters are marked in red. Right: A histogram showing the equivalent square side distribution of the Fe nanoclusters. This distribution strongly suggests that a cluster size of 9.0 Å × 9.0 Å is the most common one at a Fe coverage of 0.6 ML.

Figure 4.14.: 50 nm × 50 nm STM image of ≈ 0.1 ML of Fe on the Ge(001) surface. The Fe nanoclusters assemble into nanorows after annealing at 400 K for 60 min. (78 K, −1.5 V, 1.0 nA.)
Figure 4.15.: Low-temperature STM images of 0.3 ML of Fe on the Ge(001) surface annealed at 420 K for 30 min to form nanorow structures (or linear nanocluster arrays). (a) $V_b = 1.5 \text{ V}$, $I_t = 1.60 \text{ nA}$, size $20.0 \text{ nm} \times 20.0 \text{ nm}$, 78 K. (b) $V_b = 1.5 \text{ V}$, $I_t = 1.60 \text{ nA}$, size $3.5 \text{ nm} \times 20.0 \text{ nm}$, 78 K.
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tures have a corrugation height of 1.1 Å, the same as the single nanoclusters prior to
annealing. In the [110] direction, these nanostructures are approximately 9 Å wide. An
individual nanorow consists of several Fe nanoclusters aligned along the direction of the
Ge dimer rows [110]. The separation between the nanoclusters forming the nanorow is
approximately 4 Å. This suggests that the cluster-cluster interaction is weaker than the
interatomic interaction within a single cluster. This is in agreement with DFT results,
showing that the cluster with the size of 9.0 Å × 9.0 Å formed by sixteen Fe atoms is the
most energetically favourable on the Ge(001) surface (see Sec. 4.5).

After annealing 0.2 ML Fe on the Ge(001) surface at 570 K for 20 min Fe forms large
clusters of a size up to 4.0 nm × 4.5 nm (Fig. 4.16). These clusters are neither uniform
nor ordered. The most energetically favourable cluster size at RT is 9.0 Å × 9.0 Å and at
temperatures up to 690 K these Fe nanoclusters are stable and form Fe nanorows. How­
ever, results shown in Fig. 4.16 suggest that this stability breaks down at temperatures
higher than 690 K. Instead, Fe on the Ge(001) surface forms large Fe islands of random
size distribution, size, and orientation. It is suggested that in this case the kinetic en­
ergy of Fe on the Ge(001) surface is larger than the potential energy barrier, which is
attributed to specific surface sites and cluster sizes. For this reason Fe can migrate freely
on the Ge(001) surface and form large Fe islands.
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Figure 4.16.: 28 nm × 28 nm STM image of ≈ 0.2 ML of Fe on the Ge(001) surface after annealing at 573 K for 20 min. Fe forms larger clusters, whose position and size are not dictated by the surface anymore. (78 K, −1.5 V, 1.9 nA.)
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4.5. DFT of Fe nanoclusters on the Ge(001) surface

In order to confirm the number of Fe atoms in the nanoclusters formed on the Ge(001) surface, DFT calculations were performed using the Vienna *Ab-initio* Simulation Package (VASP) program. VASP implements a projected augmented waves basis set [83] and periodic boundary conditions. The electron exchange and correlation was simulated by local density approximation (LDA) pseudopotentials with a Ceperley-Alder exchange-correlation density functional [87]. The Ge(001) surface was simulated by periodic supercells formed by slabs consisting of six Ge unit layers and a vacuum slab of 15 Å [124]. The positions of the atoms in the layer most distant from the surface were constrained to simulate the bulk. A $(6 \times 3 \times 1)$ $k$-point grid was used to sample the Brillouin zone. The applied energy cutoff was 215 eV. The Ge system has been initially relaxed to obtain the c$(4 \times 2)$ reconstruction of the Ge(001) surface. The resulting c$(4 \times 2)$ was then used as a “substrate” to model the Fe nanocluster.

For the simulation of the Fe/Ge(001) system an energy cutoff of 287 eV was applied. The Γ-point was used to sample the Brillouin zone. Again, the positions of the atoms in the layer most distant from the surface were constrained to simulate the bulk. The Fe/Ge(001) system was then relaxed prior to any further calculations. Fe nanoclusters with 9, 12, 16, 17 and 18 atoms were considered in order to fit an experimentally observed cluster size of $9 \text{ Å} \times 9 \text{ Å}$. Simulations of 12, 17 and 18 atoms have shown that some Fe atoms diffuse into the Ge substrate. This suggests bonding between Fe and Ge, which was ruled out on the basis of the Fe X-ray absorption (XA) spectra, which have a shape typical of the XA spectrum of a metal (see Fig. 4.20 on page 77. The system with 9 atoms resulted in a smaller cluster size than experimentally observed. The Fe cluster with 16 atoms was found to have the lowest energy and a size of $9 \text{ Å} \times 9 \text{ Å}$, which is in excellent agreement with the experimental data. Six different starting configurations (geometrical positions) for the Fe nanocluster consisting of 16 atoms have been examined. Five of them either did not resemble the experimentally observed geometrical structure or had...
Figure 4.17.: Side (a) and top (b) view of the calculated relaxed structure of an Fe nanocluster, consisting of 16 Fe atoms, on the Ge(001)-c(4 × 2) reconstructed surface. The Fe atoms are denoted by large gray spheres, the Ge atoms of the surface layer by blue spheres, and the bulk Ge atoms by green spheres.
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Figure 4.18.: (a) Occupied state STM image of the Fe nanocluster (3.0 nm × 3.0 nm, \( V_b = -1.5 \text{ V} \)), left panel, compared to the simulated partial charge density (from \(-1.5 \text{ V} \) to \( E_F \)), right panel. (b) Unoccupied state STM image of the Fe nanocluster (4.0 nm × 4.0 nm, \( V_b = 1.5 \text{ V} \)), left panel, compared to the simulated partial charge density (from \( E_F \) to 1.5 V), right panel.
a higher energy than the simulated Fe nanocluster shown in Figs. 4.17 and 4.18. The resulting model of the Fe nanocluster on the Ge(001) surface is shown in Fig. 4.17. In order to further compare DFT results with the STM images, the partial charge density of the Fe on the Ge(001) surface has been simulated in the range between $-1.5\,\text{V}$ and the Fermi energy ($E_F$), as well as between $E_F$ and $1.5\,\text{V}$. The calculated images are compared with the STM data in Fig. 4.18 and show very good agreement.
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Figure 4.19.: AGM measurements of the Fe nanoclusters on the Ge(001) surface for different Fe coverages.

4.6. Magnetic measurements

4.6.1. Introduction

For magnetic measurements of the Fe nanoclusters on the Ge(001) surface with ex-situ methods the samples have been capped with a 2 nm protective layer of Au. This was done to prevent the Fe nanoclusters as well as the surface from oxidising. The methods applied were superconducting quantum interference device (SQUID) magnetometry and alternating gradient magnetometry (AGM) as well as X-ray magnetic circular dichroism (XMCD). The latter was performed at the D1011 beamline at MAX-lab synchrotron in Lund, Sweden.
4.6.2. Alternating gradient magnetometry (AGM)

AGM measurements were performed at RT for Ge(001) samples with different Fe coverage and for samples without any deposited Fe. Data indicate similar saturation magnetisations for samples with different Fe coverage as well as for the sample without any deposited Fe. This means that magnetic impurities within the Ge substrate contribute significantly to a total magnetic moment. One monolayer of Fe on the Ge(001) surface corresponds to a thickness of $\approx 0.7 \, \text{Å}$. The sample size is $0.5 \, \text{cm}^2 \times 0.5 \, \text{cm}^2$. The magnetic moment per Fe atom is $2.23 \times 10^{-20} \, \text{emu}$ and the number of Fe atoms per cubic centimetre is $6.02 \times 10^{23}$. This leads to a total magnetic moment of $\approx 1.2 \times 10^{-5} \, \text{emu}$ for 0.5 ML of Fe on Ge(001). The saturation magnetisation of the Ge substrate is about 10 times higher than the expected total magnetic moment of the deposited Fe. A distinction between the contribution by Fe and the contribution by the impurities of the Ge substrate is not possible. For high magnetic fields up to $10 \, \text{kOe}$ a slight difference in the saturation magnetisation for samples with Fe and for those without Fe is visible. However, this difference cannot be qualitatively evaluated. Samples with different Fe coverage are hardly distinguishable.

SQUID magnetometry measurements were performed for a sample with 0.5 ML of Fe deposited on the Ge(001) surface for two different temperatures (5 K and 300 K). The magnetisation behaviour for both temperatures shows a comparable saturation magnetisation for SQUID and AGM measurements. Between RT measurements and measurements performed at 5 K only a small difference is visible. This is due to a major contribution from Ge impurities to the total magnetic moment. If Fe is assumed to be the major magnetic impurity in Ge, then there are about 1 ppm Fe atoms in the Ge substrate. MaTeck GmbH (one of the manufacturer of Ge wafers) stated < 1 ppm of Fe, < 0.2 ppm of Ni and < 0.2 ppm of Co in their Ge wafer, which is in agreement with the AGM and SQUID measurements.

Element-specific magnetic measurements like X-ray magnetic circular dichroism
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(XMCD) measurements avoid difficulties in distinguishing between bulk impurity contributions and contributions from the Fe nanoclusters. The results of XMCD measurements Fe nanoclusters and nanorows on the Ge(001) surface will be presented in the next section.

4.6.3. X-ray magnetic circular dichroism (XMCD)

Germanium bulk contributions to the magnetic signal highlighted the necessity for alternative magnetic measurements. XMCD is the perfect tool because it is an element-specific technique. XMCD measurements were performed at the D1011 beamline at MAX-lab synchrotron in Lund, Sweden. The Fe/Ge(001) samples of different Fe coverage prepared at TCD and protected by 2nm Au capping layer were studied. The samples were covered with Au to prevent the oxidation of Fe. The beamline provides an omnidirectional vector field with a magnitude of up to 0.05 T. The base pressure during measurements was $\approx 2 \times 10^{-9}$ mbar. Measurements were conducted at room temperature and at 150 K. Initially Fe 2p X-ray absorption spectra (XAS) were measured without any applied magnetic field. For XMCD measurements a $+B$ and $-B$ magnetic field of 0.05 T was applied. For XAS as well as for XMCD the total electron yield was measured, and so no quantitative values for the magnetic moment can be given.

Fe 2p X-ray absorption spectra obtained from 0.5 ML of Fe on the Ge(001) surface shown in Fig. 4.20 were measured both at RT and at 150 K with the magnetic field applied in two opposite directions. The relative intensities of the spectra are normalised to the same continuum jump at the photon energy of 745 eV, after subtraction of the background measured from a clean substrate. The XA spectra have a shape typical of the XA spectrum of a metal, indicating that no significant intermixing occurs at the Fe/Ge(001) interface, which is in agreement with previous studies [27, 42].

The XMCD spectra shown in Fig. 4.20 result from the subtraction of the XA spectrum taken at the maximum magnetic field ($+B_{max}$) applied in one direction (Fig. 4.20, blue
Figure 4.20.: Fe 2p XA spectra measured from 0.5 ML of Fe on the Ge(001) surface at RT (top) and at 150 K (bottom) with the magnetic field of 0.05 T applied in two opposite directions \((-B_{\text{max}}\) and \(+B_{\text{max}}\)). The relative intensities of the spectra have been normalised to the same continuum jump at the photon energy of 745 eV, after subtraction of the background measured from a clean substrate. The XMCD spectra are multiplied by a factor of 10 for clarity.
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Figure 4.21.: Fe 2p XA spectra measured at 150 K from 0.5 ML of Fe nanorow structures on the Ge(001) surface with the magnetic field of 0.05 T applied in two opposite directions (\(-B_{\text{max}}\) and \(+B_{\text{max}}\)). The relative intensities of the spectra have been normalised to the same continuum jump at the photon energy of 745 eV, after subtraction of the background measured from a clean substrate. The XMCD spectrum is multiplied by a factor of 10 for clarity.

The XMCD measurements taken at RT and 150 K from the Fe nanorow structures grown on the Ge(001) surface also show that these structures exhibit superparamagnetic behaviour, similar to the separate Fe nanoclusters. The Fe 2p XA spectra measured from Fe nanorows at 150 K and the resulting XMCD spectrum are shown in Fig. 4.21. XMCD measurements for the Fe nanorow structures and the separate Fe nanoclusters show very small dichroism at RT and each exhibits a similar prominent dichroism at 150 K.
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(see Figs. 4.20 and 4.21). In each case no magnetic hysteresis loop with remanence was observed, in comparison to the ferromagnetic response of larger clusters and nanorods [138, 139]. This suggests that an exchange interaction between the nanoclusters within the nanorow is not strong enough, or the nanorow size is still too small, to provide a ferromagnetic response.
4.7. Conclusions

In summary, using scanning tunnelling microscopy and density functional theory calculations it was shown that the Ge(001) reconstructed surface is a suitable template for the growth of homogeneous Fe nanoclusters. The size of nanoclusters depends on the temperature of the substrate.

Relaxation of the Fe/Ge(001) system at room temperature after deposition leads to the formation of nanoclusters with 16 Fe atoms. These clusters are $9.0 \, \text{Å} \times 9.0 \, \text{Å}$ wide and $\approx 1.1 \, \text{Å}$ in height. STM measurements as well as DFT calculations show that these larger clusters exhibit an inner structure, suggesting that they comprise four of the $4.5 \, \text{Å} \times 4.5 \, \text{Å}$ nanoclusters. All Fe nanoclusters nucleate at specific sites on the Ge(001) surface. The clusters are well ordered on the substrate and have uniform size.

Annealing the Fe/Ge(001) system results in a rearrangement of the clusters. After annealing at 420 K Fe nanoclusters form nanorows on the substrate. The width of the nanoclusters is $9 \, \text{Å}$, due to cluster mobility at such temperature. The $c(4 \times 2)$ reconstruction of the Ge(001) surface determines the width of the nanorows.

X-ray magnetic circular dichroism measurements indicate that the Fe nanoclusters and nanorow structures formed on the Ge(001) surface exhibit a superparamagnetic behaviour.
5. Oxygen adatoms and Fe nanoclusters on the MoO₂/Mo(110) surface

5.1. Introduction

In this section, a summary of molybdenum, the molybdenum (110) surface and an ultra-thin film of MoO₂ on the Mo(110) surface will be given. In the first subsection, a brief overview of molybdenum and the Mo(110) surface is presented. For a more detailed discussion of the Mo(110) surface see [140, 141]. In the second subsection, an in depth description of MoO₂ is demonstrated, including the crystallographic structure and electronic properties. This description will include a comparison of experimental values of these properties as reported in the literature and DFT calculations performed within the scope of this work. In Sec. 5.3 oxygen adatoms on the MoO₂/Mo(110) surface are investigated. Finally, in Sec. 5.5 the nucleation of Fe on the MoO₂/Mo(110) surface is presented.

5.1.1. Molybdenum

Molybdenum, from the Greek meaning “lead-like”, is a chemical element with the symbol Mo and atomic number 42. The electronic configuration of Mo is [Kr] 4d⁵ 5s¹. It was discovered in 1778 by Carl Wilhelm Scheele and first isolated in 1781 by Peter Jacob Hjelm. With a density of 10.280 g cm⁻³ and a melting point at 2896 K, giving it the sixth highest melting point of any element, it is often used in high-strength steel alloys.
Molybdenum has a bcc (body-centred cubic) crystal structure, and space group Im-3m (space group number: 229) with cell parameters \(\alpha = b = c = 3.147 \text{ Å}\) and cell angle \(\alpha = \beta = \gamma = 90.00^\circ\). Mo has a well established cleaning procedure compared to other metals, which is why Mo has been widely used as a substrate for surface science studies [142, 143].

The Mo(110) surface

The densely packed Mo(110) surface is known to be the lowest energy surface of Mo [144]. The bcc (110) surface presents a distorted hexagonal primitive unit cell. However, it is often more convenient to describe this surface using the centred rectangular unit cell highlighted in Fig. 5.1.

Figure 5.1.: A diagram of the Mo(110) surface. The centred rectangular unit cell is highlighted by the black box. The blue and turquoise spheres represent the surface and second atomic layer atoms, respectively.

The Mo(110) single crystals used in these studies were obtained from Surface Preparation Laboratory [145]. They were grown by the floating-zone method from a 5N purity single Mo crystal. As-grown 5N purity crystals of refractory metals such as Mo, typically contain bulk impurities (C, K, S, etc.) in concentrations of a few parts per million. The surface was oriented to within 0.1° of the (110) crystal plane and finished by mechanical polishing to a surface roughness of 0.03 μm.

The typical procedure for cleaning refractory metal surfaces contains of cycles of an-
nealing the crystal in an O₂ atmosphere and flash-annealing. In the case of Mo a partial O₂ pressure of \(1 \times 10^{-7} \text{ mbar} \leq P_{O_2} \leq 1 \times 10^{-6} \text{ mbar}\) and elevated temperatures of (~1200–1300) K is used. At these temperatures, bulk impurities diffuse to the surface where they form chemically stable oxides. These oxides, along with the surface oxide, are then removed by flash-annealing the Mo(110) surface to high temperatures in the range \(2200 \text{ K} \leq T_{\text{flash}} \leq 2600 \text{ K}\) for short periods ((5–30) s) under UHV conditions.

These temperature flashes are accompanied by sharp pressure bursts in the UHV. For this reason, it is necessary to wait for a couple of minutes for the pressure to recover.

Initially, the surface was oxidised by annealing at between (1300–1550) K, in an O₂ atmosphere of partial pressure \(1 \times 10^{-6} \text{ mbar}\), for (30–60) min. The sample was then flash-annealed to temperatures reaching (2400 ± 200) K for (15–20) s to remove the oxide layer. It was then left to cool for (5–10) min before the next flash, which allowed the chamber pressure to recover to the low \(10^{-10} \text{ mbar}\). This cycle was repeated several times, with flash times gradually shortened to a few seconds, before the next oxidising cycle was begun. LEED, AES and STM analysis were used to assess the cleanliness and structural order of the surface. After considerable repetition (several oxidising cycles) of this procedure, it was found that a carbon peak did not appear above the detection limit of the Auger system, indicating a concentration below 1%.

The main LMM Auger transition for sulphur at 152 eV is obscured by a molybdenum peak at 148 eV. For this reason, the presence of sulphur contamination cannot be completely excluded. Nevertheless, the cleaning procedure used was assumed to produce concentrations of the same order as the carbon level. Oxygen peaks were found to persist in Auger spectra taken on the surface at this point. As a result, the oxidising treatment was abandoned and further cleaning of the surface was carried out by flash-annealing alone. The LEED and AES spectra of the clean Mo(110) surface can be seen in Figs. 5.2 and 5.3.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.2.: LEED image of the clean Mo(110) surface taken at 147 eV. The Mo[001] direction is marked by the arrow.

Figure 5.3.: AES spectra of a clean Mo(110) surface. The main Mo peaks are at 28 eV, 186 eV and 221 eV.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Positions</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>(4e)</td>
<td>0.2316</td>
<td>-0.084</td>
<td>0.0164</td>
</tr>
<tr>
<td>O$_1$</td>
<td>(4e)</td>
<td>0.1123</td>
<td>0.2171</td>
<td>0.2335</td>
</tr>
<tr>
<td>O$_2$</td>
<td>(4e)</td>
<td>0.3908</td>
<td>-0.3031</td>
<td>0.2987</td>
</tr>
</tbody>
</table>

Table 5.1.: Wyckoff positions of the atoms in the MoO$_2$ unit cell.

5.1.2. Molybdenum(IV) oxide

Molybdenum(IV) oxide (MoO$_2$) is a material which displays both high conductivity as well as high transmittance in the visible region [146]. These properties, which are uncommon for an oxide, make MoO$_2$ an important material for both scientific studies and industrial applications [146–148]. The crystal structure of MoO$_2$ is simple monoclinic with space group $P2_1/c$ ($C_{2h}^5$) (Fig. 5.4) [149]. The lattice constants and monoclinic angle are $a = 5.6109$ Å, $b = 4.8562$ Å, $c = 5.6285$ Å, and $\beta = 120.95^\circ$, respectively [149]. The MoO$_2$ structure is a slight deviation from the rutile structure. This deviation is a result of a pairing of the metal atoms parallel to the monoclinic $a$ axis in a lateral, zigzag, displacement. This pairing can be seen in the diagram of the MoO$_2$ crystal structure displayed in Fig. 5.4.

![Diagram of MoO$_2$ crystal structure](image)

Figure 5.4.: Simple monoclinic crystal structure of MoO$_2$. Mo atoms are depicted in grey and O atoms in white. The unit cell is highlighted by thick solid black lines and comprises four formula units. A pairing of the metal atoms parallel to the monoclinic $a$ axis is visible and leads to a lateral, zigzag, displacement.

The unit cell highlighted by thick solid black lines comprises four formula units (Fig.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

5.4. The Mo atoms along with the two nonequivalent oxygen atoms occupy the general Wyckoff positions (4e): ±(x, y, z), ±(x,1/2 - y, 1/2 + z) with the parameters listed in Tab. 5.1. Using standard notation, the primitive translations are:

\[
a_{M1} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -a_M \\ -a_M & 0 & 0 \end{pmatrix} \quad a_{M2} = \begin{pmatrix} -b_M & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad a_{M3} = \begin{pmatrix} 0 & 0 & c_M \sin \beta \\ 0 & 0 & -c_M \cos \beta \end{pmatrix}
\]

(5.1)
giving a unit cell with dimensions and atomic positions listed in Tabs. 5.2 and 5.3.

<table>
<thead>
<tr>
<th>Unit Vectors (Å)</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.61</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>b</td>
<td>0</td>
<td>4.86</td>
<td>0</td>
</tr>
<tr>
<td>c</td>
<td>-2.89</td>
<td>0</td>
<td>4.83</td>
</tr>
</tbody>
</table>

Table 5.2.: Dimensions of the bulk MoO$_2$ unit cell.

<table>
<thead>
<tr>
<th>Atomic Positions (Å)</th>
<th>O$_1$</th>
<th>O$_2$</th>
<th>O$_3$</th>
<th>O$_4$</th>
<th>O$_5$</th>
<th>O$_6$</th>
<th>O$_7$</th>
<th>O$_8$</th>
<th>Mo$_1$</th>
<th>Mo$_2$</th>
<th>Mo$_3$</th>
<th>Mo$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.33</td>
<td>-0.05</td>
<td>2.84</td>
<td>4.21</td>
<td>1.39</td>
<td>2.76</td>
<td>-0.12</td>
<td>-1.49</td>
<td>1.25</td>
<td>2.91</td>
<td>1.46</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>3.38</td>
<td>1.05</td>
<td>0.96</td>
<td>3.48</td>
<td>1.47</td>
<td>3.8</td>
<td>3.9</td>
<td>1.37</td>
<td>4.82</td>
<td>2.39</td>
<td>0.04</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>1.13</td>
<td>0.97</td>
<td>1.29</td>
<td>3.39</td>
<td>3.7</td>
<td>3.86</td>
<td>3.54</td>
<td>0.08</td>
<td>2.33</td>
<td>4.75</td>
<td>2.49</td>
</tr>
</tbody>
</table>

Table 5.3.: Atomic positions of the Mo and O atoms in the bulk MoO$_2$ crystal.

A structural relaxation of the MoO$_2$ unit cell was performed using VASP and the obtained structural results were then compared to reference data [149]. For the calculations, PAW pseudopotentials were used. The LDA was applied as exchange-correlation. A k-point grid of a very high density (22 × 22 × 22) was chosen in order to accurately...
calculate the band structure of MoO$_2$. The cell consisted of one MoO$_2$ unit containing 12 atoms. The cell was allowed to relax by minimising the total forces on each ion to less than 0.01 eV Å$^{-1}$. The relaxed structure had dimensions of $a = 5.520$ Å, $b = 4.853$ Å, $c = 5.609$ Å, and $\beta = 120.607^\circ$, in excellent agreement with the bulk values. The dimensions of the unit vectors and atomic positions, along with the percent change from the experimental values, is listed in Tabs. 5.4 and 5.5.

<table>
<thead>
<tr>
<th>Unit Vectors (Å)</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>5.61 (0%)</td>
<td>0 (0%)</td>
<td>0.04 (0.04%)</td>
</tr>
<tr>
<td>$b$</td>
<td>0 (0%)</td>
<td>4.85 (−0.21%)</td>
<td>0% (0%)</td>
</tr>
<tr>
<td>$c$</td>
<td>−2.84 (−1.73%)</td>
<td>0 (0%)</td>
<td>4.73 (−2.07%)</td>
</tr>
</tbody>
</table>

Table 5.4.: Dimensions of the MoO$_2$ unit cell after DFT relaxation.

<table>
<thead>
<tr>
<th>Atomic Positions (Å)</th>
<th>O$_1$</th>
<th>O$_2$</th>
<th>O$_3$</th>
<th>O$_4$</th>
<th>O$_5$</th>
<th>O$_6$</th>
<th>O$_7$</th>
<th>O$_8$</th>
<th>Mo$_1$</th>
<th>Mo$_2$</th>
<th>Mo$_3$</th>
<th>Mo$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>1.30 (−0.03)</td>
<td>1.06 (0.01)</td>
<td>2.78 (−0.06)</td>
<td>4.14 (−0.07)</td>
<td>1.36 (−0.03)</td>
<td>2.71 (−0.05)</td>
<td>−0.12</td>
<td>−1.48 (0.01)</td>
<td>1.23 (−0.02)</td>
<td>2.86 (−0.05)</td>
<td>1.43 (−0.03)</td>
<td>−0.20</td>
</tr>
<tr>
<td>y</td>
<td>3.38</td>
<td>0.96</td>
<td>3.49 (0.01)</td>
<td>1.47</td>
<td>3.79 (−0.01)</td>
<td>3.89 (−0.01)</td>
<td>3.89 (−0.01)</td>
<td>4.82</td>
<td>2.39</td>
<td>0.04</td>
<td>2.46 (−0.03)</td>
<td></td>
</tr>
<tr>
<td>z</td>
<td>1.44</td>
<td>0.97</td>
<td>1.28 (−0.01)</td>
<td>3.39</td>
<td>3.70</td>
<td>3.85 (−0.01)</td>
<td>3.55 (0.01)</td>
<td>0.08</td>
<td>2.33</td>
<td>4.75</td>
<td>2.49</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5.: Atomic positions of the Mo and O atoms after DFT relaxation of the MoO$_2$ crystal. Relative changes compared to the values listed in Tab. 5.3 are shown in brackets.
5. *Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface*

### 5.2. Surface oxide growth on Mo(110)

Up to this date, recent studies of the surface oxidation of the $4d$ series span from Ag to Rh. A developing trend from a thermodynamically stable surface oxide trilayer (oxide-metal-oxide or O-M-O) for Ag, to a slightly less stable trilayer for Pd, and a transient, kinetically stable trilayer for Rh was observed. Recent theoretical and experimental studies on the initial oxidation stages of the transition metal surfaces, Pd(111), Pd(100), Rh(111), Rh(110) and Rh(100) show that the structures of the surface oxides differ from those of the bulk oxides [150–154]. The surface oxides of these metals exhibit different thermodynamic stabilities. A common feature is that their formation involves sub-surface penetration of oxygen, thus the metal atoms of the surface oxide are sandwiched between two atomic layers of oxygen, forming O-M-O trilayer surface oxides.

However, it was recently suggested that since many of the TM oxides wet their own metal surfaces, the adhesion energy should provide extra stabilisation allowing a bulk-like surface oxide to form when the O$_2$ partial pressure is many orders of magnitude lower than required to maintain the bulk oxide [155].

For the following experiments, single crystal Mo(110) with a surface deviation from the (110) plane of less than 0.1° were used. The crystals were cleaned with the procedure outlined in section 5.1. Once a clean surface was obtained, the samples were annealed to 1275 K in an O$_2$ atmosphere of $1 \times 10^{-7}$ mbar for 2 min. The surfaces were then characterised using LEED and STM. Fig. 5.5 presents a LEED image of the molybdenum oxide overlayer. Next to the main Mo(110) LEED spots, bright satellite spots are visible in the Mo[111] direction. These satellite spots indicate the presence of a row structure on the MoO$_2$/Mo(110) surface. The rows follow the [113] direction of the Mo substrate.

Fig. 5.6 shows an STM image of the surface of Mo(110) after annealing under the same conditions discussed above. This image shows a periodic row structure aligned along the Mo[113] direction. This row structure has a period of 25 Å and a corrugation of $(0.2 \pm 0.1)$ Å. These rows are highly regular and seemingly cover the entire substrate.
5. Oxygen adatoms and Fe nanoclusters on the MoO₂/Mo(110) surface

![LEED pattern from the MoO₂/Mo(110) surface](image)

Figure 5.5.: LEED pattern from the MoO₂/Mo(110) surface, acquired at a primary beam energy of 92 eV. Next to the main Mo(110) LEED spots bright satellite spots are visible. These spots indicate the presence of a row structure on the MoO₂/Mo(110) surface. The rows follow the [113] direction of the Mo substrate. Outlined are also the [001] and [110] high symmetry directions of the Mo(110) substrate for clarity.

The periodicity and direction of these rows is consistent with the spacing of the satellite spots in the LEED pattern shown in Fig. 5.5.

5.2.1. Model of MoO₂ on the Mo(110) surface

Based on previous Raman, XPS and RHEED studies of the oxidation of molybdenum it was determined that MoO₂ is the sole oxide that grows epitaxially on the Mo(110) surface at low pressures [24, 142, 143, 156–161]. The MoO₂ bulk structure has a monoclinic-distorted rutile structure (space group $P2_1/C$) with lattice parameters $a = 5.661 \text{ Å}$, $b = 4.846 \text{ Å}$, $c = 5.628 \text{ Å}$, and $\beta = 120.95^\circ$ [149]. This gives the $a$ and $c$ axes and the angle $\beta$ dimensions similar to the overlayer imaged by STM. The axes are nearly twice that of the Mo bulk lattice constant with $\beta$ close to the angle of the quasi-hexagonal Mo(110) surface. This leads to multiple epitaxial relationships that are suitable matches for LEED data. However, considering the size and shape of the surface mesh imaged by
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

![Figure 5.6: Low-temperature STM image of the MoO$_2$/Mo(110) surface: $V_{\text{sample}} = -0.06\, \text{V}, \, I_s = 0.10\, \text{nA}$, size $22\, \text{nm} \times 22\, \text{nm}$, 78 K. The image shows a periodic row structure aligned along the Mo[113] direction with a period of 25 Å.](image)

STM, it was shown that the only compelling overlayer structure is MoO$_2$(010)/Mo(110) [24].

The MoO$_2$(010) surface is a quasi-hexagonal surface with a lattice spacing on the order of 5.7 Å and an angle of 120.95°, and very similar to the surface imaged by STM. Furthermore, the MoO$_2$(010) surface (Fig. 5.6) is built from alternating ionic planes of oxygen anions and Mo–Mo bonded dimers (Fig. 5.7). A layered oxygen-metal-oxygen (O-M-O) surface like this is a likely choice for two reasons. First, metal/polar-oxide interfaces such as this, where the oxide has only oxygen ions within the terminating plane are generally considered most stable, with adhesive energies an order of magnitude higher than non-polar interfaces [150, 151, 153, 155, 162–171].

The Mo(110) surface mesh and the MoO$_2$(010) oxygen mesh are both quasi-hexagonal with similar lattice parameters and there are three suitable orientations that can form coincidence; with either the [201] or [101] or [102] direction of the MoO$_2$ lattice parallel to Mo[113]. Comparing these three models to the LEED and STM measurements the
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.7.: The MoO$_2$(010) surface is built from alternating layers of oxygen anions (red) and Mo-Mo bonded cations (blue). In the oxygen layers, the oxygen is arranged in a quasi-hexagonal pattern with an atomic spacing of $\sim 3\,\text{Å}$. In the Mo layers, the metal forms dimers that are aligned along the MoO$_2[100]$ direction, and are arranged in a quasi-hexagonal pattern with dimensions of the MoO$_2$ unit cell.

Possible orientations were narrowed to the MoO$_2[201] \parallel$ Mo[113] orientation [24]. The overlayer in this model was skewed by $2.7^\circ$ in order to induce the required 1:1 coincidence with the Mo[113] direction that reoccurs once every 17 units along the Mo[001] direction. This leaves only a $\approx 2^\circ$ discrepancy between the MoO$_2[100]$ and the Mo[001] direction. The overlayer can now be described by a unit cell of MoO$_2[201]$ parallel to Mo[113] and MoO$_2[004]$ parallel to half a unit of Mo[997]. The surface model of MoO$_2$(010)/Mo(110) described above is presented in Fig. 5.8 and was initially proposed in [24]. The black mesh shows the overlayer unit cell in agreement with the LEED data. There is a 1:1 coincidence between the interfacial oxygen and molybdenum atoms that run along the Mo[113] direction (along the black mesh lines in that direction). The white diamond highlights the surface oxygen unit cell, and the surface oxygen are highlighted in that cell by the white dots. The surface oxygen unit cell is in perfect agreement with the STM data.

Previous DFT calculations used the reduced diamond shaped unit cell represented by the white outline in Fig. 5.9 and support this model [24]. In this model the oxide has been distorted to fit one primitive unit cell of the MoO$_2$(010) surface to the Mo(110) surface. This greatly reduced the computational cost since the slab is very small.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

**Figure 5.8.** Top view of the MoO$_2$(010) overlayer unit cell as determined by STM, LEED and DFT calculations. The larger dark grey spheres represent the Mo(110) surface atoms, the white spheres represent the O$^{2-}$ interface atoms, the grey spheres represent the Mo$^{4+}$ atoms, and the black spheres represent the surface atoms. The black rectangular grid represents the overlayer unit cell. Note that this is the “on-top” configuration and that the interface oxygen atoms are located on top of the Mo interface atoms at the intersections of the grid lines and along the Mo [113] direction [24].

**Figure 5.9.** Model unit cell used for DFT calculations with MoO$_2$(010) plane parallel to the Mo(110) surface and MoO$_2$(010) and the a and c axes aligned along the Mo[111] and [001], respectively [24].
DFT geometry optimisations for the slabs of dimensions shown in Fig. 5.9 for each of the four possible configurations of the interfacial oxygen have been previously performed [24]. These configurations are (a) on the 2-fold bridge site above the underlying Mo atom, (b) atop the surface Mo, (c) on the 3-fold hollow site, and (d) 2-fold bridge site with no underlying Mo atom (Fig. 5.10).

![Figure 5.10](image)

Figure 5.10.: DFT geometry optimisations were performed for each of the four possible configurations of the interfacial oxygen atoms that form the coincident sites seen in the LEED data. These configurations are (a) on the 2-fold bridge site above the underlying Mo atom, (b) atop the surface Mo, (c) on the 3-fold hollow site, and (d) 2-fold bridge site with no underlying Mo atom [24].

Out of the four possible interfacial oxygen coordination sites the two bridge configurations, (a) and (d), relaxed onto the 3-fold site, leaving only two stable configurations. In both cases there was a strong adhesion between the film and substrate, as expected for a polar oxide/metal interface. The adhesion energy from this system has two main components, a contribution from the metal-oxygen bonding, and a contribution arising from the electron redistribution at the interface. The latter is the result of the metal substrate transferring electrons to the interfacial oxygen atoms, which can be explained by the Pauling electronegativity of the two elements, $\chi_{Mo}(1.8) < \chi_{O}(3.5)$. This results in a polarisation of the metal at the interface, and a stronger adhesion energy. This effect was found to increase the adhesion energy by an order of magnitude for the polar Mo/MgO(111) interface compared to the nonpolar Mo/MgO(100) interface [172].
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Furthermore, with these two configurations, it was found that the case with the interface oxygen located on the 3-fold site had the lowest energy by 0.20 eV and 0.23 eV per atom at the interface as calculated by GGA and LDA, respectively. This configuration also had the shortest interlayer separation and highest work of adhesion, indicating a stronger interface bonding. The results of these calculations are shown in table 5.6.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$\Delta E^1$</th>
<th>$\Delta E^1$</th>
<th>$W^2$</th>
<th>$W^2$</th>
<th>Interlayer separation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top site</td>
<td>0.2</td>
<td>0.23</td>
<td>5.75</td>
<td>6.48</td>
<td>1.72</td>
</tr>
<tr>
<td>3-fold</td>
<td>7.13</td>
<td>8.10</td>
<td></td>
<td></td>
<td>1.18</td>
</tr>
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</table>

Table 5.6.: DFT Geometry Calculations [24].

The DFT results presented above are in good agreement with experimental data. However, due to the use of a reduced unit cell, long range surface reconstructions are not considered in these calculations. In order to identify the correct model for the MoO$_2$/Mo(110) surface (exhibiting oxide nanorows, which match the STM image), density functional theory (DFT) calculations have been performed.

The ab initio surface relaxation calculations were performed using the VASP program. A plane augmented wave basis [83] was used with an energy cutoff of 400 eV. The electron exchange and correlation was simulated by local density approximation pseudopotentials with a Ceperley-Alder exchange functional [87]. A $\Gamma$-centred $(1 \times 1 \times 1)$ k-point grid was used for all calculations to sample the Brillouin zone. For the DOS, a smearing of 0.2 eV was applied using the Methfessel-Paxton method. The global break condition for the electronic self consistent loops was set to a total energy change of less than $1 \times 10^{-6}$ eV. The unit cell was allowed to relax by minimising the total forces on each ion to less than $0.01 \text{eV} \text{Å}^{-1}$. The Mo(110) surface was modeled by three layers of molybdenum. The lowest layer of molybdenum has been constrained to simulate the bulk. An O-Mo-O trilayer, representing the ultrathin MoO$_2$ film, has been placed on top of the three Mo layers. This slab was terminated by a vacuum region to simulate the surface. The

$^1\Delta E$ is the difference in total energy for the system in eV/Atom.

$^2W$ is the work of adhesion in J m$^{-2}$. 

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resulting model of the MoO$_2$/Mo(110) surface is shown in Fig. 5.11. In order to compare DFT results with the STM images, the partial charge density of the relaxed system has been simulated in the range from the Fermi energy ($E_F$) to 0.1 V. A comparison between the calculated and the STM image is presented in Fig. 5.12 and shows an excellent agreement. This indicates that the grooves between the oxide nanorows are due to the surface topology. The MoO$_2$(010) grows as a strained-commensurate layer on Mo(110) and is slightly corrugated (see Fig. 5.11 right).

Figure 5.11.: Top (left) and side (right) views of the calculated relaxed MoO$_2$/Mo(110) structure. The Mo and O atoms are denoted by blue and red spheres, respectively.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.12.: An experimental STM image (13 nm x 13 nm, $V_b = 0.1$ V) (a) compared to the partial charge density of the relaxed MoO$_2$/Mo(110) system simulated in the range from $E_F$ to 0.1 V (b). The inset in (b) shows the surface unit cell.
5.3. Oxygen adatoms on the MoO$_2$/Mo(110) surface

5.3.1. Introduction

In this section a novel lithography system is described, in which an STM tip is used to remove single oxygen adatoms from the oxidised molybdenum surface, exhibiting well-ordered oxide nanorows. The oxygen desorption is induced by electrons tunneling from the STM tip to the sample. The process can be initiated at positive sample bias voltages above 1.5 V without a contact between the tip and the surface that substantially decrease probability to modify the tip structure and, therefore, allows reproducible atomic scale patterning. The nanoscale writing reported here does not demand extremely low temperatures because of high stability of the oxide system. Furthermore, the lateral size of the patterns on the oxydised Mo(110) can be controlled by the bias voltage applied during the STM lithography. The minimum feature size of this technique is 5 nm, which is a fundamental constraint due to periodicity of the molybdenum oxide nanorows on the Mo(110) surface. Such resolution is an order of magnitude improvement over the most cutting-edge electron beam techniques. However, for the sample preparation ultra-high vacuum conditions as well as an STM are needed which makes this type of lithography a rather impractical technique for industrial applications. Nevertheless, the method laid out here can represent an interesting avenue for the development of new procedures for future technologies.

5.3.2. Experimental

The STM experiments were performed at liquid nitrogen temperature (78 K), using a commercial instrument from Createc, in an ultra-high-vacuum (UHV) system consisting of an analysis chamber (with a base pressure of $2 \times 10^{-11}$ mbar) and a preparation chamber ($5 \times 10^{-11}$ mbar). An electrochemically-etched monocrystalline W(100) tip [133] was used to record STM images in constant current mode. The voltage $V_{\text{sample}}$ corresponds to the sample bias with respect to the tip. No drift corrections have been applied to any
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

of the STM images presented in this section. A Mo(110) single crystal (Surface Preparation Laboratory) was used as the substrate. An atomically-clean Mo(110) surface was prepared by in situ annealing at 1500 K in an oxygen atmosphere of $1 \times 10^{-7}$ mbar, followed by a series of high temperature flashes at 2200 K. The sample was heated by electron beam bombardment and temperatures were measured using an optical pyrometer (Ircorn UX20P, emissivity 0.35). The clean Mo(110) surface was verified by LEED and STM before oxidation. Once a clean surface was obtained, the sample was oxidised at 1275 K in an oxygen atmosphere of $1 \times 10^{-7}$ mbar for 2 min. The quality of the resulting oxide structure was verified by LEED and STM. In order to obtain oxygen adatoms on the MoO$_2$/Mo(110) surface the clean Mo(110) was oxidised at 1225 K in an oxygen atmosphere of $1 \times 10^{-7}$ mbar for 2 min and cooled down in an oxygen atmosphere.

5.3.3. Results and discussion

High temperature oxidation of the Mo(110) surface at 1275 K in an O$_2$ atmosphere of $1 \times 10^{-7}$ mbar for 2 min leads to the formation of an ultrathin MoO$_2$(010) layer [24, 173]. A typical LEED pattern and a STM image taken from the MoO$_2$/Mo(110) surface are shown in Figs. 5.5 and 5.6 of the previous section, respectively. The MoO$_2$(010) has an O-Mo-O trilayer structure and forms well-ordered oxide nanorows on the surface, separated by 2.5 nm (Fig. 5.6). These rows follow the [113] direction of the Mo(110) substrate and appear on STM images as bright regions with dark depressions in between. The LEED pattern (Fig. 5.5) shows characteristic satellite spots around each primary Mo(110) spot resulting from Mo oxide nanorows on the surface. Due to the formation of MoO$_2$ nanorows, the surface represents an interesting nanostructured template suitable for the controlled adsorption of atoms, nanoclusters and molecules [25, 174].

Annealing the Mo(110) surface at a slightly lower temperature (1225 K) for 2 min and cooling down in an O$_2$ atmosphere of $1 \times 10^{-7}$ mbar results in the formation of oxygen adatoms on the MoO$_2$/Mo(110) surface. A typical STM image of the MoO$_2+x$/Mo(110)
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

surface is shown in Fig. 5.14a, where oxygen adatoms appear as bright protrusions. Oxygen adatoms are adsorbed on top of the Mo oxide nanorows, which are visible in Fig. 5.14a, forming a perfectly-aligned double row structure. Each adatom results in the local formation of a MoO$_3$ cluster on the surface. The average distances between two adjacent oxygen adatoms along and perpendicular to the nanorow direction are equal to approximately 1 nm and 1.2 nm, respectively, and dictated by the MoO$_2$(010) layer.

DFT calculations have been performed to identify the correct model for the MoO$_2$/Mo(110) surface. In order to simulate the MoO$_2$/Mo(110) system, a pair of oxygen adatoms (green spheres in Fig. 5.13) was placed on the MoO$_2$/Mo(110) surface. The position of these adatoms on the surface was chosen on the basis of STM images. The resulting model of the MoO$_2$/Mo(110) surface is shown in Fig. 5.13. It is noted that oxygen adatoms lead to the local formation of MoO$_3$ clusters. As a result, the Mo atoms forming these clusters are pulled away from the surface (see Fig. 5.13 right). The partial charge density calculated in the range from $E_F$ to 1.5 V is compared to experimental STM data in Fig. 5.14 and shows a very good agreement.

![Figure 5.13.: Top (left) and side (right) views of the calculated relaxed O-MoO$_2$/Mo(110) structure. The Mo and O atoms are denoted by blue and red spheres, respectively. The two oxygen adatoms are indicated by green spheres.](image)

Oxygen adatoms are stable on the MoO$_2$/Mo(110) surface if imaged by STM at any negative bias or at a positive bias smaller than 1.5 V applied to the sample. At a positive bias higher than 1.5 V oxygen adatoms can be desorbed from the surface. Fig. 5.15 shows consecutive images taken from the same area of the MoO$_2$/Mo(110) surface.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.14.: An experimental STM image (12.5 nm x 15.5 nm, $V_b = 1.5$ V) (a) compared to the partial charge density of the relaxed MoO$_{2+x}$/Mo(110) system simulated in the range from $E_F$ to 1.5 V (b). The inset in (b) shows the surface unit cell.

...after applying positive voltage pulses of 3 V and 4 V for a short time (100 μs). The voltage pulse of 4 V leads to the desorption of oxygen adatoms from the surface area, which is 7 nm in diameter (approximately three oxide nanorows). In turn, the 3 V pulse removes oxygen from the smaller area, which is 5 nm in diameter.

Desorption of atoms from a surface by STM can occur by several mechanisms. The STM system consists of an atomically-sharp metal tip, a sub-nanometer sized vacuum gap, and a conducting sample upon which a bias voltage is placed. The bias voltage allows electrons to quantum mechanically tunnel through the vacuum and these electrons can be responsible for atom desorption. The phenomenon, when tunneling electrons are used for a controlled excitation of adsorbed atoms or molecules, which leads to manipulation and charging of atoms and molecules or bond breaking between the molecular fragments, is called inelastic electron tunneling [13, 175–178]. In this process low energy tunneling electrons (or holes) are injected to the atom (or molecule) located on a surface by positioning the tip above the target. The tunneling electron energy is transferred to an atom/molecule through a resonance state leading to various (single and multi-
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.15: A sequence of low-temperature STM images taken from the same area of the MoO$_{2+x}$/Mo(110) surface (size 30 nm × 40 nm, $V_{sample} = 1.5$ V, $I_t = 1.0$ nA, 78 K): (a) the initial STM image, (b)–(d) STM images after applying 4 V pulses. White crosses on panels (a)–(d) show the positions where the pulses were applied.
5. Oxygen adatoms and Fe nanoclusters on the MoO_2/Mo(110) surface

In this process, the maximum tunneling-electron-energy can be controlled by adjusting the applied bias, and the probability and the excitation rate can be varied by changing the tunneling current (i.e. the number of tunneling electrons per second). Another consequence of the voltage applied across such a small distance is that a large electric field is created between the sample and the tip. Such a field can be used for manipulation of polarised atoms and molecules, which will experience either attractive or repulsive force depending on the bias polarity [185]. In the following, a distinction between these two phenomena will be drawn by examining effects of the bias voltage and tip-sample separation on desorption of adatoms.

![Graph](image)

**Figure 5.16:** The dependencies of threshold desorption voltage on the pulse length. The dependencies of the threshold voltage on the pulse duration measured at different tip-sample distances indicates that the threshold voltage at all distances and pulse lengths is not lower than 1.5 V. A strong dependence of the threshold voltage on the tip-sample distance it also observed.

The dependencies of threshold desorption voltage on the pulse length (Fig. 5.16) as well as the calculated DOS associated with the oxygen adatom on the oxidised molyb-
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

denunm surface (Fig. 5.17) favour the inelastic tunneling induced desorption scenario. The dependencies of the threshold voltage on the pulse duration measured at different tip-sample distances (Fig. 5.16) reveal two distinct features. First, the threshold voltage at all distances and pulse lengths is not lower than 1.5 V. This is in agreement with the calculated PDOS of the oxygen adatom demonstrating the unoccupied states just above 1.5 eV (Fig. 5.17). Therefore, tunneling into these empty states can produce vibrational excitations leading to breaking chemical bonds between the oxygen adatom and MoO$_2$ tri-layer structure underneath. Fig. 5.16 also demonstrates strong dependence of the threshold voltage on the tip-sample distance. This is in agreement with the inelastic tunneling induced oxygen desorption. Indeed, higher voltages are needed to reach the same tunneling current at larger tip-sample distances. At the same time, the tunneling current should be above a critical, minimal value because of the finite vibrational lifetime for the oxygen adatom on the MoO$_2$/Mo(110) surface similarly to that for Si-H system discussed in the first publications on inelastic tunneling desorption [13]. The necessity to reach minimal current value rather than cumulative number of electrons transferred is responsible for the different saturation threshold voltages observed at different tip-sample distances in Fig. 5.16. This also explains the dependence of the desorbed area on the bias voltage at the same tip-sample distance (Fig. 5.15). Because of strong exponential dependence, the tunneling current is maximal under the tip while the number of electrons flowing through the laterally shifted surface atoms is substantially smaller. It can be insufficient for initiation of vibrational excitations on further located oxygen adatoms. At increasing bias voltages (consequently, tunneling currents) vibrational excitations on the oxygen adatoms located further from the tip apex increase and therefore the size of the area cleared from adatoms.

A controlled lithography via desorption of atoms from surfaces due to inelastic electron tunneling has been previously demonstrated on the H-passivated Si(100) surface [13]. Model calculations have indicated that the extremely high current densities present in the STM can produce multiple-vibrational excitation through inelastic electron tunneling.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.17.: Calculated DOS associated with the oxygen adatom on the oxidised molybdenum surface. The PDOS of the oxygen adatom demonstrates unoccupied states just above 1.5 eV. Tunneling into these empty states can produce vibrational excitations leading to breaking chemical bonds between the oxygen adatom and MoO$_2$ tri-layer structure underneath.
and in some cases the deposited energy can be sufficiently high to cause desorption. It was observed that, when the energy of incident electrons was greater than the threshold energy (achieved by applying 6.5 V bias to the surface), the H atoms have been desorbed from the Si(100) surface at a nearly constant yield [13]. Our data support the proposed mechanism of multiple-vibrational excitation as a result of inelastic electron tunneling. The observed threshold bias of 1.5 V for an oxygen desorption indicates that the O-MoO$_2$ bond is weaker than the H-Si bond.

In order to study the influence of an electric field on the extra-oxygen-molybdenum bond DFT calculations have been performed on a MoO$_3$ cluster to minimise calculation time. An electric field of different strength has been applied and the system has been relaxed. The changes in total energy of the O-MoO$_2$/Mo(110) system as a function of an extra-O-Mo distance calculated for electric fields of different strength (up to $\pm 1.25\text{ eV }\AA^{-1}$) are shown in Fig. 5.18. For both “positive” and “negative” electric fields applied perpendicular to the O-MoO$_2$/Mo(110) system, which correspond to the positive and negative sample bias, respectively, the field strength is not sufficient to break the O-MoO$_2$ bond for an oxygen adatom removal. Even at a very high field of $-1.25\text{ eV }\AA^{-1}$ (which corresponds to approximately $-10\text{ V}$ sample bias) the energy barrier necessary to overcome for an adatom removal is reduced by 40% only. Furthermore, results for the positive sample bias, when the desorption of oxygen adatoms has been observed, show no significant reduction of the energy barrier. This indicates that an electric field can not be responsible for the desorption of oxygen adatoms. Note also that applying high bias voltages at distances when tunneling current was below the noise level in STM experiments did not initiate the oxygen adatom desorption. This also highlights the importance of tunneling electrons rather than electric field for the desorption of oxygen adatom from the MoO$_{2+x}$/Mo(110) surface.

The use of tunneling electrons to desorb oxygen adatoms from the MoO$_{2+x}$/Mo(110) surface makes controlled STM lithography with nanometer resolution possible. Tip movement along the surface produces a nanoscale pattern, with a minimum feature size of
Figure 5.18.: The total energy of the O-MoO₂/Mo(110) system as a function of an extra-O-Mo distance plotted for electric fields of different strength. The left graph shows results for a positive sample bias. The right graph shows results to a negative sample bias.

just 5 nm. By moving the STM tip in a controlled fashion, information can be written, read and erased by applying specific biases between the surface and the tip. An example of nanoscale writing is shown in Fig. 5.19.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.19.: The words TCD, NANO and SFI are written on the MoO$_{2+x}$/Mo(110) surface by moving the STM tip in a controlled fashion.
5. Oxygen adatoms and Fe nanoclusters on the $\text{MoO}_2$/Mo(110) surface

5.4. Conclusion

In summary, using scanning tunnelling microscopy and density functional theory calculations it was shown that high-temperature oxidation of the Mo(110) surface under specific conditions results in the oxygen rich $\text{MoO}_{2+x}/\text{Mo}(110)$ surface, exhibiting perfectly-aligned double rows of oxygen adatoms. These adatoms can be removed from the surface by scanning (or pulsing) at positive sample biases greater than 1.5 V. Experimental data and DFT calculations suggest that inelastic electron tunneling is responsible for the adatom desorption. Tip movement along the surface can be used for controlled lithography at nanoscale, with a minimum feature size of just 5 nm. By moving the STM tip in a predetermined fashion, information can be written, read and erased by applying specific biases between the surface and the tip.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

5.5. Nucleation of Fe on the MoO$_2$ surface

5.5.1. Introduction

In this section the MoO$_2$/Mo(110) surface is used as a template for the growth of ordered arrays of Fe nanoclusters. We employ scanning tunnelling microscopy (STM), density functional theory (DFT) simulations and X-ray magnetic circular dichroism (XMCD) to study the nucleation, structure, and magnetic properties of the Fe nanoclusters. The results obtained provide important information on Fe nanoclusters grown on the oxidised Mo(110) surface and will be of value for the development of spin-electronics.

5.5.2. Experimental

The Mo(110) single crystal was prepared as described in the previous section. The quality of the substrate was verified by LEED and STM before the deposition of Fe. Fe was deposited from an electron-beam evaporator at a rate of 0.1 monolayer (ML) per minute. The substrate was kept at RT during deposition. After deposition, the sample was transferred into the STM and cooled down to 78 K. XMCD measurements of the Fe/MoO$_2$/Mo(110) system were performed at the D1011 beamline at MAX-lab synchrotron in Lund, Sweden. Fe 2p X-ray absorption (XA) spectra were recorded using sample drain current. The relative intensities of the spectra were normalised to the same continuum jump at the photon energy of 745 eV. The photon energy resolution was set to 200 meV at the Fe L$_3$-edge ($\approx$ 710 eV). For XMCD measurements, a switchable magnetic field of 0.05 T was applied.

5.5.3. Results

MoO$_2$ grows on the Mo(110) surface in the form of an O-Mo-O trilayer, which exhibits well-ordered oxide nanorows separated by 2.3 nm [24]. These rows are oriented along the [113] crystallographic direction of the Mo(110) surface. Deposition of 0.3 ML of Fe on the MoO$_2$/Mo(110) surface leads to the formation of small nanoclusters, which have a
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.20.: STM images of 0.3 ML of Fe on MoO$_2$/Mo(110), $V_b = -0.5$ V, $I_t = 1.10$ nA, 40 nm $\times$ 40 nm, 78 K.

Figure 5.21.: STM images of 0.7 ML of Fe on MoO$_2$/Mo(110), $V_b = 1.2$ V, $I_t = 1.00$ nA, 40 nm $\times$ 40 nm, 78 K.
round shape and are 6 Å in diameter (Fig. 5.20). Most of these nanoclusters are found as individual structures on the surface. However, some of them form larger structures with rectangular, triangular and square shapes, consisting of two, three and four small Fe nanoclusters, respectively. All these nanostructures are located on top of the oxide rows, with a variable separation between them. In the case of higher Fe coverage ((0.6–0.9) ML) the separation between nanoclusters on the MoO$_2$/Mo(110) surface becomes much smaller. It is clear from Fig. 5.21 that at such coverage the Fe nanoclusters self-assemble into linear nanocluster arrays. These arrays follow the [113] direction of the substrate oxide rows.

In order to confirm the number of Fe atoms in the round shaped nanoclusters formed on the MoO$_2$/Mo(110) surface, DFT calculations were performed using the VASP software.

![Figure 5.22.](image)

Figure 5.22.: Top (left) and side (right) views of the calculated relaxed Fe/MoO$_2$/Mo(110) structure. The Mo, O and Fe atoms are denoted by blue, red and grey spheres, respectively.

The MoO$_2$/Mo(110) system has been initially relaxed as described in Sec. 5.2 using VASP. The resulting surface was then used as a “substrate” to model the Fe nanocluster. VASP was also employed for the simulation of the round shaped Fe nanocluster on the MoO$_2$/Mo(110) system. Here, an energy cutoff of 300 eV was applied. The Γ-point was used to sample the Brillouin zone. The Fe/MoO$_2$/Mo(110) system was relaxed prior to any further calculations. Fe nanoclusters with 4, 7, 9, 10, and 11 atoms were considered in order to fit an experimentally observed cluster size with a diameter of 6 Å. Simulations of 9 and 11 atoms have shown that some Fe atoms diffuse into the MoO$_2$/Mo(110)
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.23.: Occupied state STM image of the Fe nanocluster (1.4 nm x 1.4 nm, $V_b = 1$ V), left panel, compared to the simulated partial charge density (from $E_F$ to 1 V), right panel.

substrate. This suggests bonding between Fe and MoO$_2$, which was ruled out on the basis of the Fe X-ray absorption (XA) spectra, which have a shape typical of the XA spectrum of a metal (see Fig. 5.26). The system with 7 and 10 atoms resulted in a smaller cluster size than experimentally observed.

The Fe cluster with 4 atoms was found to have the lowest energy and a size of 6 Å in diameter, which is in good agreement with the experimental data. Four different starting configurations (geometrical positions) for the Fe nanocluster consisting of 4 atoms have been examined. Three of them either did not resemble the experimentally observed geometrical structure, diverged or had a higher energy than the simulated Fe nanocluster shown in Figs. 5.22 and 5.23. The resulting relaxed model of the Fe nanocluster on the MoO$_2$/Mo(110) surface is shown in Fig. 5.22. In order to further compare DFT results with the STM images, the partial charge density of the Fe on the MoO$_2$/Mo(110) surface has been simulated in the range between the Fermi energy ($E_F$) and 1 V. The calculated image is compared with the STM data in Fig. 5.23 and show very good agreement. However, the simulated image exhibits more features than the measured STM image. The reason for this could be the neglect of the tip-sample convolution within partial charge density simulations.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.24.: Top (left) and side (right) views of the calculated relaxed three Fe nanoclusters on the MoO$_2$/Mo(110) structure. The Mo, O and Fe atoms are denoted by blue, red and grey spheres, respectively.

Figure 5.25.: Occupied state STM image of the Fe nanocluster (1.4 nm x 1.4 nm, $V_b = 1$ V), left panel, compared to the simulated partial charge density (from $E_F$ to 1 V), right panel.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

![Fe L\textsubscript{3} spectra](image)

Figure 5.26.: Fe 2p XA spectra measured at 150 K from 0.7 ML of Fe nanocluster arrays on MoO$_2$/Mo(110) with the magnetic field of 0.05 T applied in two opposite directions ($-B_{max}$ and $+B_{max}$). The XMCD spectrum is multiplied by a factor of 10 for clarity.

In order to simulate the triangular Fe nanocluster on the MoO$_2$/Mo(110) surface, the MoO$_2$/Mo(110) slab size needed to be doubled. This led to a quite large number of atoms ($\approx 400$) within the unit cell. Three of the 4 Fe atoms nanoclusters were positioned in close proximity to form a triangle. The results of the relaxed system are presented in Fig. 5.24. The partial charge density of the Fe on the MoO$_2$/Mo(110) surface has been simulated in the range between the Fermi energy ($E_F$) and 1 V, in order to further compare DFT results with the STM images. Fig. 5.24 shows the comparison of the calculated image with the STM data. The two images are in very good agreement and suggest that triangular Fe nanoclusters are consisting of three smaller clusters.

The XA spectra from the Fe nanocluster arrays on the MoO$_2$(010)/Mo(110) surface were measured at RT and 150 K at normal X-ray incidence and grazing X-ray incidence. A magnetic field of 0.05 T was applied in two opposite directions. Fig. 5.26 shows the grazing X-ray incidence spectra taken at 150 K. The Fe $L_3$ spectra exhibit two structures: the main asymmetric peak A and a high-energy shoulder A*. The latter indicates that
some intermixing occurs at the Fe/MoO₂ interface, resulting in bonding between some of the Fe atoms and the top O layer of the substrate. However, the energy and the shape of the main peak A are typical for the XA spectrum of Fe metal. Grazing X-ray incidence XMCD measurements for the Fe nanocluster arrays show very small dichroism at RT and a prominent difference between the two opposite magnetic field directions at 150 K (Fig. 5.26). The same results were obtained for the separated nanoclusters on MoO₂/Mo(110). This indicates a superparamagnetic behaviour of both the Fe nanocluster arrays and separated Fe nanoclusters on the MoO₂/Mo(110) surface. No magnetic hysteresis loop with remanence was observed at 150 K, similar to the case of Fe/Ge(001). This suggests that the individual nanoclusters within the array are still too well-separated from each other to result in a ferromagnetic response of the whole system.

5.6. Nucleation of Fe on the MoO₂+x surface

The initial nucleation of Fe was also studied on the MoO₂+x/Mo(110) surface exhibiting extra oxygen (see Fig. 5.15 on page 101). Again, Fe was deposited from an electron-beam evaporator at a rate of 0.1 ML min⁻¹. The substrate was kept at RT during deposition. After deposition, the sample was transferred into the STM and cooled down to 78 K.

Deposition of 0.5 ML of Fe on the MoO₂+x/Mo(110) surface leads to the formation of elongated nanowires, which have a zigzag shape and are up to 20 nm in length (Fig. 5.27). Most of these nanowires are found as individual structures on the surface. All these nanowires are located on top of the oxide rows and follow the [113] direction of the substrate oxide rows.

It is suggested that Fe interacts with the oxygen to form Fe oxide nanowires on the MoO₂+x/Mo(110) surface. There are two types of oxygen structures within the top two layers of the MoO₂+x/Mo(110) surface: (i) oxygen adatoms forming linear arrays along the oxide nanorow with an average separation of 1 nm between them and (ii) the rows of oxygen atoms forming the top layer of the MoO₂ oxide. The angle between those two
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

Figure 5.27.: STM images of 0.5 ML of Fe on MoO$_{2+x}$/Mo(110), $V_b = -0.5$ V, $I_t = 1.10$ nA, 40 nm x 40 nm, 78 K. Deposition of Fe on the MoO$_{2+x}$/Mo(110) surface leads to the formation of elongated nanowires (left panel), which have a zigzag shape and are up to 20 nm in length (right panel).

structures is $30^\circ$ (see Fig. 5.12 on page 96 and Fig. 5.14 on page 100). The position of Fe atoms on the surface is defined by oxygen atoms forming the top layer. However, Fe atoms nucleate around oxygen adatoms. This leads to the formation of zigzag structures.
5. Oxygen adatoms and Fe nanoclusters on the MoO$_2$/Mo(110) surface

5.7. Conclusion

In summary, using scanning tunnelling microscopy and density functional theory calculations it was shown that the MoO$_2$/Mo(110) surface is a suitable template for the growth of well-ordered, uniformly-sized Fe nanoclusters and nanocluster arrays.

At low coverage, Fe self-assembles into small clusters, which are well separated on the MoO$_2$/Mo(110) surface. Linear Fe nanocluster arrays that follow the Mo oxide rows are spontaneously formed on the MoO$_2$/Mo(110) surface at room temperature if the Fe coverage exceeds 0.5 ML. The observed Fe nanoclusters and nanocluster arrays show a superparamagnetic behaviour as measured by X-ray magnetic circular dichroism. Deposition of Fe on the MoO$_{2+\delta}$/Mo(110) surface leads to the formation of continuous, zigzag-shaped nanowires with a length of up to 20 nm.
6. Conclusions

6.1. Fe nanostructures on the Ge(001) surface

AES, LEED and STM and XMCD have been used to study the self-assembly and magnetic properties of Fe nanoclusters on the Ge(001) substrate. The Ge(001) surface exhibits the well known (2 × 1) surface reconstruction at RT as measured by LEED and the c(4 × 2) reconstruction at 78 K as measured by LTSTM. The results obtained show that the Ge(001) reconstructed surface is a suitable template for the growth of homogeneous Fe nanoclusters. The size of the nanoclusters depends on the temperature of the substrate.

Deposition of (0.05–0.30) ML of Fe at RT and immediate cooling results in the formation of 4-atom Fe nanoclusters. The Fe nanoclusters are 9 Å × 9 Å wide and ≈ 1.1 Å in height. The Fe nanoclusters nucleate at specific sites on the Ge(001) surface. The clusters are well ordered on the substrate and have uniform size. Relaxation of the Fe/Ge(001) system at room temperature after deposition leads to the formation of nanoclusters with 16 Fe atoms.

Annealing the Fe/Ge(001) system results in the rearrangement of the clusters. After annealing at 420 K, Fe nanoclusters form nanorows on the substrate. The width of the nanostructures is 9 Å, due to cluster mobility at such temperature. The c(4 × 2) reconstruction of the Ge(001) surface determines the width of the nanorows. At higher annealing temperatures larger unordered non-uniform clusters are formed. At initial nucleation, the interaction between Fe and the Ge(001) surface is strong enough to pro-
vide equivalent nucleation sites. At the beginning Fe atoms adsorb on top of Ge dimers breaking the dimer bonds. After that, additional Fe atoms diffuse on the surface to form nanoclusters around the initial nucleation sites. This indicates quite a strong Fe–Fe interaction. In turn, Fe nanoclusters grow up to a limited size at RT. This means that the strength of the Fe–Fe interaction depends significantly on the size of the self-assembled Fe nanocluster.

It has been shown that an element-specific method like XMCD is required to measure the correct magnetisation of the deposited Fe. Other bulk sensitive methods like SQUID and AGM are problematic because of the high magnetic contribution from substrate impurities. This contribution is found to be 10 times larger than the one expected from the small amount of Fe deposited. XMCD measurements indicate that the Fe nanoclusters and nanorow structures formed on the Ge(001) surface show a superparamagnetic behaviour.

6.2. Oxygen adatoms on the MoO$_2$/Mo(110) surface

The oxidation of Mo(110) was studied and it was found that a bulk-like oxide of MoO$_2$(010) grows epitaxially on the surface at 1275 K and $1 \times 10^{-7}$ mbar oxygen pressure. LEED and STM data were used to give a detailed analysis of the oxide surface structure. From this experimental data, and through the use of DFT calculations, a model was built. It was shown that a strained bulk-like MoO$_2$(010) film is in excellent agreement with the experimental data. Slightly changing the oxidation temperature to 1225 K leads to the formation of oxygen adatoms on the oxide rows of the MoO$_2$/Mo(110) surface. DFT calculations suggest that the presence of these oxygen adatoms is responsible for the localised formation of MoO$_3$.

It has furthermore been shown that tunneling electrons can be used to desorb oxygen adatoms from the MoO$_2$+$\Delta$+/Mo(110) surface. This effect makes controlled STM lithography with nanometer resolution possible. Tip movement along the surface produces a
nanoscale pattern, with a minimum feature size of just 5 nm. By moving the STM tip in a controlled fashion, information can be written, read and erased by applying specific biases between the surface and the tip.

6.3. Nucleation of Fe on the MoO$_2$/Mo(110) and MoO$_{2+x}$/Mo(110) surface

The results obtained show that the MoO$_2$/Mo(110) surface is a suitable template for the growth of well-ordered, uniformly-sized Fe nanoclusters and nanocluster arrays. At low coverage, Fe self-assembles into small clusters, which are well separated on the MoO$_2$/Mo(110) surface. Linear Fe nanocluster arrays that follow the Mo oxide rows are spontaneously formed on the MoO$_2$/Mo(110) surface at room temperature if the Fe coverage exceeds 0.5 ML. The observed Fe nanoclusters and nanocluster arrays show a superparamagnetic behaviour as measured by XMCD. Deposition of Fe on the MoO$_{2+x}$/Mo(110) surface leads to the formation of continuous, zigzag-shaped nanowires with a length of up to 20 nm.
7. Future work

As potential future work the deposition of other magnetic TM (e.g. Co, Ni) and/or a combination of these on the Ge(001) and the MoO₂/Mo(110) surface could be studied. Here the question of whether these elements cluster in the same manner as Fe or not arises.

The deposition of Fe, Co and Ni on other, similar substrates like the Si(001) and W(110) surface could be investigated by STM measurements and DFT calculations. Si(001) has similar properties to the Ge(001) surface. For example, the Si(001) surface exhibits the same surface reconstructions as the Ge(001) surface, i.e., a (2 x 1) surface reconstruction at room temperature and a c(4 x 2) reconstruction at lower temperatures. A suppressed p(2 x 2) reconstruction is also present on this surface. These surface reconstructions could lead to similar nucleation sites for, e.g., deposited Fe. The W(110) surface also has properties similar to the Mo(110) surface. Oxidising the W(110) surface also leads to the formation of oxide nanorows which can act as a template for deposited materials like, e.g., Fe. Here, a potential question to be answered would be whether or not Fe also forms nanoclusters on W(110) and if these nanoclusters have similar properties to those deposited on the Mo(110) surface.

As another future work, spin-polarised DFT calculations to simulate the magnetic properties of the Fe nanoclusters deposited on the Ge(001) and the Mo(110) surface could be performed. It is also possible to simulate XMCD spectra using the ELK DFT code. These simulated XMCD spectra could be compared to the measured XMCD spectra presented in this thesis.
7. Future work

Furthermore, other substrates suitable for self-assembly could be identified. The deposition of Fe, Co, and Ni on these newly identified surfaces could be studied by STM measurements. Ideally, a surface would be identified on which the cluster size of e. g. deposited Fe exceeds the superparamagnetic size limit and exhibits ferromagnetic properties.
A. Single crystalline W[001] tips

In quantum mechanics, a single-electron state in an atom is described by a set of wave functions associated with a particular electron energy, orbital momentum, spin and momentum projections on the quantization axis. The spatial distribution of these wave functions (atomic orbitals) determines the probability for an electron with quantum numbers $n, l, m_l, m_s$ to be detected in a particular volume of space. This theoretical formalism allows one to explain the behavior of the electron systems on the atomic level. However, for a long time the electron orbitals could not be directly observed in experiments. This only became possible with the invention of scanning probe microscopy (SPM) methods [182-184]. These use sharp tips to image [48] and manipulate [185] atomic structures, to identify the chemical nature of atomic species [186, 187] and to reveal magnetic contrast [188] on surfaces.

The ultimate vertical resolution of scanning tunneling microscopy (STM) is determined by exponential dependence of the tunneling current between a sample and a tip [189]. The lateral resolution can be limited by the technical characteristics of a microscope. One of the first theoretical explanations of the atomic resolution was proposed by Tersoff and Hamann [190, 191] who considered a spherically symmetric $s$-wave tip. The theory was further advanced by Chen [192-194] who showed that the tunneling matrix elements are proportional to the derivatives of the wave functions of electrons involved in the tunneling process. Therefore, a variety of electron states can contribute to experimental images and, consequently, the limit of lateral resolution is physically restricted by spatial distribution of the tip and surface wave functions. However, it took
two decades after the invention of STM to measure the asymmetric charge distribution related to apex atomic orbitals in atomic force microscopy (AFM) [195, 196] and STM [197–199] experiments. The observed subatomic features [195–199] still could not be unambiguously identified with single-electron orbitals. Recently, two legs of the MnNi tip $d_{x^2}$-orbital ($l = 2, m_l = 1$) were resolved in STM experiments on a Cu(014)-O surface [200, 201]. Essential distance dependence of the atomically resolved Cu(014)-O STM images [201, 202], however, did not allow to reveal the conditions where this tip orbital channels most of the tunneling current. The observed distance dependence, leading to chemical selective imaging of either copper or oxygen atomic rows of the Cu(014)-O surface [187, 201, 202], was attributed to the change of relative contribution of different electron orbitals of the surface atoms. However, the distance-dependent contribution of different $d$-orbitals could be proved experimentally only by direct experiments demonstrating subatomic features of different symmetry at different gap spacings. For example, such experiments can be done using a combination of $d$ electron tip states and $s$ or $p_z$ surface electron states.

In this work, Chaika et al. use the reciprocity principle of STM, and probe different $d$-orbitals of the W[001] tip atom by localised carbon orbitals of the highly oriented pyrolytic graphite (HOPG) surface atoms at different bias voltages and tip-sample separations. Using distance-dependent STM measurements with sub-Ångström lateral resolution and density functional theory (DFT) calculations the possibility of selecting a particular tip electron orbital for high-resolution imaging was demonstrated. This is
A. Single crystalline W[001] tips

Figure A.2.: (a) Schematic view of a W[001] tip with the \( d_{3z^2-r^2} \) (left), \( d_{x\pm yz} \) (centre) or \( d_{x^2-y^2} \) (right) orbital at the apex above the graphite surface. (b)–(d) Pseudo 3D images of the atomic features measured with W[001] tips at different tunneling parameters as indicated in Fig. A.6. The images are explained by overwhelming contribution of \( d_{3z^2-r^2} \) (b), \( d_{x\pm yz} \) (c) or \( d_{x^2-y^2} \) (d) electron states of the tip atom. 2.5 Å × 2.4 Å STM images were plotted with the WSxM software [204].
A. Single crystalline W[001] tips

Figure A.3.: (a)–(d) 11 Å × 11 Å STM images of HOPG(0001) measured with polycrystalline W tips. The images demonstrate a typical hexagonal pattern (a) and subatomic features with two- (b), three- (c) and four-fold (d) symmetry. The tunneling parameters are \( U = -30 \text{ mV}, I = 0.25 \text{ nA} \) (a); \( U = -25 \text{ mV}, I = 0.25 \text{ nA} \) (b); \( U = -200 \text{ mV}, I = 0.4 \text{ nA} \) (c); \( U = 45 \text{ mV}, I = 0.25 \text{ nA} \) (d). The STM images were background subtracted and smoothed by 5 × 5 matrix.

confirmed by reproducing the shapes of the W 5\( d_{x^2-y^2} \) and 5\( d_{z^2} \) atomic orbitals.

The experiments were carried out in an ultra-high vacuum (UHV, \( p < 1 \times 10^{-10} \text{ mbar} \)) chamber equipped with a room temperature STM (GPI-300). STM images were measured in the constant current mode. Tungsten tips were fabricated from [001]-oriented 0.5 mm × 0.5 mm × 310 mm single crystalline bars using electrochemical etching. Fig. A.1 shows typical scanning electron microscopy (SEM) images of chemically etched W[001] tips. Before the experiments, the tips were cleaned from contaminants and sharpened in the UHV chamber by electron beam heating and Ar ion bombardment [203]. Only clean W[001] tips which could to resolve a honeycomb surface structure (Fig. A.2(a)) directly after tip approach were used for all experiments. All other tip treatments (e.g., continuous scanning or voltage pulses) which could lead to a mass transport from the sample to the tip were excluded. The distance dependence of the STM images was measured by varying the gap resistance with fixed bias voltages applied to the sample. Only sequences without tip changes were analysed.

Fig. A.2(a) shows the atomic structure of graphite. Carbon atoms within each layer are strongly bonded via \( sp^2 \) bonds and form in-plane honeycomb patterns while the neighbouring layers are weakly bonded via van der Waals forces. The honeycombs in the adjacent layers are shifted in the \((x - y)\)-plane so that only three of six carbon atoms
A. Single crystalline W[001] tips

Figure A.4.: Partial DOS associated with s- and p-orbitals of graphite(0001) surface atoms.

in each hexagon (namely, α atoms) lie directly above the atoms of the underlying layer, while the three others are located above the hollow sites (β atoms). Because of their non-equivalence, α and β atoms demonstrate different relaxations interacting with a SPM tip [205]. As a result, for most tunneling conditions [205–207], only one of two carbon atoms is resolved in HOPG(0001) STM images (Fig. A.5(a)). Partial density of electron states (PDOS) calculations, performed for a 20-layer graphite slab within the tight-binding (TB) method (Fig. A.4), show that both α and β atoms have $p_z$ electron states near the Fermi level ($E_F$) that are suitable for studies of the fine tip electronic structure effects in SPM. The subatomic features with two-, three-, and four-fold symmetry have been observed previously in AFM experiments [196] and explained by [011]-, [111]-, and [001]-oriented clusters at the apex of polycrystalline W tips. Similar subatomic features were observed in our STM experiments with polycrystalline W tips (Fig. A.5(b)–(d)). In

\[\text{The TB parameters for } s- \text{ and } p-\text{states of graphite were taken from the tables given in the book of Harrison [208] with the } V_{ppr} \text{ coefficient reduced by a factor of 2 as suggested in Problem 3.3 in Chapter 3 of that book. The interactions within three nearest-neighbour coordination spheres were taken into account.}\]
order to improve resolution, W[001] tips were used, which would be more stable because of higher apex atom coordination and would reveal a greater number of details on the subatomic scale [196]. In experiments with W[001] tips (Fig. A.5(b)) STM images were reproducibly acquired demonstrating a regular lattice of well-resolved four-fold split subatomic features although for most tunneling conditions typical hexagonal patterns (Fig. A.5(a)) were observed. The experimental image in Fig. A.5(c) qualitatively reproduces the shape of the W 5d_{x^2-y^2} electron orbital calculated within the Thomas-Fermi approximation shown in Fig. A.5(d). The difference between the calculated and experimental features (Fig. A.5(b), (d)) could be caused by slight tip tilting and strong tip-sample interaction affecting the tip electronic structure and increasing experimental noise because of graphite surface layer oscillations [209]. The observation of four subatomic maxima was found to be both bias and gap resistance dependent. The bias voltage allows to select the range of energies of the electron states involved in the tunneling. The partial density of electron states for the W[001] tip (Fig. 13 of Ref. [202]) suggests that one can apply a bias voltage in the way that either the d_{x^2-y^2} or d_{3z^2-r^2} states of the tip could provide maximum contributions. Small positive voltages (up to 50 mV) would be optimal for achieving highest lateral resolution because of large PDOS associated with d_{3z^2-r^2} tip states slightly below E_F [202]. In contrast, at a sample bias around -100 mV one can expect a significant contribution from the d_{x^2-y^2}-orbital (Fig. A.5(b), (c)). The ideal situations when d_{3z^2-r^2} or d_{x^2-y^2} atomic orbitals of the tip can be responsible for STM imaging are shown in Fig. A.7(b). In fact, STM images with four-fold split atomic features at small negative voltages (up to -150 mV) could be resolved. Additionally, the spatial distribution of electron wave functions can result in a strong dependence of STM images on the tip-sample distance [201, 210, 211]. This is illustrated by gap resistance dependences of HOPG(0001) STM images at different bias voltages shown in Fig. A.6. The biases were selected on the basis of PDOS calculations [202], to achieve situation when tunneling current is controlled by d_{x^2-y^2} (Fig. A.6(a)), d_{3z^2-r^2} (Fig. A.6(b)) or a sum of different d-states (Fig. A.6(c)). For all sequences at larger distances (smaller
A. Single crystalline W[001] tips

Figure A.5.: (a), (b) 6Å x 6Å STM images of HOPG(0001) surface measured with a W[001] tip at $I = 0.7\,\text{nA}$ (a) and $I = 1.6\,\text{nA}$ (b). $U = -100\,\text{mV}$. (c) A 2Å x 2Å region indicated by the dashed square in panel (b). (d) Electron probability density distribution for the W 5$d_{z^2}$-orbital in the plane $z = 1.0\,\text{Å}$ from the nucleus. This plane was selected because of necessity of extremely small tip-sample separations for subatomic imaging and due to the fact that carbon orbitals are less localised than tungsten orbitals (see text and Fig. A.8).

currents) the honeycomb pattern is resolved in accordance with TB calculations (Fig. A.4). With increasing current (i.e. decreasing distance) it transforms into a hexagonal pattern where every second carbon atom is resolved [205]. However, the most interesting results were obtained at smaller gap resistances.

For $U = -100\,\text{mV}$, at intermediate gap resistances (Fig. A.6(a), $I = 0.7\,\text{nA}$) the $d_{3z^2-r^2}$-orbital of the tip is mainly responsible for the observed images with spherically symmetric atomic features. Then, with increasing current the atomic features become asymmetric and at some currents (Fig. A.6(a), $I = 1.6\,\text{nA}$ and $I = 1.7\,\text{nA}$) four-fold split subatomic features are observed due to the substantial contribution of $d_{x^2-y^2}$-orbital. The images in Fig. A.2(d) and 5(c) correspond to the situation when this tip orbital is responsible for the STM imaging. Evidently, this can be achieved by a suitable choice of both voltage and distance (Fig. A.6).
A. Single crystalline W[001] tips

Figure A.6.: (a)-(c) Gap resistance (tip-sample separation) dependence of 7 Å × 7 Å HOPG(0001) STM images measured with W[001] tips at three bias voltages of −100 mV (a), 23 mV (b), and −35 mV (c). The tunnelling currents are indicated on each particular frame. The images were background subtracted and smoothed by 5 × 5 matrix. The dashed squares in panels (a), (b) and (c) indicate the regions shown in Fig. A.2(d), 2(b), and 2(c), respectively.
A. Single crystalline W[001] tips

The best resolution can be achieved when the tip $d_{3z^2-r^2}$-orbital is responsible for the tunnelling current. This is demonstrated by the measurements at a sample bias of 23 mV (Fig. A.6(b)). One can see an enhancement of lateral resolution at tunneling currents between (1.0 and 3.9) nA. The most impressive resolution is achieved at $I = 3.9$ nA (Fig. A.6(b)) when the full width at half maximum of the atomic features is slightly below 1 Å. This is close to the physical limit of the resolution related to the spatial distribution of the carbon $p_z$-orbital. The left part of Fig. A.2(a) illustrates the situation when the $p_z$-orbital is imaged with the $d_{3z^2-r^2}$-orbital. With decreasing distance, the atomic features become broader but distinct subatomic features could not be resolved unambiguously.

The most informative tip-sample distance dependence was obtained at $U = -35$ mV which is partially shown in Fig. A.6(c). Firstly, one can see an enhancement of the resolution with decreasing distance. Then, the atomic features become smeared and at some currents ($\approx 5.3$ nA) transformed into double features. Then, in the current range from (5.3–7.2) nA the double features become sharper. And finally, they are rapidly transformed into features with four-fold symmetry ($(7.7–9.1)$ nA). It is seen that in a very narrow range of the tunneling currents, the subatomic features demonstrate a three-fold symmetry ($(7.5–7.6)$ nA) that can be related to simultaneous contribution of both $d_{xz,yz}$ and $d_{x^2-y^2}$ electron orbitals. This sequence proves that the explanation based on the tip cluster orientation [196] can only be partially correct and is not valid in a general case: Different subatomic features can be resolved with the same tip while the most frequently observed double features can be measured in a significantly wider range of the tip-sample distances. The STM image transformation shown in Fig. A.6(c) is determined by two factors: i) the difference in spatial localisation of $d$-orbitals with different $m$ which implies that they can be probed by a carbon $p_z$-orbital at different tip-sample separations and ii) gradually decreasing density of states (DOS) on the further extended tip orbitals ($d_{3z^2-r^2}$ and then $d_{xz,yz}$) because of their substantial overlapping with the carbon $p_z$-orbital. At small distances the PDOS associated with the tip $d_{3z^2-r^2}$-orbital becomes smaller and the experimental conditions can correspond to the models depicted in the
central and right parts of Fig. A.2(a). In these cases two or four distinct maxima can be resolved typical for the $d_{x^2-y^2}$ (Fig. A.2(c)) and $d_{x^2-y^2}$ (Fig. A.2(d)) wave functions.

DFT calculations of the PDOS at the W tip atom interacting with the graphite cluster were performed to prove this interpretation. The ab initio DOS calculations were performed using the VASP program. A plane augmented wave basis [83] was used with an energy cutoff of 400 eV. The electron exchange and correlation was simulated by local density approximation pseudopotentials with a Ceperley-Alder exchange functional [87]. A Γ-centred $(1 \times 1 \times 1)$ $k$-point grid was used for all calculations to sample the Brillouin zone. For the DOS a smearing of 0.2 eV was applied using the Methfessel-Paxton method. The global break condition for the electronic self consistent loops was set to a total energy change of less than $1 \times 10^{-6}$ eV.

The simulated graphite(0001) surface consisted of two constrained unit layer slabs. To model the W tip a pyramid in [001] orientation constructed out of seven unit layer slabs (128 atoms in total) was used. For the tip all atom positions were constrained as well. Tip-sample separations from 1.25 Å up to 4.0 Å were applied to calculate the PDOS dependence on the distance. The spacing between the back of the tip slab and the HOPG was ≈ 7.5 Å for a distance of 4 Å, for all other distances it was correspondingly larger.

The results of DFT calculations presented in Fig. A.7(a) are in a good agreement with the above discussion. The PDOS associated with the $d_{3z^2-r^2}$-orbital decreases drastically when the separation is close to the interatomic distances (below 3.0 Å). The tip $d_{x^2-y^2}$-orbital can dominate at small distances and small negative bias voltages, while $d_{xz}$ and $d_{yz}$ orbitals are not equivalent at distances below 2.25 Å due to the tip-sample interaction, which can lead to doubling subatomic features. Note that PDOS calculations of the fully relaxed W[001] tip-graphite system (to be published elsewhere) give qualitatively the same results. According to the DFT calculations (Fig. A.7(a)), the best lateral resolution can be obtained at small positive sample biases and distances around 3 Å, but four-fold splitting can, in principle, be resolved at very small gap spacings in some ranges of the bias voltages. However, at negative biases from (−50—150) mV the four-
Figure A.7: (a) PDOS associated with different d-orbitals of the W[001] tip apex atom interacting with the graphite(0001) surface. The distances between tip and surface atom nuclei are indicated on each panel. (b) Schematic models of the tunnelling process in the W[001] tip-graphite(0001) system for STM imaging in the empty (left panel) and occupied (right panel) surface state regimes. The PDOS for the models (b) was taken from Ref. [202].
fold splitting can be achieved at somewhat greater distances because the DOS associated with the $d_{x^2-y^2}$ tip orbital exceeds the DOS for other orbitals in the corresponding energy interval of the empty tip electron states (Fig. A.6(a)). It is assumed that the strong tip-sample interaction, inducing uncontrollable fluctuations of the gap spacing at small distances \cite{209}, is the most probable reason why the four-fold splitting could not be observed clearly at positive bias voltages in our experiments. In contrast, the splitting was evident at negative biases (e.g., see Fig. A.5 and Fig. A.6(a), (c)) although the appearance of the four-fold split features is not fully identical. The latter is tightly related to the fact that appearance of four distinct subatomic maxima is essentially distance dependent: very small change in the tip-sample separation can easily modify the shape of the subatomic features or even completely suppress the effect. This is illustrated by calculated electron density maps for the fully-relaxed W[001] tip-graphite system shown in Fig. A.8. In this case the final W-C interatomic distance is 2.38 Å (1.75 Å before allowing atomic relaxations). This slightly exceeds the W-C bond length in tungsten carbide and can be realized in experiments. Fig. A.8(a) reveals that carbon orbitals protrude much further into vacuum than tungsten $d$-orbitals. For that reason even the highly localised W $d_{x^2-y^2}$-orbital (Fig. A.8(b)) can be probed by carbon orbitals. Comparison of the calculated electron density maps in (001) planes located (0.4–0.6) Å below the apex core (Fig. A.8(b), (c)) shows that transition from imaging two-fold to imaging four-fold split subatomic features requires a small (around 0.2 Å) change in the tip-sample separation. This is in line with the tunneling current values indicated in Fig. A.2(c). The experimental tip-sample distances corresponding to imaging particular electron orbitals of the W[001] tip atom can be estimated from the distance dependence of STM images (Fig. A.6) and PDOS calculations shown in Fig. A.7(a). It is reasonable to assume that spherically symmetric features start to smear out at gap spacings corresponding to fading PDOS associated with the $d_{3z^2-r^2}$-orbital. This is observed at distances slightly below 3.0 Å. For our experiments these distances correspond to tunneling currents of (0.7, 3.9 and 2.7) nA at bias voltages of (−100, 23 and −35) mV, respectively. From the values
A. Single crystalline W[001] tips

Figure A.8.: (a)–(c) Calculated electron density distribution for the W[001] tip atom interacting with a graphite(0001) atom shown as a (100) slice through the apex atom (a) and 2 Å x 2 Å (001) slices located 0.4 Å (b) and 0.6 Å (c) below the apex atom. The asymmetrical orbitals in panels (b) and (c) are due to the tip interaction with the surface which is not two-fold symmetrical along the tip axis.

of tunneling currents required for imaging symmetric and four-fold split features (Fig. A.6(a), (c)), and assuming the exponential distance dependence, one can suggest that four-fold and two-fold split subatomic features are observed in the tip-surface separation range of (2.0–2.5) Å. The observed rapid transition from symmetric to multiple subatomic features can be one of the reasons why subatomic contrast was earlier detected with AFM but could not be observed in simultaneous STM experiments [196]: the required distance was not reached in the STM regime but occurred during the tip-surface approaching phase of the probe vibrations in the AFM mode.

For all dependences, at the smallest distances one can see a reverse transformation from hexagonal to honeycomb pattern (lower panels in Fig. A.2(a)-(c)). This is consistent with a “current-distance” dependence observed in [207]. In this regime the honeycomb patterns can mostly be determined by the repulsive tip-sample interaction due to drastically decreased PDOS near $E_F$ (Fig. A.7).

In conclusion, one can fabricate a single crystalline tip with a certain set of wave functions at the apex and adjust the tunneling parameters to select one of them for STM imaging. Note that a tip suitable for high-resolution studies on one surface may not be as effective on another sample because of the necessity of applying different bias voltages. The relative contributions of different atomic orbitals are simultaneously bias-
A. Single crystalline W[001] tips

and distance-dependent because of the overlapping of the tip and sample wave functions. STM topographic images can bear important information on the tip and surface electronic structure that cannot be obtained even with sophisticated spectroscopic techniques. And finally, the single-electron wave functions can be probed in real space and controllably selected for high-resolution STM studies. This possibility can provide the key to success in improving spatial resolution and controllable chemical analysis on an atomic scale.
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