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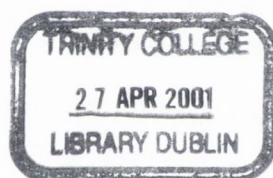
Surface studies of the Fe/Mo(110) and Fe/W(100) epitaxial systems

A thesis submitted to the University of Dublin, Trinity College,
in application for the degree of Doctor in Philosophy
by

Shane Murphy

Physics Department
Trinity College Dublin

October 2000



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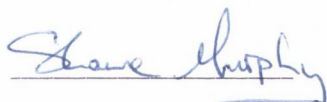
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Shane Murphy

October 2000

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Abstract

This thesis describes the investigation of ultrathin Fe film growth on the Mo(110) and W(100) surfaces, using scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). A general review of the current understanding of epitaxial film growth is given, covering both thermodynamic and kinetic aspects of theory. The experimental set-up and conditions under which the Fe/Mo(110) and Fe/W(100) epitaxial systems were studied are described. This includes a description of the preparation procedure for novel STM tips of MnNi, Fe and Cr, that were used in the study.

For the Fe/Mo(110) system, films in a thickness range of $0.3 \leq \theta \leq 4.7 \text{ ML}$ were deposited on a Mo(110) surface with an average terrace width of $185 \pm 60 \text{ \AA}$. Depositions were carried out at substrate temperatures in the interval $300 \leq T \leq 525 \text{ K}$ and at deposition rates in the range of $0.2 \leq D \leq 1.0 \text{ ML.min}^{-1}$. Near room temperature, the first two Fe layers grow in a layer-by-layer (LBL) fashion - predominantly by the step-flow mechanism, but with some 2D island growth. The first Fe layer is strained pseudomorphically on the Mo(110) surface, despite a large lattice misfit (-8.9 %). Dislocation lines appear in the second Fe layer, which develop into a quasi-hexagonal 2D dislocation network at higher coverages. This corresponds to a transition between LBL growth below 2 ML and layer-plus-island (Stranski-Krastanov) growth above this coverage. The first and second Fe layers display different adsorption characteristics, with an ordered $p(2 \times 2)$ adlayer structure resolved exclusively on the Fe bilayer. This structure is attributed to oxygen originating from the Fe source during deposition. It is not resolved on the first layer, which shows a disordered $p(2 \times 2)$ structure, or on

thicker layers where the 2D dislocation network is observed.

At elevated temperatures, growth of the first and second Fe layers proceeds exclusively by the step-flow mechanism. A $p(2 \times 2)$ structure is also resolved on the Fe bilayer of films grown in this temperature range. At higher coverages, Fe not contained in the pseudomorphic first layer agglomerates into islands with a characteristic wedge shape, which is due to surface free energy minimisation. A transition between an array of evenly-spaced dislocation lines and a 2D network (similar to that observed on room-temperature grown films) is observed as the local film thickness increases from 2 to 3 *ML*.

An oxygen-induced $p(3 \times 1)$ missing-row structure was observed on the W(100) surface during the early stages of sample cleaning. Deposition of Fe on this surface was characterised by the formation of a high density of Fe clusters. The average size of these clusters increases with increasing deposition temperature and total coverage. There is no evidence of a pseudomorphic first layer formed on this surface. For 2 *ML* Fe deposition on the clean surface, the growth mode appears to be Stranski-Krastanov at 330 *K* and Volmer-Weber at 565 *K*. The latter film exhibits rectangular islands with local thicknesses reaching 8 *ML*. On the larger of these islands, a square dislocation network is observed, corresponding to the insertion of an extra Fe atom for every twelve W atoms along the [001] and [010] directions.

Publications

S. Murphy, J. Osing and I.V. Shvets. *Atomically resolved $p(3 \times 1)$ reconstruction on the $W(100)$ surface imaged with magnetic tips.* *J. Magn. Magn. Mat.*, 198-199:686, 1999

S. Murphy, J. Osing and I.V. Shvets. *Fabrication of submicron-scale manganese-nickel tips for spin-polarized STM studies.* *Appl. Surf. Sci.*, 144-145:497, 1999

J. Osing, S. Murphy and I.V. Shvets. *Enhanced gas-particle adsorption on strained pseudomorphic Fe films on $Mo(110)$.* *Surf. Sci.*, 454-456:280, 2000

List of abbreviations

- 1D - one dimensional
- 2D - two dimensional
- 3D - three dimensional
- AES - Auger electron spectroscopy
- CMA - cylindrical mirror analyser
- DLA - diffusion limited aggregation
- DOS - density of states
- e-beam - electron beam
- ECG - electrostatic centre of gravity
- HT - high-temperature
- L - Langmuir
- LBL - layer-by-layer
- LDOS - local density of states
- LEED - low energy electron diffraction
- LT - low-temperature
- LTSTM - low-temperature scanning tunneling microscopy
- MBE - molecular beam epitaxy
- ML - monolayer
- RFA - retarding field analyser
- RT - room temperature
- RTSTM - room-temperature scanning tunneling microscopy

SPM - scanning probe microscopy

SPSTM - spin polarised scanning tunneling microscopy

STM - scanning tunneling microscopy

STS - scanning tunneling spectroscopy

TMR - tunneling magneto resistance

TPD - temperature programmed desorption

TSP - titanium sublimation pump

UHV - ultra high vacuum

XRD - x-ray diffraction

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Chapter 1

Introduction

Ultrathin epitaxial film systems have attracted much interest due to their novel electronic, magnetic and catalytic properties [1–4]. Because the structure and electronic properties of ultrathin films are intimately related, an understanding of the mechanisms behind the formation of specific film morphologies leads to the possibility of controlling growth conditions to produce films with tailor-made properties. Among the diverse bimetallic systems that have stimulated interest, the Fe/W and Fe/Mo epitaxial systems have received particular attention regarding the effects of film-substrate d-band hybridisation and misfit strain on the chemisorptive and magnetic properties of Fe films [5–9]. An example of the phenomena encountered is the enhancement of the Fe magnetic moment above its bulk value, when the lattice parameter of the film is dilated due to the large lattice misfit with a refractory metal (Mo or W) substrate. Moreover, there is considerable interest in investigating the suitability of these systems as candidates for spin-polarised scanning tunneling microscopy (STM) experiments, as discussed by Osing [10]. In a practical sense, there is the additional advantage that the tungsten and molybdenum surfaces are relatively easy to clean for surface studies, while surface alloying

can be neglected in both systems¹.

In this study, the morphology of ultrathin Fe films grown epitaxially on the Mo(110) and W(100) surfaces is investigated using STM, low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The Fe/Mo(110) epitaxial system has not been studied in great detail, though previous work has indicated that it exhibits a similar film growth behaviour to that of the more widely studied Fe/W(110) system. The Fe/W(100) system has been the subject of extensive study, using a variety of techniques including LEED, AES and temperature programmed desorption. However, it does not appear that any considerable amount of STM work has been published on this system. For full reviews of the surface-sensitive techniques used in this study, the reader is referred to references [11–13]. A brief discussion of the practical aspects of the LEED and AES techniques is given in chapter 3. The main body of this work begins with a review of selected topics related to ultrathin film epitaxy.

¹The Fe/Mo epitaxial film system does not undergo alloying below 800 K, while the Fe/W epitaxial film system does not alloy up to the desorption of Fe.

Chapter 2

Epitaxial ultra-thin film growth

2.1 Thermodynamics of crystal growth

Though this approach does not model the non-equilibrium conditions normally inherent in thin film epitaxy or the atomistic processes which influence growth, it is still extremely valuable in forming a qualitative understanding of the driving forces behind epitaxial growth. A review of the thermodynamics of surfaces and crystal growth is given by Kern *et al.* [14]. The thermodynamical treatment begins with the definition (after Gibbs [15]) of the specific surface free energy γ , which is *the reversible work per unit area required to create a surface*. For a polyhedral crystal of n identical atoms at constant temperature T and pressure P , the cost in Gibbs free energy dG to create a surface area dA perpendicular to the j^{th} crystallographic direction is given by:

$$dG = \gamma_j dA_j \quad (2.1)$$

where the area of every other face of the crystal is kept constant and γ_j is a constant.

The total change in Gibbs free energy as the crystal grows by the addition

of n atoms is given (for homogeneous growth) by:

$$\Delta G(n) = -n\Delta\mu + \sum_j \gamma_j A_j \quad (2.2)$$

While the second term of this relation accounts for the energy cost associated with creating new surfaces, the first term deals with the work done to increase the crystal volume. It is the competition between these surface and volume terms which determines the critical cluster size at which spontaneous crystal growth occurs. The volume term is related to the variation in chemical potential $\Delta\mu$ associated with the addition of a single atom to the crystal from the vapour phase, which is given by:

$$\Delta\mu = k_B T \ln \left(\frac{P_{vap}}{P} \right) \quad (2.3)$$

where k_B is Boltzmann's constant, P_{vap} is the vapour pressure and P is the saturated vapour pressure. From this relation it is apparent that when $\Delta\mu$ is positive the vapour is supersaturated, while it is negative for an undersaturated vapour.

As the crystal is described by a polyhedron, its volume can be expressed as the summed volumes of pyramids whose bases are faces of the polyhedron with area A_j . These pyramids have a height h_j perpendicular to the j^{th} face, originating from a point O that joins the vertices of all the pyramids. Thus the volume of the polyhedron is:

$$V = \frac{1}{3} \sum_j A_j h_j \quad (2.4)$$

An infinitesimal change in this volume is given by:

$$dV = \frac{1}{3} \left(\sum_j A_j dh_j + \sum_j h_j dA_j \right) \quad (2.5)$$

Alternatively, dV can be described as a displacement of the surface area A_j by an infinitesimal distance dh_j so that:

$$dV = \sum_j A_j dh_j \quad (2.6)$$

Combining these two equations, the change in volume can be written solely in terms of the change in surface area:

$$dV = \frac{1}{2} \sum_j h_j dA_j \quad (2.7)$$

Taking $v = V/n$ as the volume per atom, equation (2.2) for the change in total free energy can also be written solely in terms of the change in surface area:

$$d(\Delta G) = -\frac{\Delta\mu}{2v} \sum_j h_j dA_j + \sum_j \gamma_j dA_j \quad (2.8)$$

Under equilibrium, the total free energy is minimised so that this equation equals zero, therefore, the crystal can only present surface facets which satisfy the equality:

$$\frac{2\gamma_j}{h_j} = \frac{\Delta\mu}{v} \equiv W \quad (2.9)$$

This is Wulff's theorem, where W is known as Wulff's constant and is related to the total energy required for crystal formation. This theorem is the basis for a geometrical method for the construction of the equilibrium crystal form, illustrated in figure 2.1. The crystallographic $[hkl]$ directions of the crystal lattice are mapped through a fixed point O in space. Commencing from this point vectors of length $h_{[hkl]}$ (proportional to $\gamma_{[hkl]}$) are drawn along these directions. At the end of each vector the normal plane is constructed. The inner envelope of these planes will correspond to the equilibrium form of the crystal.

Calculated surface energies for a number of metals are presented in table 2.1. There can be significant differences in the values obtained using different

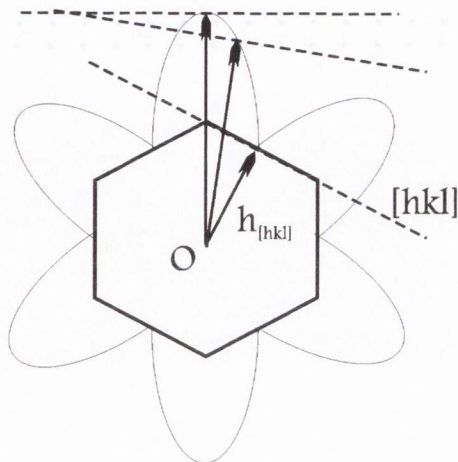


Figure 2.1: Illustration of Wulff's construction: Vectors $\vec{h}_{[hkl]}$ are drawn from the centre of the crystal O , whose ends are situated on the outer envelope of the construction. Assume for the 2D case that l , which lies in the direction normal to the page, is equal to zero. The dashed lines represent the possible $[hkl]$ index faces which lie perpendicular to these vectors. The surface energy is minimised for faces which appear at cusps in the outer envelope. These faces will determine the equilibrium shape of the crystal, given by the inner envelope of the construction (dark lines).

techniques, so that a comparison of values is only valid if they are taken from the same source. Some experimentally obtained values are also listed in table 2.2. The low-index surfaces (100), (110), (111) form the most stable surfaces of equilibrium crystals, with the lowest values of $\gamma_{[hkl]}$. This is because they are the most closely packed atomic planes where the interaction between neighbouring atoms is strongest.

On vicinal surfaces, the macroscopic plane of the surface is oriented to within a few degrees of a low-index surface. In these cases, there is a tendency for the surface atoms to rearrange themselves into low-index facets separated by atomic steps. The faceted surface retains the original macroscopic plane,

but has a lower total surface free energy than it would as a high index surface - even with the necessary increase in surface area. A fuller discussion of this topic is given by Bennema [16].

2.1.1 Heteroepitaxy and interface energy

In the previous section the case was considered for a single-component, unsupported crystal. In heteroepitaxy, where the crystal is supported on a substrate of a different material, the crystal-substrate interface can have a strong influence on the equilibrium shape. It is assumed that the substrate surface is free from defects and that no alloying between the crystal (film) and substrate occurs.

The Wulff's theorem can be extended to include an interfacial energy term by considering a polyhedral crystal with a face of surface energy γ_{cry} supported on a substrate of surface energy γ_{sub} . The interface free energy per unit area σ is then:

$$\sigma = \gamma_{cry} + \gamma_{sub} - \beta \quad (2.10)$$

which is known as Dupré's relation, where the additional term β is the free energy of adhesion. The specific interface free energy is a constant and is independent of the size or shape of the interface. For highly miscible systems it will be strongly attractive.

The change in Gibbs free energy of this system can be written as:

$$\Delta G(n) = -n\Delta\mu + \sum_j \gamma_j A_j + (\sigma - \gamma_{sub}) A_{int} \quad (2.11)$$

where for one of the free surfaces of the free-standing crystal, an interface of area A_{int} has been substituted. The generalised form of Wulff's theorem is then:

$$\frac{\gamma_j}{h_j} = \frac{(\sigma - \gamma_{sub})}{h_{int}} = \frac{(\gamma_{cry} - \beta)}{h_{int}} = \frac{\Delta\mu}{2v} \quad (2.12)$$

Surface	γ^a [J/m^2]	γ^b [J/m^2]	Surface	γ^a [J/m^2]	γ^b [J/m^2]
Ni (100)	1.57	2.426	Fe (100)		2.222
(110)		2.368	(110)		2.430
(111)	1.44	2.011	(111)		2.733
			(310)		2.393
Cu (100)	1.29	2.166	Ta (100)	2.328	3.097
(110)		2.237	(110)	1.980	3.084
(111)	1.18	1.952	(111)		3.455
			(310)	2.512	3.139
Ag (100)	0.70	1.200	Mo (100)	2.100	3.837
(110)		1.238	(110)	1.829	3.454
(111)	0.62	1.172	(111)		3.740
			(310)	2.070	3.626
Au (100)	0.92	1.627	W (100)	2.924	4.635
(110)		1.700	(110)	2.575	4.005
(111)	0.79	1.283	(111)		4.452
			(310)	3.036	4.303

Table 2.1: Calculated surface free energies for fcc metals. γ^a values from Gumbsch and Daw [17] for fcc and from Ackland and Finnis [18] for bcc metals. γ^b values taken from Vitos *et al.* [19].

Metal	γ^a	γ^b	γ^c
Ag	1.25	1.14	1.246, 1.250
Au	1.55	1.41	1.506, 1.500
Mn	1.6		1.543, 1.600
Cu	1.85	1.67	1.790, 1.825
Pd	2.1		2.003, 2.050
Ni	2.45	1.85	2.380, 2.450
Co	2.55		2.522, 2.550
Fe	2.55	2.15	2.417, 2.475
Pt	2.55	2.34	2.489, 2.475
Mo	2.95		2.907, 3.000
Ta	3.05		2.902, 3.150
W	3.3	2.9	3.265, 3.675
V			2.622, 2.550

Table 2.2: Experimental values of the surface free energies for fcc and bcc metals. Values are taken from sources referenced in: γ^a Gradmann [1], γ^b Somorjai [3] and γ^c Vitos *et al.* [19].

where h_{int} is the distance from the centre of the polyhedron to the crystal-substrate interface. This distance, which is determined by the relation between the surface free energy of the crystal γ_{cry} and the free energy of adhesion β , denotes the extent to which wetting of the surface can occur. A summary of possible scenarios is illustrated in figure 2.2.

2.1.2 Bauer criteria - the three growth modes

Developing on the generalised Wulff's theorem, Bauer [20], in 1958, proposed the description of three principle equilibrium growth modes, characterised by the relationship between the free energies of the film, substrate and interface:

$$\Delta\gamma = \gamma_{cry} + \sigma - \gamma_{sub} \quad (2.13)$$

Volmer-Weber mode $\Delta\gamma > 0$: In the terminology of the last section, this refers to the case where $h_{int} < h_{cry}$, when $\beta \ll 2\gamma_{cry}$ (see figure 2.2). This is the case of purely 3D growth, resulting in a macroscopically rough film. The adatoms form clusters upon deposition onto the substrate surface, preferring to form bonds with one another than with substrate atoms so that surface wetting is energetically unfavourable.

Frank-van der Merwe mode $\Delta\gamma < 0$: In this case $h_{int} = -h_{cry}$ as $\beta \rightarrow 2\gamma_{cry}$ giving purely layer-by-layer (LBL) growth. The adatom-substrate interaction is stronger than the adatom-adatom interaction, thus favouring wetting of the substrate surface by the film. The resulting film will be macroscopically smooth with (ideally) completion of each successive atomic layer before nucleation of the next.

Stranski-Krastanov mode: Continued LBL growth is experimentally rare as the interfacial energy varies with increasing thickness *i.e.* successive atomic layers will not experience the same interfacial energy as the first atomic

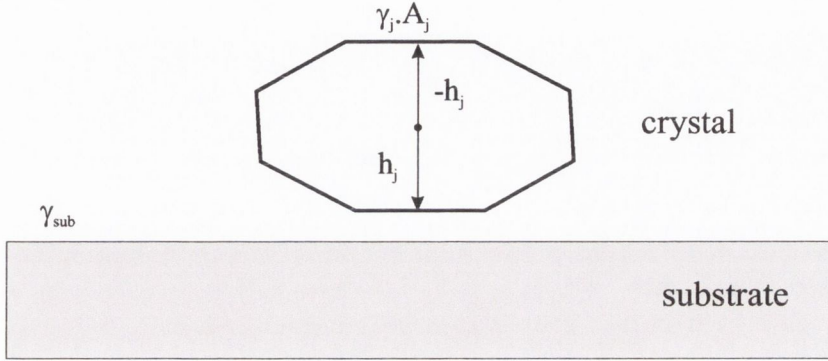
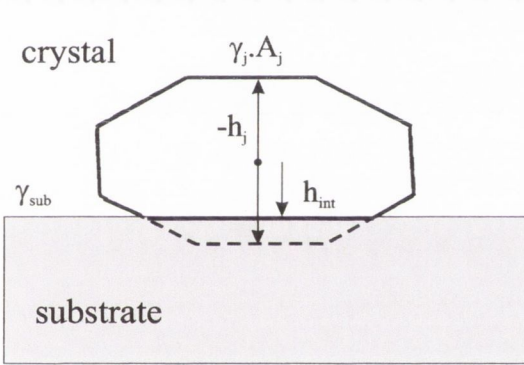
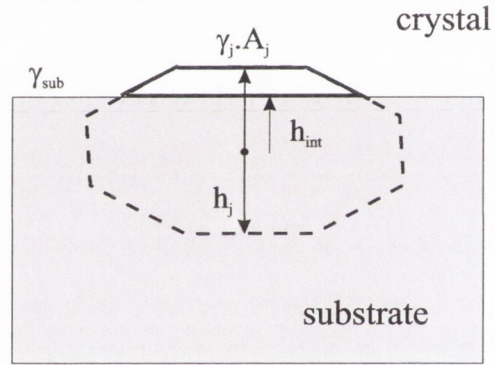

 (a) $\beta = 0, h_{int} = h_j$

 (b) $0 < \beta < \gamma_j, 0 < h_{int} < h_j$

 (c) $\beta \rightarrow 2\gamma_j, h_{int} \rightarrow -h_j$

Figure 2.2: Illustration of the possible equilibrium crystal growth modes using the generalised Wulff's theorem. A_j and γ_j are the area and surface energy of the j^{th} face of the crystal respectively, while $\vec{h}_j$ is the vector normal to the face that originates from the crystal centre. γ_{sub} is the surface free energy of the substrate, while $\vec{h}_{int}$ is the vector normal to the crystal-substrate interface from the crystal centre. The three cases shown are: (a) the crystal remains unsupported by the substrate, (b) heteroepitaxial 3D growth and (c) nearly-2D heteroepitaxial growth.

layer to wet the surface. Additionally, in heteroepitaxial systems the lattice misfit between film and substrate will introduce a misfit strain energy that increases with thickness. Consequently, at some critical thickness there is a transition in growth mode between LBL and 3D growth. The formation of 3D islands is energetically favourable as it allows for some relaxation of the misfit strain at the island-edges. The resulting film represents an intermediate case consisting of 3D islands growing on a pseudomorphic first layer, this is known as *Stranski-Krastanov* growth.

For metal-on-metal growth, the interfacial free energy is generally an order of magnitude smaller than the surface free energies so that σ may be ignored [1].

2.2 Lattice misfit and interface stress

In heteroepitaxial growth, there will be a misfit m between the film and substrate lattices due to the difference in their equilibrium lattice parameters a_f and a_s respectively:

$$m = \frac{a_f - a_s}{a_s} \quad (2.14)$$

If the film grows on the substrate by pseudomorphic LBL growth this misfit can be accommodated by elastically straining the film to bring it into registry with the substrate lattice. If this involves a contraction (expansion) of the film lattice parameter, the strain is said to be *compressive* (*tensile*) and the sign of the lattice misfit will be positive (negative).

For a simple 1D model, the film strain ε will be equal to the lattice misfit. In three dimensions, while the film maintains in-plane registry with the substrate, it can distort in the normal direction to maintain its unit cell volume. The film strain is then given by a second rank tensor ε_{ij} which is

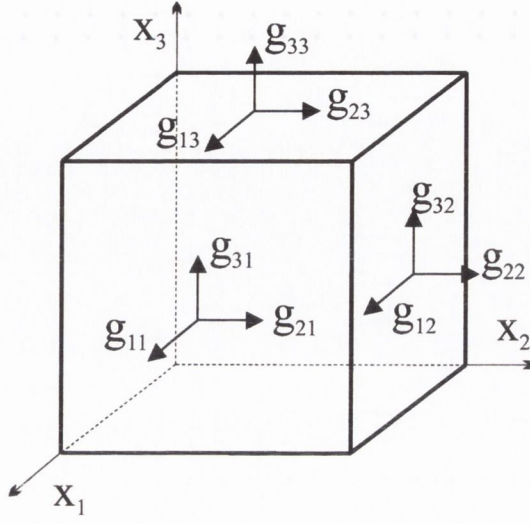


Figure 2.3: The components of the second rank stress tensor g_{ij} are illustrated as forces on a simple cube with orthogonal axes x_1 , x_2 and x_3 . The components of g_{ij} correspond to forces in the x_i direction, acting on the plane normal to the x_j direction. Therefore the g_{ii} components correspond to normal forces, while g_{ij} ($i \neq j$) are shear components.

related by some elastic constant B to the *interface stress* g_{ij} . The *interface stress* g_{ij} is defined as *the reversible work done to strain one phase relative to another*¹. For uniaxial stress in a film the elastic constant B is equal to the Young's modulus Y , while for isotropic biaxial stress $B = Y/(1 - \nu)$, where ν is the Poisson's ratio [22].

The lattice parameter b' for the out-of-plane distortion of the film (see figure 2.4) is given by [22]:

$$b' = \frac{a(1 + m)(1 + \nu)}{(1 - \nu)} \quad (2.15)$$

The energy per unit area associated with elastic strain ε parallel to the film

¹It is sometimes appropriate to define a second form of the interface stress h_{ij} , as *the reversible work done to equally stretch both phases* [21]

plane is given by [23]:

$$E_\varepsilon = \varepsilon^2 B h, \quad B = \frac{2G(1+\nu)}{(1-\nu)} \quad (2.16)$$

where h is the film thickness and G is its shear modulus. The elastic strain energy per unit area in the film is given by:

$$E_\varepsilon = \frac{2G(1+\nu)m^2h}{(1-\nu)} \quad (2.17)$$

where the misfit m is substituted for the strain ε . The elastic strain energy increases with increasing thickness until a critical thickness h_c where the strain is partially relieved by the introduction of misfit dislocations. The misfit m is then shared between strain ε and dislocations, for the 1D case:

$$m = \varepsilon + \delta \quad (2.18)$$

where δ is the misfit accommodated by dislocations. The energy associated with the formation of an edge dislocation at the interface is given by:

$$E_{dis} = \frac{1}{2} D b [\ln(R/b) + 1], \quad D = \frac{G_f G_s b}{\pi(G_f + G_s)(1-\nu)} \quad (2.19)$$

where R is the extent of the dislocation's strain field and G_f , G_s are the shear moduli of the film and substrate respectively. b is the Burger's vector of the dislocation (see figure 2.4). The energy associated with two perpendicular, non-interacting dislocation arrays is:

$$E_\delta = D \delta [\ln(R/b) + 1] \quad (2.20)$$

The critical thickness is found by determining the strain ε^* at which the total energy $E = E_\varepsilon + E_\delta$ is minimised and setting $\varepsilon^* = m$. The result is [23]:

$$h_c = \left(\frac{D}{2Bm} \right) [\ln(h_c/b) + 1] \quad (2.21)$$

With increasing film thickness the dislocation density increases until the misfit strain has been completely relieved and the film reaches its equilibrium lattice parameter. The thickness at which this occurs is roughly equal to the separation p between the dislocations [1, 24]:

$$p = \frac{a_s \times a_f}{a_s - a_f} \quad (2.22)$$

where a_s and a_f are the substrate and film lattice parameters respectively. Alternatively, this may be written as $p = b/\delta$ [23], where b is the magnitude of the Burger's vector of the dislocation. The transition between pseudomorphic growth and 3D island growth has already been mentioned as another means of reducing misfit-strain. In real systems, the overall relaxation of the film will often be a combination of both these processes.

An alternative solution for the critical thickness for misfit dislocation has been outlined by Cammarata [21] where:

$$h_c = \frac{-2(g - \sigma + f - \gamma)}{Bm}, \quad B = \frac{Y}{(1 - \nu)} \quad (2.23)$$

This approach considers three terms:

- the elastic energy per unit area $\varepsilon^2 B h$, where h is the film thickness and ε is the uniform radial strain in the film.
- the work required per unit area to change the defect structure at the interface $2(g - \sigma)\varepsilon$. The strain associated with the interface stress g , will change the interface structure (by increasing the dislocation density for example) and therefore causes a change in the interface free energy σ . The factor of 2 reflects the 2D nature of the planar strain.
- the work done to strain the surface of the film $2(f - \gamma)\varepsilon$. This last term introduces the contribution of the intrinsic quantity f , the *surface stress* which is discussed in the next section. γ is the surface free energy.

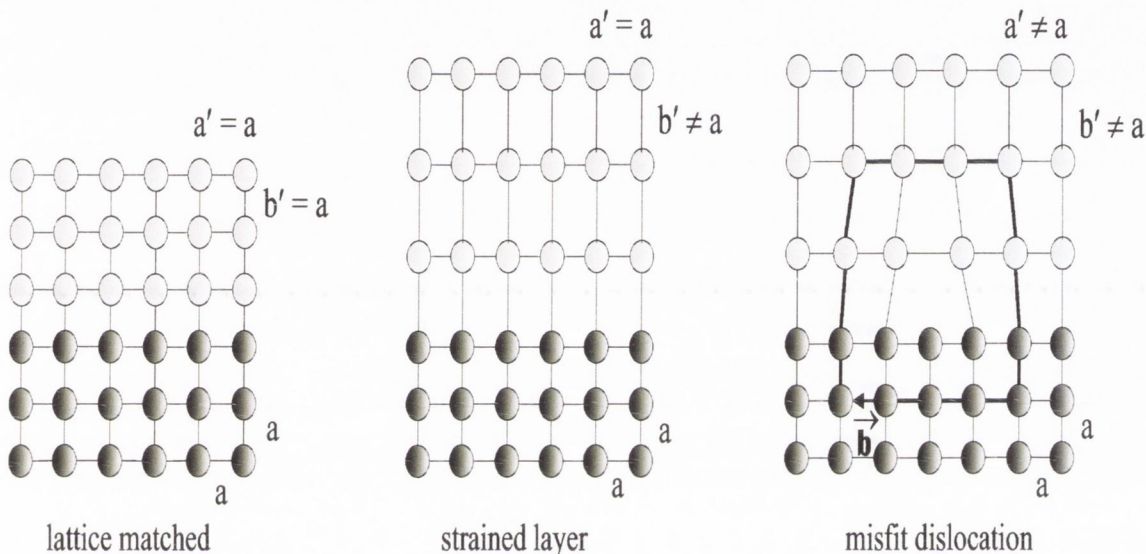


Figure 2.4: Illustration of the effects of introducing a lattice misfit into LBL epitaxial growth. Lattice misfit may be accommodated by elastically straining the film to be in registry with the substrate, though some out-of-plane distortion results. Above a critical thickness h_c the strain energy is sufficiently high to necessitate the formation of edge-type dislocations to alleviate the strain. The Burger's vector $\vec{b}$ for the dislocation is marked. This defines the difference between the starting and finishing points of a cyclic path encompassing the dislocation.

2.3 Surface stress

The *surface stress* f_{ij} may be defined qualitatively as *the reversible work per unit area needed to produce an elastic strain at a surface*. This is a second rank tensor quantity which relates the change in the total excess free energy of the surface γA to a change in the surface area by an infinitesimal elastic strain, $d\varepsilon_{ij}$:

$$d(\gamma A) = A f_{ij} d\varepsilon_{ij} \quad (2.24)$$

Since $d(\gamma A) = \gamma dA + A d\gamma$, and $dA = A \delta_{ij} d\varepsilon_{ij}$ (where δ_{ij} is the Kronecker delta function) this becomes:

$$f_{ij} = \delta_{ij} \gamma + \frac{\partial \gamma}{\partial \varepsilon_{ij}} \quad (2.25)$$

For surfaces of three-fold and higher rotational symmetry the surface stress is isotropic and reduces to a scalar quantity, so this equation reduces to:

$$f - \gamma = \frac{\partial \gamma}{\partial \varepsilon} \quad (2.26)$$

This equation, due to Shuttleworth [25], shows that the difference between surface stress and surface free energy is equal to the change in surface free energy per unit change in the elastic strain of the surface. For clean surfaces, surface stress values are usually of the same order of magnitude as the surface free energies, but while γ is always positive, f may be positive or negative leading to cases of tensile ($f > 0$) and compressive ($f < 0$) stress respectively. Calculated values for the surface free energy and surface stress of various metals are shown in table 2.3, after Cammarata [21].

For a liquid surface, the surface free energy does not change as the surface is strained², the term on the right vanishes so that $\gamma = f$, which is then known as the surface tension.

²When a liquid surface is stretched, the atoms or molecules within the interior can readily move, without resistance from the bulk, to the surface to fill the expanded area.

Surface	f_{xx} [J/m^2]	f_{yy} [J/m^2]
Ni (100)	1.27	
(111)	0.43	
Cu (100)	1.38	
(111)	0.86	
Ag (100)	0.82	
(111)	0.64	
Au (100)	1.79	
(111)	1.51	
Pt (100)	2.69	
(111)	2.86	
V (100)	2.424	
(110)	1.939	0.263
Nb (100)	2.532	
(110)	2.168	0.301
Ta (100)	3.249	
(110)	2.535	0.392
Mo (100)	2.241	
(110)	2.019	0.775
W (100)	3.032	
(110)	2.385	0.271

Table 2.3: Calculated surface surface stresses f_{xx} and f_{yy} , for fcc metals (from Gumbsch and Daw [17]) and bcc metals (from Ackland and Finnis [18]). For the anisotropic stresses of bcc (110) surfaces f_{xx} lies along the $[1\bar{1}0]$ direction while f_{yy} lies along the $[001]$ direction. Some of the corresponding surface energy values are listed under column γ^a in table 2.1.

2.3.1 Origin of surface stress

This property originates as a result of breaking the high-symmetry environment of the bulk crystal at its surface. The difference in bonding geometry at a newly formed surface is responsible for a charge distribution at the surface which differs from that within the bulk. Here, the case is considered for metallic surfaces where cohesion is provided by a delocalised charge distributed between metal ion cores, that lacks the directionality of covalent bonds. In the absence of an atomic layer lying above it, the charge distribution within the surface layer accumulates both *a*) between the ion cores comprising the surface layer and *b*) in the interlayer region between this layer and the first sub-surface layer. The increase in charge density in the interatomic region between the ion cores of these layers produces a net Coulombic force which acts to shorten the equilibrium bond length between them. In case (*a*), the lateral (in-plane) constriction of the surface is restricted by the symmetry requirements of the bulk lattice. The bulk constrains the surface layer to lie in registry with the bulk lattice, the surface is stretched beyond its ideal configuration and therefore experiences a tensile stress. In case (*b*), there is no out-of-plane restriction to an interlayer relaxation between the surface layer and the first sub-surface layer. This phenomenon, which is known as *surface relaxation*, is described further in section 2.4.2.

2.3.2 Adsorbate-induced stress

Bearing in mind from the above discussion that the intrinsic stress of clean metal surfaces has its origins in the redistribution of charge at the surface, it is natural to expect that the chemisorption of species onto these surfaces will alter their stress. The magnitude of these changes will depend upon the extent

to which the adsorbed species can accommodate electrons i.e. the polarity of the surface-adlayer bond. In the case of adsorbates which are electronegative with respect to the surface, the bonds between surface and adsorbate will remove some of the excess charge distributed between the surface atoms, leading to a reduction in the tensile stress associated with the clean surface. It is possible in some cases that these bonds will remove sufficient charge to reverse the sign of the surface stress from tensile to compressive. Where the adsorbate is inclined to donate charge to the surface, the tensile stress can be enhanced.

There will obviously be some dependence of these changes on the coverage of the adlayer. Some experimental results are shown in figure 2.5 (reproduced after Ibach [26]). The dependence is linear in the low-coverage region, but becomes non-linear at higher coverages. Part of this non-linearity may be due to the repulsion experienced between the adsorbates as they form heteropolar bonds with the surface, though this contribution is considered to be small [26]. Another possibility may be the switching of the adsorption process to alternative adsorption sites with increasing coverage - to accommodate the higher density of adsorbates - which will affect the nature of the bond to the surface and therefore the induced stress.

2.4 Stress related phenomena

2.4.1 Role of stress in surface reconstruction

Though most clean low-index metal surfaces maintain the (in-plane) symmetry of the underlying lattice, in some cases surface instability results in the repositioning of surface-layer atoms so that they no longer lie in perfect (1×1) registry with the bulk - this is known as surface reconstruction. A

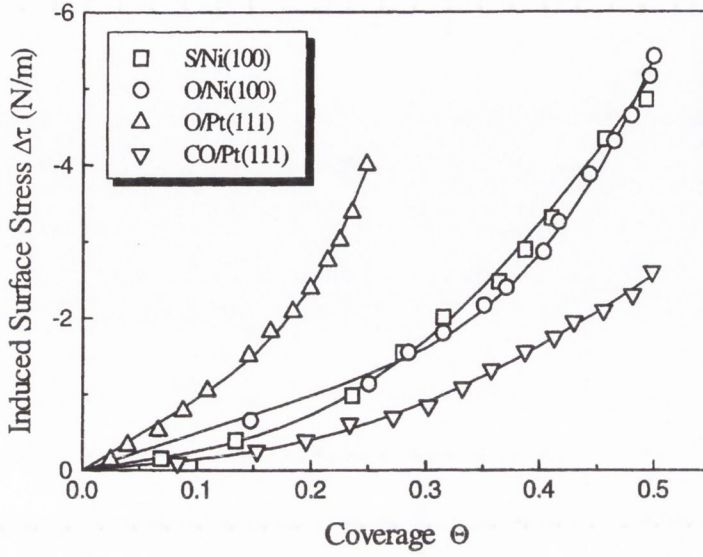


Figure 2.5: Experimental data revealing the coverage dependence of adsorbate-induced stresses in a number of adsorption systems. Note that in these cases the trend is towards an increasingly compressive stress. Data are taken from [27–29].

sufficiently large surface stress can contribute to this surface instability in one of two ways:

(i) The derivative term of the Shuttleworth equation (2.26) can be viewed as a thermodynamic driving force to change the surface atom density [30]. Where $\partial\gamma/\partial\epsilon < 0$, there is a tendency to remove atoms from the surface, while $\partial\gamma/\partial\epsilon > 0$ favours an increase in the surface atom density. The surface will be inclined to reconstruct to a state where $\partial\gamma/\partial\epsilon = 0$, this is valid for surfaces under tensile or compressive stress. However, reconstruction may only occur when this driving force exceeds the increase in energy due to the surface layer breaking symmetry with the underlying lattice. An example of surface densification is the $(23 \times \sqrt{3})$ reconstruction on Au(111) which has

been described as an insertion of an extra row of atoms every twenty-three rows on the surface [31].

(ii) The crystal lattice near the surface may be pictured as an array of identical atoms held together by springs representing the various interatomic bonds. Surface phonons may be taken as elastic vibrations propagating through this array, whose magnitude and frequency will depend upon the restoring forces of the various springs. Surface stresses contribute to the stiffness of these springs by increasing the restoring forces in the tensile case and reducing them in the compressive case. For an extremely large compressive stress the relaxation of the restoring forces can lead to a vanishing phonon frequency - known as phonon softening. Under the resulting surface instability the surface reconstructs along the displacement vectors of the phonon. This type of reconstruction differs from the one mentioned above in that the surface atom density does not change. An example of this type of reconstruction is that of the Ni(100) surface in the presence of carbon or nitrogen [32].

In the latter example adsorbate-induced changes in stress play an important role in forming the reconstruction. For reconstructions originating in tensile stress of the surface, adsorption can serve to remove the reconstruction by reducing the tensile stress and may even produce a different reconstruction due to compressive stress.

Reconstruction can be a multilayer phenomenon, originating in the low-symmetry environment induced in a sub-surface layer as the layer above it reconstructs. No longer restricted to high-symmetry sites, rearrangement of atomic positions can occur in these layers, allowing some propagation of the top-layer reconstruction into the next few sub-surface layers.

It should be noted that surface stress is not the only contributing factor to the phenomenon of surface reconstruction - for example, the surface density

of states of a metal can have important implications regarding its stability against reconstruction. A full account of this phenomenon is given in review articles by Inglesfield [33] and Pick [34].

2.4.2 Surface relaxation

Surface relaxation has been observed experimentally using LEED, ion-beam and atom-beam scattering techniques which have confirmed that the top layer of ion cores in a metal surface can be shifted inwards or outwards by 1-10 % of the interlayer separation. A summary of relaxation values and directions for a number of bcc, fcc and hcp low-index surfaces is given in table 2.4, reproduced after Kiejna and Wojciechowski [35]. From this, it is apparent that the relaxations are significantly larger for the less densely-packed bcc (100), (111) and fcc (110) surfaces than for the more closely-packed fcc (100), (111), bcc (110) and hcp (0001) surfaces. It should be noted that surface relaxation can provide a significant negative term contribution to the surface free energy.

The treatment describing the origins of surface relaxation of the simple metals (Al, Na, etc.), after Finnis and Heine [38], differs somewhat from that of the transition and noble metals (W, Au, etc.) due to the different orbitals that give cohesion to each metal. For the simple metals, where cohesion is mediated by delocalised s- and p-orbitals, the conduction electrons have only a weak interaction with the metal ion cores. The charge distribution within these metals may be treated as an electron gas uniformly spread throughout the bulk, composed of weak ionic pseudopotentials representing the ion cores, and terminating abruptly at its surface. Within the bulk each ion core resides in its own symmetrical Wigner-Seitz cell wherein it experiences no net electrostatic field from the charge distribution within this volume. However,

Structure	Metal	Relaxation [%] at crystal plane		
fcc		(111)	(100)	(110)
	Al	+1 ~ +2.5	0	-5 ~ -15
	Ag	0	0	-6 ~ -10
	Cu	0 ~ -4	0	-6 ~ -10
	Ir	-2		-7
	Ni	-1	-3 ~ +2	-5 ~ -9
	Pb			-17
	Pd		+2	
	Pt	0 ~ +1	0	
	Rh	0	0	-3
bcc		(110)	(100)	(111)
	Fe	0 ~ +1	-1	-15
	Mo		-9 ~ -11	
	Na	0		
	V		-7	
	W	0	-4 ~ -11	0
hcp			(0001)	
	Be		0	
	Cd		0	
	Co		0	
	Gd		-3.5	
	Ti		-2	
	Zn		-2	

Table 2.4: Surface relaxation values for the low-index planes of various metals. Negative values represent a contraction, while positive values represent an expansion of the interlayer spacing. Data taken from Jona [36], Inglesfield [33] and van der Veen [37].

if this cell is assymetrical as is the case in an abruptly terminated surface, the ion core experiences a net electrostatic field which will require it to move inwards to minimise its energy in a new electrostatic centre of gravity (ECG). This explains why surface relaxations are larger for the less densely-packed surfaces, where the surface Wigner-Seitz cell is more assymetrical and requires greater distortion to reach the ECG. The experimental relaxations are generally smaller than the values calculated using this treatment since the charge distribution at the surface undergoes some redistribution and does not terminate abruptly. In some cases, this charge redistribution which screens the ionic pseudopotentials and the repulsion of electrons from within the volume of the closed ion cores may lead to an expansion of the interlayer separation being more favourable.

For the transition metals, localised d-orbital electrons, which are much more directional than s- and p-orbitals, are responsible for cohesion, therefore the Finnis and Heine treatment [38] cannot really apply. In the bulk, the d-orbital electrons outside the closed ion cores contribute to the cohesion by pulling the ion cores together, leading to broadening of the d-bands. On the other hand, the outer s- and p-orbital electrons are repelled from the closed ion cores and so favour an increase in the atomic volume. At the surface, these s-, p-electrons can spill over into the vacuum, allowing the d-electrons to pull the ion cores closer to the substrate.

The propagation of ion core shifts into the first few sub-surface layers as a multilayer relaxation has also been observed experimentally by LEED [39–41] on various surfaces. These are damped-oscillatory relaxations *i.e.* the sign of the relaxation changes from layer to layer, while the magnitude decreases as the relaxation propagates into the bulk. Typically, if the first interlayer separation is contracted by 10 %, the second interlayer separation will expand

by 2-5 % while the third interlayer separation will contract by 1-2.5 %. This can be understood as the second interlayer separation compensating for the accumulation of excess charge around the first sub-surface layer (due to the contraction of the surface layer) and so forth.

2.5 Kinetics processes in crystal growth

As already mentioned, the basic thermodynamic treatment of crystal growth represents an equilibrium situation where the film grows on a defect free surface without any intermixing. Normally, epitaxial films are grown under conditions which are very far from equilibrium. For instance, films are often grown using molecular beam epitaxy (MBE) where the film is deposited using a supersaturated atomic or molecular beam of the deposit species. The rate of arrival of adatoms at the surface is given by the deposition rate R , given by:

$$R = \frac{P}{\sqrt{2\pi m k_B T}} \quad [m^{-2}s^{-1}] \quad (2.27)$$

where P is the vapour pressure (Pa), m is the molecular mass (kg), k_B is Boltzmann's constant and T is the temperature (K). Near-equilibrium conditions can be achieved if the deposition rate R is low and/or the substrate temperature is high. However, non-equilibrium growth modes can be forced under extreme conditions, leading to the formation of novel metastable phases.

The morphology of films grown under non-equilibrium conditions will depend upon the defect nature of the substrate surface and the atomic processes which adatoms may undergo upon deposition. A summary of the principle processes is given in figure 2.6. The particular growth mode is derived from the competition of processes such as diffusion, nucleation, intermixing, re-

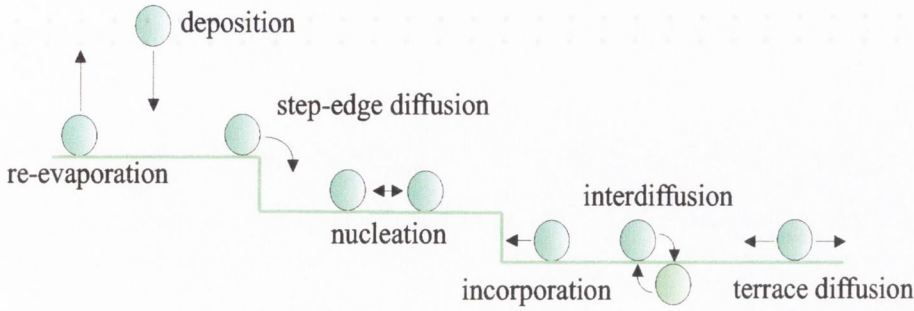


Figure 2.6: An illustration of the atomic processes at work during far from equilibrium growth.

evaporation and incorporation at special sites such as step-edges, vacancies and kinks. The latter point and line defects act as sinks for adatoms since they offer high coordination sites for binding.

These competing processes may reasonably be modelled using rate equations [42] such as the simple equation for the rate of change of adatom concentration n_a :

$$\frac{dn_a}{dt} = R - \frac{n_a}{\tau} \quad (2.28)$$

where $1/\tau$ is the inverse adatom lifetime, which is determined by the rates of the competing processes - adsorption/desorption, nucleation, capture *etc.*:

$$\frac{1}{\tau} = \frac{1}{\tau_{a/d}} + \frac{1}{\tau_n} + \frac{1}{\tau_c} \quad (2.29)$$

The rate of an atomic process that occurs during growth usually has the form:

$$\tau^{-1} = \tau_0^{-1} \exp\left(\frac{-E}{k_B T}\right) \quad (2.30)$$

where E is the activation energy for the process and τ_0^{-1} is the effective attempt frequency, which is of the order of an atomic vibration frequency (1-10 THz) for adsorption and diffusion.

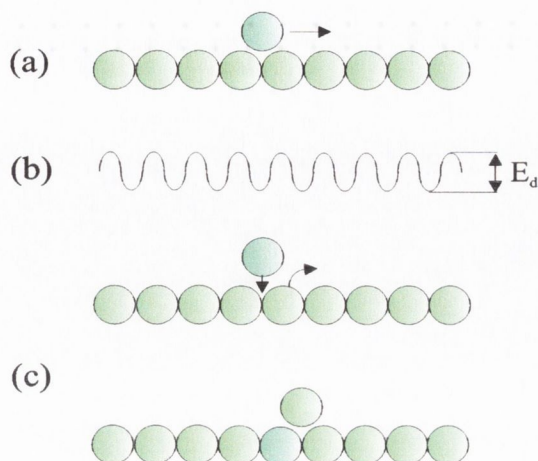


Figure 2.7: (a) Terrace diffusion by the hopping mechanism, (b) the corresponding potential curve with the activation barrier E_d marked and (c) terrace diffusion by the exchange mechanism.

2.5.1 Diffusion of adatoms on a terrace

During the time that the adatom is absorbed on the surface it can diffuse about before undergoing some other process. The motion of the adatom is limited by the periodic potential it experiences due to the surface, as illustrated in figure 2.7. The adatom must travel along the potential curve between local minima, which correspond to favourable binding sites, by passing across local maxima (saddle points), where the adatom may be in an unfavourable coordination. The energy difference between these maxima and minima represents the activation barrier E_d for the diffusion process. Two mechanisms for terrace diffusion can be identified, these are the *hopping* and *exchange* mechanisms, figure 2.7. The latter mechanism has been observed for self-diffusion on fcc(001) surfaces *e.g.* Pt/Pt(001) [43] and Ir/Ir(001) [44].

The diffusion parameter (or diffusivity) D can be classified in one of two groups. *Intrinsic* and *mass transfer* diffusion refer to the case where

the number of diffusing species remains constant or varies with temperature respectively. This is the simple random walk process where adatoms have no mutual interaction. The diffusivity is related to the mean-square displacement $\langle |\vec{r}|^2 \rangle$ by the *Einstein relation*:

$$2\alpha D\tau = \langle |\vec{r}|^2 \rangle = N\ell^2 \quad (2.31)$$

where α is the dimensionality of diffusion, τ is the time taken to observe N jumps and ℓ is the shortest jump distance. N is related to the difference in Gibbs free energy of the adatom at the minima and maxima of the surface potential curve:

$$N = \nu_d \tau \exp\left(\frac{-\Delta G}{k_B T}\right), \quad \Delta G = E_d - T\Delta S \quad (2.32)$$

so that it can be rewritten as:

$$N = \nu_d \tau \exp\left(\frac{-\Delta S}{k_B}\right) \exp\left(\frac{-E_d}{k_B T}\right) \quad (2.33)$$

The entropy term in single atom diffusion is so small that it can be ignored so that D can be written as:

$$D = D_0 \exp\left(\frac{-E_d}{k_B T}\right) = \frac{\nu_d \ell^2}{2\alpha} \exp\left(\frac{-E_d}{k_B T}\right) \quad (2.34)$$

For metals D_0 lies in the range of $10^{-3} < D_0 < 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}$ [45]. The diffusivity is sensitive to the particular crystallographic direction along which the adatom diffuses on the surface. This is because the periodicity and corrugation of the surface potential, experienced by the adatom, changes as a function of interatomic spacing and charge density, thereby affecting the shortest jump distance and the activation barrier respectively.

Chemical and *tracer* diffusion refer to the case where a chemical potential gradient is present or absent respectively. A chemical diffusivity D_C may be

defined which is related to the tracer diffusivity D by:

$$D_C = D \frac{\partial(\mu/k_B T)}{\partial \ln C} \quad (2.35)$$

where C is the adsorbate concentration. If this is sufficiently low, the mutual interaction between adsorbates is weak so that the derivative term approaches unity. A comprehensive database of diffusion parameters is provided by Seebauer and Allen [45].

2.5.2 Nucleation

At the beginning of film growth, adatoms arriving on a defect-free surface with deposition rate R will diffuse until they meet other diffusing adatoms and form clusters which will be stable and immobile at sufficiently low T . As the deposition continues, the concentration of these nuclei will increase linearly until it equals the free (non-nucleated) adatom concentration. Beyond this point the probability of a diffusing adatom adding to these clusters will be equal to the probability of forming a new nucleus. At a sufficiently high cluster density, diffusing adatoms will only contribute to the growth of pre-existing clusters. This density is called the *saturation island density* and marks the transition between the *pure nucleation regime* and the *steady-state regime*. At the saturation island density, the mean free path of diffusing adatoms is equal to the mean island separation ℓ_m . It has been shown that for a simple model excluding re-evaporation, ℓ_m is related to the adatom diffusivity D and the deposition flux F by [46]:

$$\ell_m \propto \left(\frac{D}{F} \right)^{\frac{1}{6}} \quad (2.36)$$

The flux F is equivalent to the deposition rate R and is given in units of $ML.s^{-1}$. The rate equations that predict adatom and island densities are

complicated by the fact that there is an adatom concentration gradient within the vicinity of each island due to the capture process at its edges. However, in the *mean-field nucleation theory*, it is assumed that outside the islands the adatom concentration is constant. The solution of these rate equations in the mean-field approximation leads to the relation between the saturation density of stable clusters n_i , and the ratio D/F :

$$n_i \propto \left(\frac{D}{F}\right)^{-\chi} \exp \left[\frac{E_i}{(i+2) k_B T} \right] \quad (2.37)$$

with:

$$\chi = \frac{i}{i+2} \quad (2.38)$$

where i is the critical cluster size ($i = 1$ for a dimer *etc.*) and E_i is its binding energy. The mean-field theory has its drawbacks when faced with modelling realistic island size distributions and coalescence, so that it is only applicable at the very early stages of film growth.

It should be noted that adatoms can continue to be mobile after deposition has been stopped. Without the interruption of other adatoms arriving at the surface they can diffuse far enough to attach to existing islands, leading to *post-growth*, or form new nuclei, which is known as *post-nucleation*.

2.5.3 Effect of step-edges

A surface consists of flat terraces separated by atomic steps which will have some finite kink density. The step and kink densities and the terrace width distribution will depend on the temperature and the macroscopic orientation of the surface. The presence of these steps will introduce an additional barrier, known as the *Schwoebel-Ehrlich* barrier [47, 48], to adatom diffusion. Analogous to terrace diffusion, there are *hopping* and *exchange* mechanisms for diffusion across steps, as illustrated in figure 2.8 for step-down diffusion.

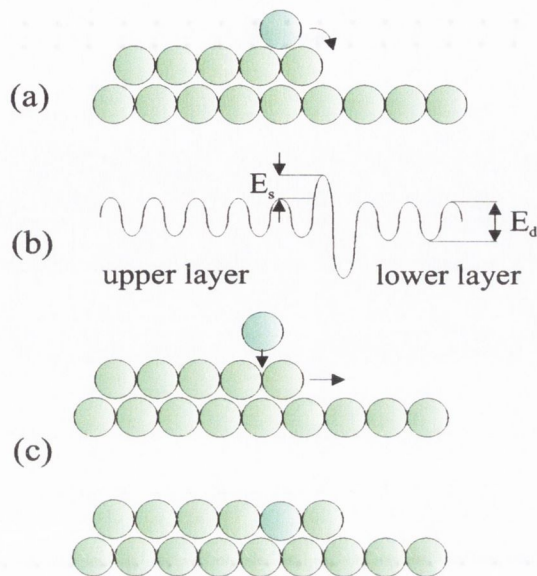


Figure 2.8: (a) Step-down diffusion by the hopping mechanism, (b) the corresponding potential curve with the additional activation barrier E_s marked and (c) step-down diffusion by the exchange mechanism.

The additional effective barrier E_s to step-down diffusion occurs because the adatom must leave a binding site and move into a very low coordination site as it crosses the step-edge. The barrier to step-up (or ascending) motion is higher as the adatom must leave a very high coordination binding site, at the step-edge, to make the transition.

With the concepts of terrace and step diffusion, it is now possible to define two modes of adatom mass transport. *Intralayer* mass transport refers to the case where diffusion occurs exclusively on the terrace onto which the adatom is deposited, while *interlayer* mass transport refers exclusively to the case of (ascending or descending) step-diffusion. The extent of *intralayer* mass transport during the nucleation stage will influence the saturation island density and island size distribution, which the film will build upon during subsequent growth. It will also determine the regularity with which adatoms may

reach substrate step-edges and adatom island-edges, thereby affecting the rate at which processes such as incorporation and step-diffusion can occur. The amount of *interlayer* mass transport will ultimately decide whether the growth will be 3D, LBL or a mixture (Stranski-Krastanov). Depending upon the heights of the Schwoebel-Ehrlich barriers at the step- and island-edges, impinging adatoms may diffuse across or be reflected.

An illustration of the possible scenarios is given in figure 2.9. The 3D (Volmer-Weber) growth mode is precipitated where all the step- and island-edges are reflective to adatom diffusion *i.e.* the *interlayer* mass transport is low. This growth mode may also be facilitated by a very low adatom mobility on top of the flat regions of the substrate and islands. This reduces the rate at which adatoms visit island-edges (and so the *interlayer mass transport*) and increases the probability that they will be captured to form new nuclei.

Pure LBL growth requires that all step- and island-edges are non-reflective to adatom diffusion. Usually however, as the adatom islands approach coalescence, the probability that an adatom will reach an island-edge before participating in a nucleation event decreases. Therefore, a critical coverage θ_C may be defined, at which nucleation on top of the growing islands occurs. If this coverage is much greater than the coverage θ_{coal} at which coalescence into a fully connected layer (percolation) begins, then the growth will be LBL. However, if $\theta_C < \theta_{coal}$, then the growth will be 3D.

A particular case of LBL growth is the *step-flow* growth mode, which can often be observed for early film growth under near-equilibrium conditions. This growth mode does not require any *interlayer* mass transport, adatoms are sufficiently mobile on terraces that upon deposition they immediately diffuse to step-up edges where they are incorporated. Hence, there is a net growth of the step in the direction normal to its step-edge, see figure 2.9(d).

A mixture of the 3D and LBL modes can occur if step-edges are not reflective but island-edges are. This situation can correspond to the build-up in strain energy discussed earlier for Stranski-Krastanov growth.

Adatoms can diffuse *along* step-edges as well as across them. In this direction mass transport will depend strongly on the density of kinks, which act as sinks for adatom capture. At very low temperatures films can adopt characteristics of fractal growth due to the reduced mobility along island edges. The classical explanation of this phenomenon is the diffusion limited aggregation (DLA) theory where the adatom is assumed to stick irreversibly at the first point it reaches [49]. However, with oriented dendritic growth commonly observed in STM studies under such conditions, modified theories that allow for site-dependent sticking coefficients [50] and *hit-and-miss* factors [51] have been introduced.

2.5.4 Ripening effects

At a finite temperature, islands which are larger than the critical cluster size are not necessarily stable. If the island is not close to its equilibrium state it will try to reach this state in which its surface energy is minimised. This will depend on the mobility of adatoms at the island edges.

Also, the island size distribution will vary as smaller islands tend to dissociate in favour of contributing to the further growth of their larger counterparts. This is known as *Ostwald ripening* and is driven by the Gibbs-Thomson effect (*cf.* equation 2.2) which favours an increasing radius of curvature r_c in islands which exceed the critical cluster size [52].

As film growth proceeds, coalescence can be inhibited by the presence of anti-phase domain boundaries between the growing islands. This occurs where islands nucleate at sites determined by the underlying lattice symme-

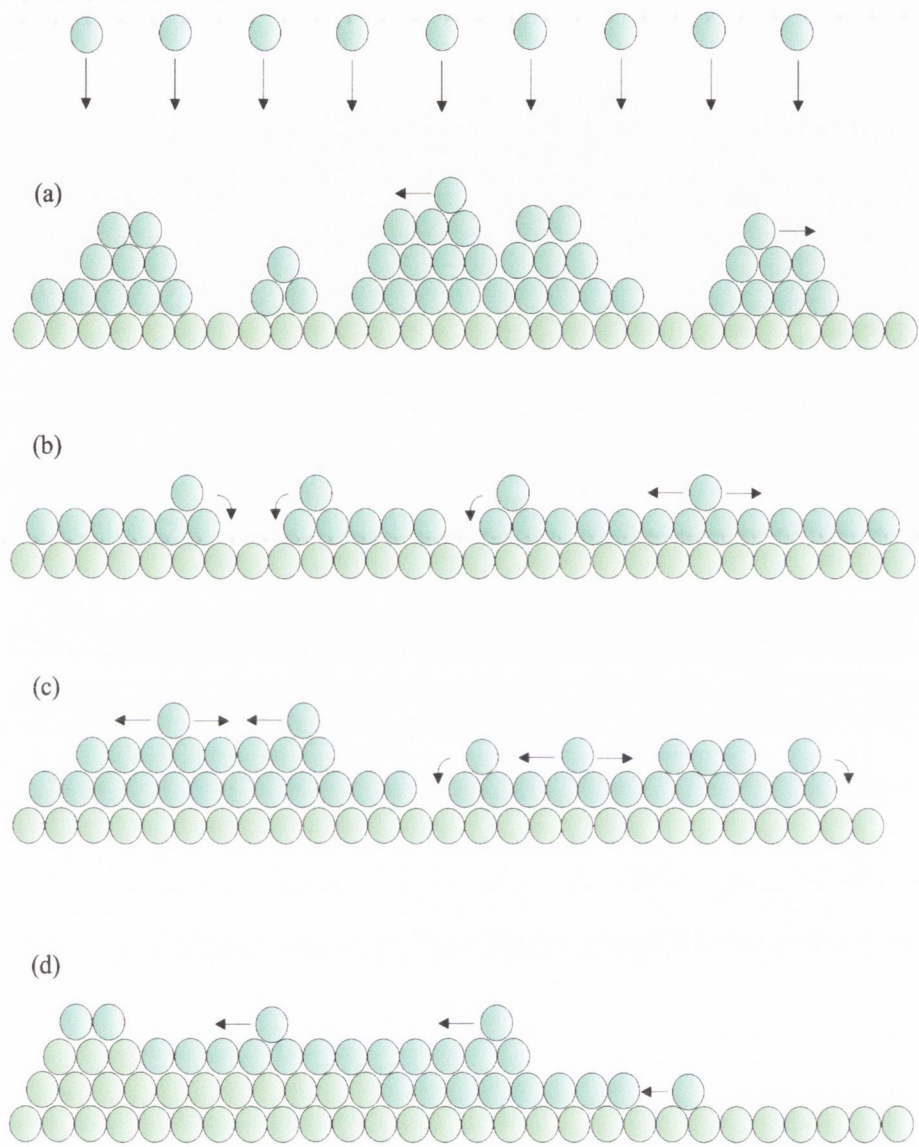


Figure 2.9: Various growth modes which depend upon the reflectivity of step- and island-edges to adatom diffusion. (a) 3D growth: all edges are reflective, (b) LBL growth: all edges are non-reflective, (c) intermediate case: step-edges are non-reflective while island-edges are reflective and (d) step-flow growth: there is no interlayer mass transport or nucleation on terraces, adatoms diffuse to step-up edges where they are incorporated.

try (two-, three-fold hollow sites *etc.*), but where stacking faults lead to a mismatch between the edges of the islands [53]. Domain boundaries can also be seen in heteroepitaxial Volmer-Weber growth, where the nucleation site is also determined by the substrate lattice, but the adatom islands grow with their own equilibrium lattice parameter. If coalescence proceeds, there will be an increase in the strain energy of the film as atoms are forced into the interstitial region between the mismatched edges.

2.5.5 The effect of strain on diffusion and nucleation

Earlier, it was highlighted that lattice mismatch in heteroepitaxial growth introduces a strain in the film that decreases with successive layers. It is natural to expect that the strain variation in the uppermost layers of these films may in some way affect the diffusion and nucleation kinetics of adatoms deposited on their exposed regions. The outcome of such layer-dependent kinetics is a strong thickness-dependence in island density, such as that observed by STM in the Ni/Ru(0001) system [54]. Several theoretical studies have also proposed the dependence of kinetic processes on strain [55, 56].

Another experimental example of layer-dependent island density is the Ag/Pt(111) system [57], where the lowest island density is found on top of the first pseudomorphic Ag layer. This has been attributed to the compression of the Ag lattice spacing by 4.3 %, which lowers the binding energy of adatoms to the surface [58]. The related diffusion barrier for adatoms on top of Ag layers is thus found to increase with decreasing compressive strain, so that the island density increases for thicker layers where the film relaxes towards its bulk configuration.

In addition to the effect of strain on intralayer mass transport in this system, it has been proposed that strain is responsible for an increase in

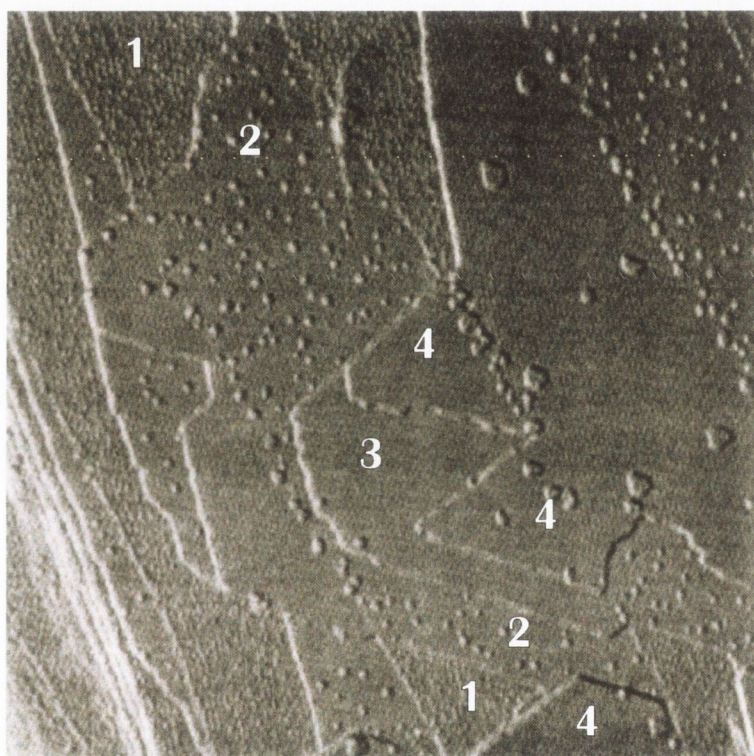


Figure 2.10: ($4000\text{\AA} \times 4000\text{\AA}$) STM image reproduced from reference [54], showing an example of the layer dependence of island density upon local film thickness in the Ni/Ru(0001) system. The local thickness of the Ni film is numbered in ML on a single Ru terrace.

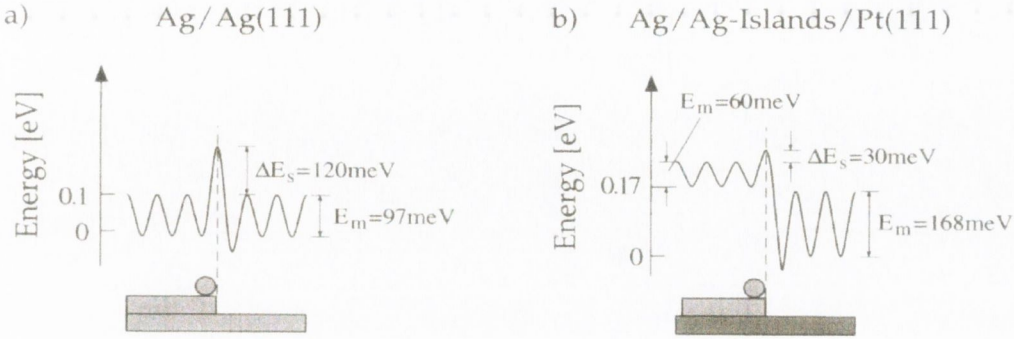


Figure 2.11: Potential energy diagrams for (a) Ag/Ag(111) homoepitaxy and (b) Ag/Pt(111) heteroepitaxy. E_m is the barrier to terrace diffusion, while ΔE_s is the additional activation barrier for step-diffusion. Reproduced from [59].

interlayer mass transport over the homoepitaxial Ag/Ag(111) case. The additional activation barrier for step-down diffusion (figure 2.11) is reduced to 25 % of the homoepitaxial value for the Ag/Ag(1ML)/Pt(111) system [59]. It is proposed that outward relaxation at the Ag island-edges is prompted by the compressive strain and that this facilitates the exchange mechanism for step-down diffusion.

Strain fields develop around line defects such as steps and dislocation edges due to the relaxation of interatomic spacings in their vicinity. This arises because atoms occupying positions at the step-edges are in a lower coordination than terrace atoms. The result is analogous to surface relaxation, the lower coordination at the step-edges causes small atomic displacements so that equilibrium atom separations are shortened. This relaxation propagates for some distance into the step, thereby creating the strain field.

It has been suggested that the interaction of the strain fields due to successive steps causes the step-step repulsion which stabilises some vicinal

surfaces against *step bunching* [26]. This is because the overlap of strain fields where atoms are displaced in the same sense is energetically unfavourable, leading to the repulsive interaction, while strain fields of opposite sense are attractive. More complicated anisotropic strain fields will develop around defects such as screw dislocations and partial dislocations (domain boundaries caused by stacking faults). The repulsive interaction between the latter dislocations can result in highly ordered features. These anisotropic strain-fields can act attractively or repulsively to adatoms leading to preferential nucleation at (attractive) or in between (repulsive) these dislocations. This can produce regularly spaced islands with a narrow size distribution *e.g.* Ni nucleation on the ($\sqrt{3} \times 22$) reconstructed Au(111) surface [60].

2.6 Surfactants

In discussing the kinetic processes that control epitaxial growth, and such quantities as island density and critical island area, some attention must be given to the matter of surfactant growth. Surfactants are impurities which are added to (or already present in) an epitaxial system to promote and regulate LBL growth. Some examples of surfactant induced LBL growth are: O for Fe/Fe(110) [61], Sb for Ag/Ag(111) [62], O for Pt/Pt(111) [63], O for Cu/Cu(111) [64] and Sb for Co/Cu(111) [65]. The main characteristics of these impurities are a low surface energy, high mobility and low reactivity with film (and substrate), so that they float on top of the growing film without being incorporated into it. Originally, their action was understood in terms of lowering the surface free energy of the film, thereby promoting surface wetting and 2D growth. However, since surfactant action is often observed in homoepitaxial systems, a fuller understanding of the atomistic processes

at work is now being approached.

A number of mechanisms for surfactant action have been proposed which affect interlayer mass transport, critical island area and island density:

- The surfactant decorates island- and step-edges where it lowers the diffusion barrier across the step-down edges. This is due to the usually weaker interaction between the adatom and surfactant than the adatom-adatom interaction.
- If the substrate holds the adlayer under tensile stress, chemisorption of an electronegative adsorbate at an island-edge may weaken the lateral bond of edge atoms towards the island. This could result in an outward relaxation of edge atoms which would facilitate the exchange mechanism for step-down diffusion.
- Surfactant atoms at the step-edges reflect atoms approaching the step-edge from the lower terrace, thereby reducing interlayer mass transport in the step-up direction and increasing the island density on the terrace.
- Surfactant atoms adsorbed onto the terrace can act as nucleation centres, and reduce adatom mobility on terraces, to increase island density. By having a high density of small-area islands, adatoms arriving on top of the incomplete monolayer have a higher probability of reaching step-edges before nucleating a new layer.
- Surface impurities produce a potential energy gradient which attracts adatoms to step-edges, thus enhancing the arrival rate at edges and so increasing the probability for an adatom to diffuse from one layer down to a lower one.
- By lowering the mobility of adatoms on top of islands, surfactant atoms effectively increase the barrier to diffusion across the terrace. As a result, the difference between the terrace diffusion barrier and the step-edge diffusion

barrier is reduced, allowing greater interlayer mass transport.

- Inclusion of surfactant atoms at the step-edges may enhance the diffusion of adatoms along these edges, thereby promoting dendritic growth. This greatly reduces the diffusion length required to reach a step-edge.

2.7 Interface alloying

The question of miscibility in metal epitaxial systems is a technologically important issue. For magnetic multilayer devices, interface mixing between two epitaxial layers can reduce charge transport across the interface, or affect the extent to which one layer is magnetically ordered with respect to the next [66, 67]. The novel catalytic properties of surface alloys are also an extensive field of research [3, 68].

The first consideration is the bulk miscibility of the two metals - alloying in the bulk generally indicates the likelihood of interdiffusion or alloying at the 2D interface. There are numerous examples of bulk-miscible systems which have been grown epitaxially, whose intermixing was studied using STM - Cu/Au [69], Fe/Cu [70], Ag/Pt [71] and Pd/Cu [72]. As a rule, when the surface free energy of the deposit is higher than that of the substrate a thermodynamic driving force towards intermixing is present. If the surface free energy of the deposit is lower than that of the substrate, then the deposit should wet the substrate surface.

However, there are a number of cases where 2D alloys are formed which have no analogue in the bulk. Examples are the Au/Ni [73], Ag/Cu [74], Ag/Ni [68] and Pb/Cu [75] systems, where STM studies have confirmed intermixing in the sub-monolayer regime. The tendency towards intermixing in these systems is controlled by the coordination of the surface - which deter-

mines the number of substrate bonds that must be broken - and the lattice mismatch which determines the amount of deposit that can be accommodated within the substrate surface - due to the size difference between the atoms. A full discussion of this topic is given in reference [68].

Where a sharp interface is required, an epitaxial system with a low lattice mismatch and largely disparate surface free energies must be chosen. For magnetic films, refractory metal surfaces are favoured substrates because of their large cohesive energies, high melting points and moderate lattice mismatch. Examples are the Ni/W [76] and Fe/W [77, 78] systems where no intermixing is observed up to re-evaporation of the deposit, and Fe/Mo where intermixing only begins at 800 K [79].

Chapter 3

Experimental details

3.1 Ultra-high vacuum

3.1.1 Vacuum requirements

As discussed earlier, the presence of adsorbates on a surface can have a variety of effects such as altering surface stress, causing surface reconstruction, quenching magnetic moments *etc.* Therefore, the presence of contaminants can significantly affect results obtained with surface-sensitive techniques such as STM, LEED, AES, ESD *etc.* Consequently, a high degree of surface cleanliness (≤ 1 at%) is required during the observation time of an experiment in order to obtain a meaningful result.

The period during which the surface contamination will be within an acceptable limit, will be determined primarily by the rate at which gas-particles (atoms or molecules) impinge upon the sample surface, given by equation 2.27:

$$R = \frac{P}{\sqrt{2\pi mk_B T}} \quad [m^{-2}s^{-1}] \quad (3.1)$$

which at constant temperature is largely dependent upon the gas pressure

P(mbar)	10^3	1	10^{-3}	10^{-6}	10^{-12}
	-Low-	-Med.-	-HV-	-UHV-	-XHV
P(Pa)	10^5	10^2	10^{-1}	10^{-4}	10^{-10}

Table 3.1: The various ranges of vacuum, defined in units of *mbar* and *Pa*, where 1 atmosphere = 760 torr = 1013 millibar = 1.013×10^5 pascal. HV, UHV and XHV refer to high-, ultra-high and extreme-high vacuum respectively. Reproduced from [80].

within the experiment environment. Reducing this gas pressure will increase the longevity of a clean surface. As a result, most surface sensitive techniques require a vacuum environment for operation - table 3.1 lists the various ranges of vacuum.

When considering vacua, it is useful to calculate the *molecular mean free path* λ , which is the average distance travelled by a gas-particle before it collides with another particle.

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \quad [\text{m}] \quad (3.2)$$

where πd^2 represents the collision cross-section of the particle, d is the particle diameter and n is the number density of particles, given by:

$$n = \frac{P}{k_B T} \quad [m^{-3}] \quad (3.3)$$

A *monolayer formation time* τ_m can be defined, which is the time taken to form a complete particle layer on the surface. In addition to the impingement rate, τ_m will depend on the *sticking probability* $s(\theta)$ of the gas-particle on the surface, for sub-monolayer coverages, this can be given by a relation of the type:

$$s(\theta) = s_0(1 - \theta) \quad (3.4)$$

P (mbar)	P (Pa)	n (m^{-3})	λ (m)	R ($m^{-2}.s^{-1}$)	τ_m
1013	1.013×10^5	2.5×10^{25}	6.6×10^{-8}	2.9×10^{27}	1.7 ns
1.33×10^{-3}	0.133	3.2×10^{19}	5.1×10^{-2}	3.8×10^{21}	1.3 ms
1.33×10^{-6}	1.33×10^{-4}	3.2×10^{16}	5.1	3.8×10^{18}	1.3 s
1.33×10^{-9}	1.33×10^{-7}	3.2×10^{13}	5.1×10^4	3.8×10^{15}	22 min.
1.33×10^{-11}	1.33×10^{-9}	3.2×10^{11}	5.1×10^6	3.8×10^{13}	36.5 hrs.

Table 3.2: Gas-particle density n , mean free path λ , arrival rate R and monolayer formation time τ_m on the W(100) surface at various P for N_2 at 300K.

The sticking probability is dependent upon the fraction of the surface already covered θ . Beginning with an *initial sticking probability* s_0 , it falls off as the fraction of available adsorption sites $(1 - \theta)$ decreases. Assuming that the sticking probability is constant and that when the gas-particle strikes the surface there is a one-to-one correspondence between the gas and surface atoms, the monolayer formation time τ_m is:

$$\tau_m = \frac{n_s}{RN s_0} \quad (3.5)$$

where n_s is the total number of surface atoms and N is the number of atoms per gas-particle.

As an example the monolayer formation time is calculated for N_2 adsorption on the W(100) surface at room temperature for various pressures in table 3.2. The sticking coefficient is assumed to be equal to unity, while the molecular mass is taken as 4.65×10^{-26} kg and the molecular diameter is taken as $3.7 \text{ \AA}^2$ [81]. The lattice parameter of bcc tungsten is $3.165 \text{ \AA}$, so that the atomic density of the W(100) surface n_s is $9.98 \times 10^{18} m^{-2}$.

For surface studies of transition metals such as Fe, Mo and W, which are highly reactive, with a particularly strong affinity for oxygen, a high degree

of surface cleanliness can only be achieved for long periods under ultra-high vacuum (UHV) conditions.

3.1.2 Pumping

The pumping time required to reach a specific vacuum pressure will depend on the gas flow rate from the chamber being evacuated. The gas flow rate, or *throughput* Q is given by:

$$Q = \frac{d(PV)}{dt} \quad [Pa.m^3.s^{-1}] \quad (3.6)$$

which is related to the *mass flow rate* by:

$$\frac{dM}{dt} = \frac{mQ}{k_B T} \quad [kg.s^{-1}] \quad (3.7)$$

while Q is related to the *volume flow rate* S by:

$$Q = SP \quad (3.8)$$

There are three main gas flow regimes, all of which will be encountered during a pump-down from atmospheric pressure to UHV. These are the (1) *turbulent*, (2) *viscous or laminar* and (3) *molecular* flow regimes. The factors which determine the particular regime are:

- the magnitude of the flow rate
- the pressure difference across the vessel through which there is gas flow
- the surface finish and geometry of this vessel
- the nature of the gas being pumped (molecular weight *etc.*)

The nature of the gas flow can be defined by two dimensionless numbers, the *Reynolds number* R_e and the *Knudsen number* K_n , where:

$$R_e = \frac{\rho v D}{\eta} , \quad K_n = \frac{\lambda}{D} \quad (3.9)$$

where ρ is the gas density (kg.m^{-3}), v is the flow velocity (m.s^{-1}), η is the gas viscosity (N.s.m^{-2}) and D is the diameter of the vessel.

Turbulent flow: This regime is encountered very briefly during the initial stages of pump-down. At this point there is a high pressure gradient between the pump inlet and the main body of the vessel. The mean free path for particle collisions is much smaller than the dimensions of the vessel. With a Reynolds number $Re > 2100$, it is characterised by chaotic flow with many eddies and vortices.

Laminar or viscous flow: With a Reynolds number $Re < 1100^1$ and a Knudsen number $Kn < 0.001$, this flow regime is encountered in the early stages of pump-down, at moderate pressure gradients. It is characterised by ordered flow which is proportional to the pressure gradient and the viscosity. The viscosity limits the flow since collisions between gas-particles occur more frequently than collisions with the vessel walls. Only particles near the walls collide with them, so that the velocity decreases near these surfaces.

Molecular flow: As the mean free path of the gas-particles approaches the dimensions of the vessel, the flow reaches an intermediate stage between viscous and molecular flow. However, when $Kn > 1$ more collisions occur with the vessel walls than with other gas-particles. This is the molecular flow regime, where the motion of the gas-particles is random, but there is a net flow from regions of higher to lower particle concentration. Pumping in this regime is based on the concept of capturing the particles that stray into the pump inlet.

The various pipes through which the vessel is pumped offer resistance to all forms of gas-flow, resulting in a pressure gradient ΔP between its opposite

¹ A Reynolds number in the range $1200 < Re < 2200$ can correspond to either turbulent or laminar flow, depending on the surface roughness and geometry of the vessel.

ends. The *conductance* of a pipe or bellows is the reciprocal of this resistance and is defined as:

$$C = \frac{Q}{\Delta P} \quad [m^3.s^{-1}] \quad (3.10)$$

Capacitance C and pumping speed S are conventionally given in units of $L.s^{-1}$ (or equivalently in $m^3.hour^{-1}$). For the conductance of pipes in parallel, the total conductance C_T is:

$$C_T = C_1 + C_2 + \dots + C_n \quad [L.s^{-1}] \quad (3.11)$$

while for pipes in series:

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} + \dots + \frac{1}{C_n} \quad (3.12)$$

For a pump with nominal pumping speed S ($L.s^{-1}$) connected to a pipe of conductance C , the effective pumping speed is limited by the conductance of the pipe as:

$$\frac{1}{S_{eff}} = \frac{1}{S} + \frac{1}{C} \quad (3.13)$$

It is clear that the conductance of a pipe will depend upon its surface finish and geometry, while the smallest conductance between the pump and the chamber will determine the effective pumping speed within it.

The ultimate pressure in a system is obtained when an equilibrium is reached between the throughput due to pumping and the throughputs due to processes which deliver gas-particles into the system. These are:

- Leaks from the atmosphere side through misaligned flanges or cracked welds.
- Virtual leaks from trapped air pockets, such as those formed when a screw is threaded into a blind hole. Gas escapes slowly along the helical path of the thread.

- Surface and volume outgassing of gas-particles which have been adsorbed onto and absorbed into materials present inside the chamber - the major adsorbed contaminant is water. All materials chosen for vacuum applications have an extremely low vapour pressure so that they will not sublime or evaporate in vacuum. The outgassing process is usually speeded up by thermal activation through baking of the vacuum system.
- The materials used for construction of vacuum systems, glass, stainless steel, viton rubber *etc.* will be permeable to the lighter elements. For example hydrogen can diffuse through stainless steel. This is a continuous process as gas-particles can enter the vacuum system from the atmosphere side by diffusion.

A fuller discussion of these topics, including flow calculations is available in references [82] and [83].

3.1.3 The UHV system

The original UHV system was designed and constructed by Dr. I.V. Shvets, Dr. A. Quinn and Dr. J. Osing. Consisting of three main chambers: the room-temperature STM (RTSTM) chamber with an annexe for LEED/AES analysis, the preparation chamber for tip and sample preparation and the low-temperature STM (LTSTM) chamber, the layout of this system is shown schematically in figure 3.1. A full description of the construction and operation of the RTSTM and preparation systems is given by Quinn [83], while the LTSTM system is detailed by Osing [10].

During the course of this work, the UHV system was extensively modified, involving the replacement of the LTSTM and preparation chambers, installation of three new pumps and an Auger electron spectroscopy (AES) subsystem. The layout of the system as it is now, is shown schematically in

figure 3.2. Construction diagrams and port tables for both new chambers are included in appendices A and B.

Each chamber can be valved off from the rest of the system via a series of UHV gate valves (VAT [84]) and brought to atmospheric pressure for maintenance without breaking vacuum in the rest of the system. Samples and STM tips are introduced to the system via a fast-entry loadlock connected to the preparation chamber by a gate valve. When not in use, this loadlock is usually maintained in the low 10^{-10} mbar range by a 20 L.s^{-1} differential ion-pump (Perkin-Elmer [85]). Tip and sample transfer throughout the chamber is facilitated by a series of wobblesticks and magnetically-coupled linear drives (Vacuum Generators Ltd. [86]) which can access each sample stage. The pressure in each chamber is monitored using nude Bayard-Alpert type ionisation gauges (Perkin-Elmer). The entire system is supported on a stainless steel box-section frame which can be floated on pneumatic dampers to isolate the system from building vibrations during STM operation. The box-section is filled with gravel to minimise hollow pipe vibrations.

The preparation chamber

The preparation chamber was designed by the author to replace the original chamber (a customised nine-way cross [83]) with a larger chamber allowing greater access and manipulation room. Manufactured by Caburn-MDC [87], it is an O.D. 209 mm $\times$ 3.0 mm stainless steel (304 grade) cylinder approximately 0.8 m long, with one hemispherical end and one plated end. There are a total of twenty-seven access ports, listed in the port table in appendix B. It contains all the facilities for *in-situ* tip and sample preparation: electron-beam and resistive heaters, quartz crystal deposition monitor (Inficon [88]), liquid N₂ cooled evaporator, ion-gun (VG Microtech [89]) and precision leak

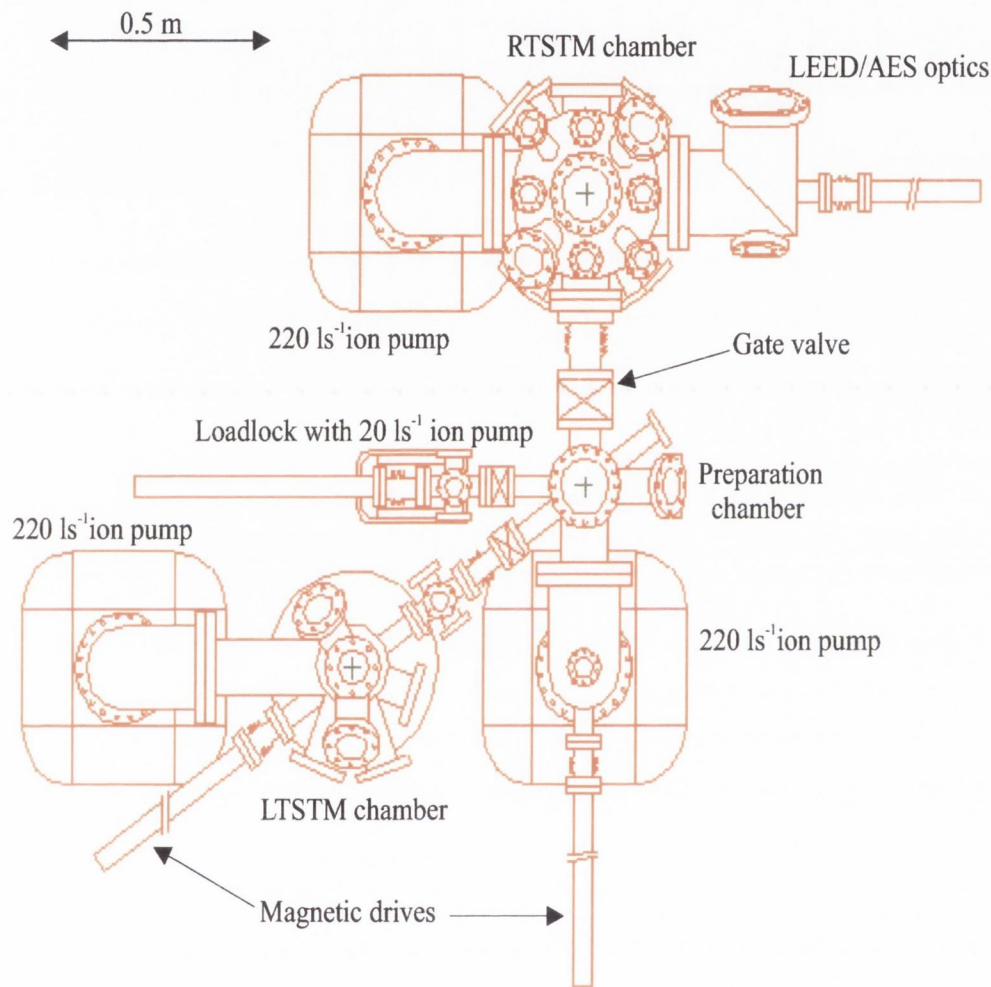


Figure 3.1: Top view schematic of the UHV system layout prior to modification. The original preparation chamber was a modified nine-way cross, which was attached via a mitred elbow to a 220 $L.s^{-1}$ differential ion pump.

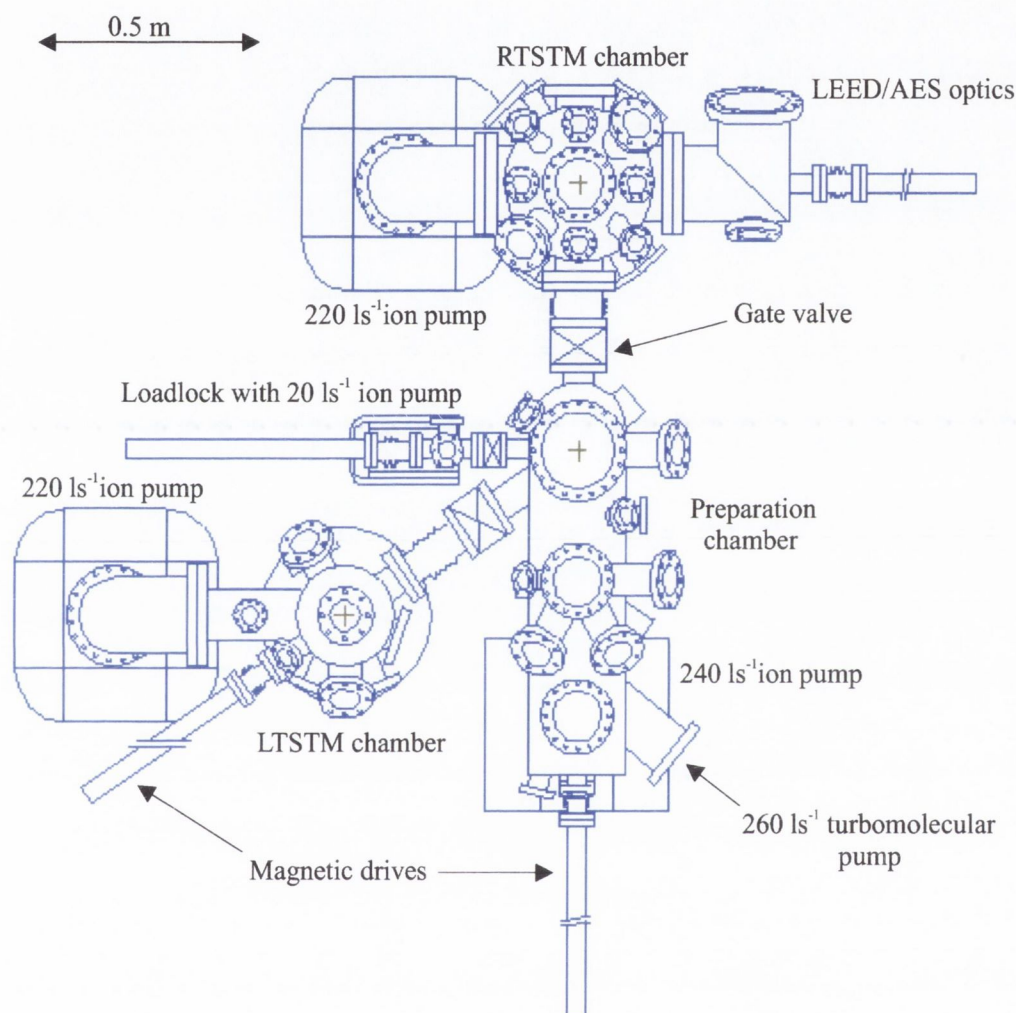


Figure 3.2: Top view schematic of the UHV system after installation of the new LTSTM and preparation chambers. The original LTSTM and preparation chambers have been replaced with larger chambers, offering more access ports.

valves for controlled introduction of high purity oxygen and argon gases². In addition, the preparation chamber also contains a cylindrical mirror analyser (CMA) based AES subsystem (Perkin-Elmer), which will be discussed later.

The chamber is usually baked for 2 days at 170-180 °C by three heating tapes with a total radiative power of 2175 W. The temperature is measured by two thermocouples, the first feeds the Eurotherm 91e controller which controls the bakeout [83], while the second feeds an Omega CN375 controller which acts as a fail-safe against over-heating. The chamber is wrapped in aluminium foil and a heavy bakeout blanket to provide thermal insulation. A number of pumps are used to achieve UHV conditions in the chamber:

- a water-cooled TMU 260 $L.s^{-1}$ turbomolecular pump (Pfeiffer Vacuum [90]) is connected directly to the preparation chamber via a DN 100 CF gate valve (VAT) to minimise the drop in effective pumping speed. This pump is backed by a 0.7 $L.s^{-1}$ two-stage rotary vane pump³. The TMU260 is used for pumping the chamber down from atmosphere and handling heavy gas loads during ion-etching and oxidation procedures. This set-up has a superior pump-down time to the original set-up which used a 60 $L.s^{-1}$ turbo connected to the chamber via a four-way cross. A base pressure in the low 10^{-6} mbar region can usually be reached within 5-6 hours after pump-down from atmospheric pressure. It is fitted with a 100 W heating jacket to heat the pump inlet to ~ 120 °C during bakeout.

- a double-ended 240 $L.s^{-1}$ differential ion-pump (Physical Electronics [85])

²An additional gas line has recently been installed by the author, for controlled introduction of molecular hydrogen into the system.

³Though there is the possibility of some back-streaming of oil vapours with this pump, it was chosen over a dry diaphragm pump as it improves the ultimate pressure attainable by the turbo pump [91].

is used to maintain UHV conditions. The pump is fitted with four external 200 W heating strips for baking. This ion-pump is located below and away from the Auger set-up so that the latter is not affected by stray magnetic fields.

- a liquid N_2 cryoshroud is inserted in the base flange of the ion-pump which houses a titanium sublimation pump (TSP). The maximum pumping speed obtainable when titanium is deposited on a surface at 300 K is $3\text{--}9\text{ L.s}^{-1}.\text{cm}^{-2}$ for hydrogen and oxygen, while it is increased by a factor of 2-5 upon cooling to 70 K [82].

- a non-evaporable getter pump (NEG) from SAES Getters [92] is positioned mid-way along the chamber. This pump carries a cartridge of St 172 (ZrVFe alloy) high porosity sintered disks mounted on a 0.D. 70 mm flange. It works in a similar manner to the titanium sublimation pump, by chemically reacting with gases. However, the getter material diffuses into the bulk of the getter, so that the pumping speed is controlled by this diffusion rate. This can be increased by heating the getter cartridge with an insulated W filament located inside it. This pump is particularly effective at pumping hydrogen with a maximum pumping speed of roughly 400 L.s^{-1} at room-temperature.

A base pressure in the mid- 10^{-11} mbar is usually obtained in this chamber after bakeout.

The LTSTM chamber

The LTSTM chamber was also designed by the author and built by Caburn-MDC. It has dimensions O.D. 209 mm $\times$ 3.0 mm $\times$ 270 mm (height) with one dished end. There are fifteen ports, which are listed in appendix A. The chamber is connected to the UHV insert of a 60 L liquid He cryostat, for cryogenic experiments. The system is pumped from atmosphere by a 60 L.s^{-1}

turbo pump which is connected via a right-angle UHV valve (VG) and a 1 metre long formed bellows. A bakeout system has not yet been constructed for this system, the chamber is pumped by a 220 L.s^{-1} differential ion-pump with TSP and cryoshroud and a NEG pump. A base pressure of $1 \times 10^{-9} \text{ mbar}$ is usually obtained.

The RTSTM chamber

The RTSTM chamber is a standard O.D. 457 mm commercial chamber (Perkin-Elmer) with two modified ports, there are a total of twenty-one ports. The RTSTM is mounted inside this chamber via the O.D. 254 mm base flange. A customised mitred elbow (VG) to the side of the main chamber provides the annexe that houses the four-grid LEED/Auger optics. This chamber also contains a tip and sample storage carousel. The chamber is pumped by a 220 L.s^{-1} differential ion-pump with TSP and cryoshroud, which is connected to a mitred elbow on the opposite side of the chamber. This eliminates stray magnetic fields from the vicinity where LEED and (magnetic) STM experiments are carried out. The chamber is pumped down from atmosphere in the same fashion as the LTSTM chamber. The effective pumping speed is probably restricted to a few L.s^{-1} by pumping in this manner. The chamber is baked inside a custom-designed oven [83] which encloses the chamber, LEED annexe and ion-pump. There are two 840 W radiative heaters mounted on the base of the oven, while the ion-pump houses eight 200 W heating strips. The temperature inside this oven is maintained at 120-130 °C (this temperature is below the maximum withstandable temperature of the STM I-V pre-amplifier) for 2-3 days to achieve a base pressure in the mid- 10^{-11} mbar .

3.2 Sample preparation

3.2.1 Sample cleaning - the e-beam heater

As-grown 5N purity crystals of refractory metals such as W and Mo, typically contain bulk impurities (C, K, S, *etc.*) in concentrations of a few parts per million. The typical procedure for cleaning refractory metal surfaces involves annealing the crystal in an O_2 atmosphere of partial pressure $1 \times 10^{-7} \leq P_{O_2} \leq 1 \times 10^{-6}$ mbar at elevated temperatures ~ 1200 - 1300 K. At these temperatures the 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 surface to very high temperatures, in the range $2200K \leq T_{flash} \leq 2600K$ for short periods (5-20 seconds) under UHV conditions. These flashes are accompanied by sharp pressure bursts in the vacuum, so that some time must be allowed between flashes to allow the sample to cool and the vacuum to recover.

Conventional resistive heaters are not suitable for rapidly heating samples to such high temperatures. Instead, an electron beam heater, designed and assembled by Dr. J. Osing [10], was used. A schematic illustration of the e-beam set-up is shown in figure 3.3. The sample is clamped in a sample holder between a Ta cap that screws onto a Mo body, the thread is deliberately machined for a loose fit. These measures are taken to prevent the two pieces of the sample holder from welding together. This holder is mounted into a Ta stage which is held at a potential of $+1$ kV. A current ($2.5A \leq I \leq 4.5A$) is passed through a grounded thoriated tungsten filament ($\phi 0.15$ mm, 0.6 % Th) which generates thermionic emission of electrons. These electrons are accelerated towards the cap of the sample holder, where upon collision, their kinetic energy is transferred to the sample as heat. Because the filament

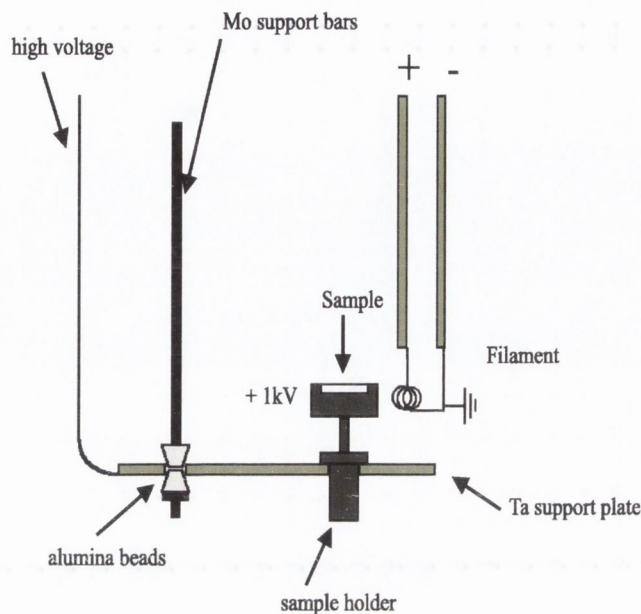


Figure 3.3: A schematic illustration of the e-beam heater used to clean refractory metal samples. Reproduced from [10].

is situated to one side of the sample there will be a temperature gradient across the sample, however, this set-up produces a contamination free surface. Surface temperatures are measured from outside the chamber using an infrared pyrometer (Altimex UX-20/600 [93]) using an emissivity value of $\varepsilon = 0.35$ for both W and Mo. The absolute accuracy of these measurements is hindered by the position of the filament, which will contribute to the level of radiation measured. However, the temperatures measured are within a similar range to the values used by other groups to obtain clean surfaces [94,95].

3.2.2 Fe film deposition

The ultrathin Fe films were deposited using an electron beam evaporator (see figure 3.4) designed and assembled by C. Kempf. The principle of operation is the same as that for the e-beam heater. Electrons originating from a hot

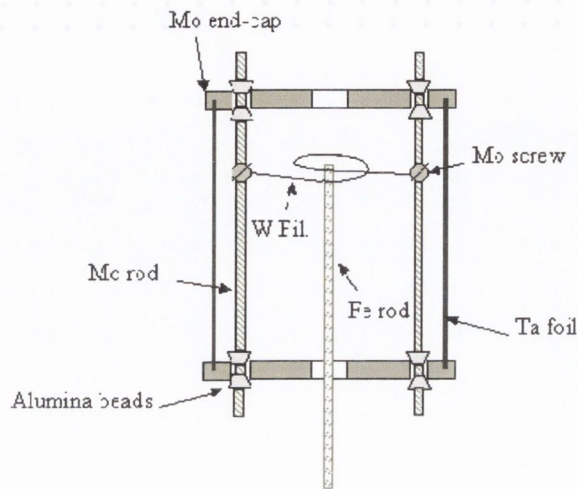


Figure 3.4: A schematic illustration showing a cross-sectional view of the e-beam evaporator used to deposit ultrathin Fe films. Reproduced from [83].

(thoriated tungsten) filament are accelerated towards a 3N purity $\phi 1.6$ mm Fe rod which is at a potential of $+1.9$ kV with respect to ground. A heat-shield is formed around the Fe rod and filament by a tube of Ta foil which sits into grooves cut in the Mo end-caps of the cell. Alumina beads isolate the filament from these end-caps. Apertures in each Mo cap allow the Fe rod into the cell at one end and the evaporated Fe out through the other. The entire cell fits inside a double-walled liquid N_2 cooled cryoshroud. During operation, cooling this cryoshroud minimises outgassing from the environs of the evaporator. A new Fe rod is outgassed for several hours before it is suitable for use, it is also outgassed for a further 3-4 hours before each subsequent deposition. Typical values for the filament and emission currents during deposition are 2.5 A and 4 mA respectively. The chamber pressure usually rises to no more than the mid- 10^{-10} mbar.

The sample sits upside-down inside a resistive heater (described later),

which has an aperture machined in its base. This set-up allows the sample surface to be heated for depositions at elevated temperatures. This heater stage is also equipped with a water-cooled quartz crystal balance and deposition monitor (Inficon). The quartz crystal balance measures the mass of iron arriving at its surface by the dampening effect of this mass on the resonant oscillations of the quartz crystal sensor. The measured mass may be converted into a film thickness value by the deposition monitor, which is programmed with values for the density of bcc Fe (7.86 g.cm^{-3}) and the exposed sensor area (diameter = 8 mm). However, the thickness value determined by this method is inaccurate as it assumes that the Fe deposited on the sensor surface grows as bcc Fe, which may not be the case. Therefore, it is safer to measure the mass arriving at the sensor surface per second and from this calculate the incident flux F_{Fe} (measured in $\text{kg.s}^{-1}.\text{m}^{-2}$) for deposition on the sample surface.

The heating stage and crystal sensor are mounted on a linear drive so that alternately, the sample or quartz monitor can be moved into position over the evaporator aperture. During a deposition the quartz crystal is first positioned over the evaporator aperture. The filament current is slowly increased until a stable deposition rate is achieved, this is usually about 0.5 ML.min^{-1} (0.015 Å.s^{-1}). Then the sample, which is cleaned 20-45 minutes prior to deposition, is rapidly moved into the deposition beam - this takes roughly 10 seconds. As a result the amount of material deposited upon the surface is not exactly controlled, however, the deposition rate is typically so low that only a very small fraction of the total coverage can be deposited in this time. Once the required deposition time has elapsed the filament current and accelerating voltage are quickly ramped down.

3.2.3 The resistive heater

The heater was designed by C. Kempf and assembled and calibrated by J. Naumann. The heater consists of an alumina crucible with a spiral groove machined along its circumference along which a $\phi 0.2\text{ mm}$ W wire is wrapped. The sample sits inside a Ta insert which fits inside the crucible. Both the crucible and the Ta insert have concentric apertures machined in their bases. The sample can be inserted face-down for film depositions or face-up for Ar^+ ion bombardment. The crucible fits inside a stainless steel can which is connected to the feedthrough for the quartz crystal monitor. This feedthrough comprises two water cooling pipes and a BNC feedthrough to carry the quartz crystal signal to the monitor. A separate feedthrough carries the connections to the heater filament and a K-type (Omega) thermocouple which is spot-welded to the Ta insert. The heater was calibrated for temperature ($^{\circ}\text{C}$) *versus* filament power (W) with the thermocouple attached in this position and to the face of a sample-holder mounted face-down in the heater. The calibration curves for different filaments are given in appendix C.

3.2.4 The ion gun

The preparation chamber is fitted with a cold-cathode type ion gun (VG Microtech), which is used for Ar^+ ion etching of STM tips and for some sputtering experiments. During operation, the chamber is pumped using the 260 L.s^{-1} turbo pump. The argon gas is introduced by leak-valve directly into the gas-cell of the ion-gun, the base pressure in the chamber rises to $5 \times 10^{-6} \leq P_{\text{Ar}} \leq 1 \times 10^{-5}\text{ mbar}$. The gas-cell contains a cylindrical anode, while the casing of the cell acts as the cathode. Applying a potential difference of a few kilovolts between these electrodes strikes an electric discharge in the

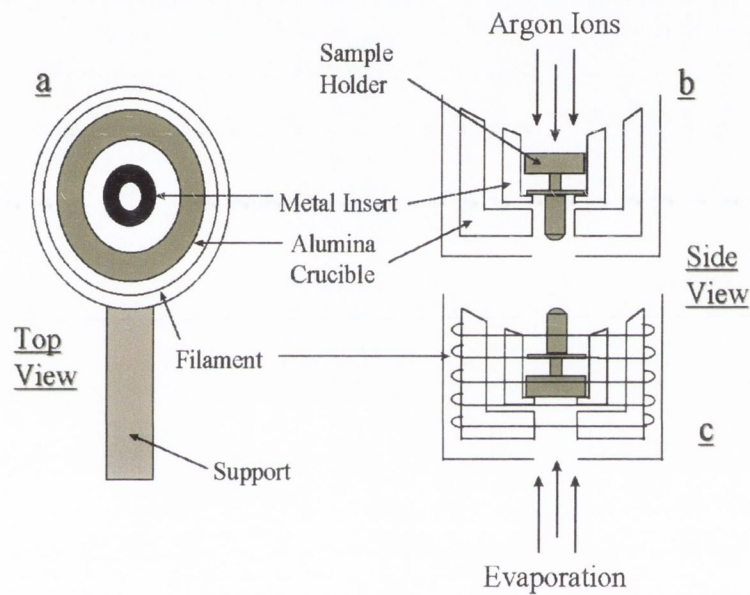


Figure 3.5: Schematic illustration of the resistive heater. The sample can sit face-down in the heater so that Fe can be deposited on it through the aperture in the base. Alternatively, the sample (or tip) is inserted face-up for ion-etching. Reproduced from [96].

cell, which generates the positive ions. These ions are confined in a helical path in the cell by an externally mounted cylindrical permanent magnet. The ion beam is accelerated with a beam energy between 500 eV and 5 keV, through the gas-cell aperture and focussed by a series of concentric electrostatic lenses. The spot size could be varied between 19 and 25 mm with a sample/gun working distance of 250 mm.

The target diameter is taken as 11 mm, which is the diameter of the circular Ta insert in the resistive heater, into which the sample is mounted for ion-etching. This insert is isolated from ground by the surrounding ceramic crucible. The thermocouple spot-welded to this insert allows the target current to be measured. This is typically of the order of $3.0 \leq I \leq 12.0 \mu A$ for a 1-2 keV beam energy and a chamber pressure of 1×10^{-5} mbar. Figure 3.6 shows a plot of target currents measured for various beam energies using two argon pressures. The target current is measured using the ion-gun control unit, which biases the sample with +15 V to suppress low energy secondary electrons generated by the impacting ions.

An estimate of the amount of material removed from the surface by sputtering can be calculated knowing the incident ion flux (calculated from the target current) and the sputter yield Y (the number of target atoms ejected per incident ion). The sputter rate ν is obtained from the relation [97]:

$$\nu = \frac{JYM}{\rho e N_A n} \quad [m.s^{-1}] \quad (3.14)$$

where J is the ion current density ($A.m^{-2}$), Y the sputter yield (atoms/incident ion), M the molar mass of the target matrix ($kg.mol^{-1}$), ρ the density ($kg.m^{-3}$), e the electron charge ($A.s$), N_A is Avogadro's constant (mol^{-1}) and n the number of components yielded per matrix molecule ($n = 1$ for an elemental target). For a circular target, this can be re-written

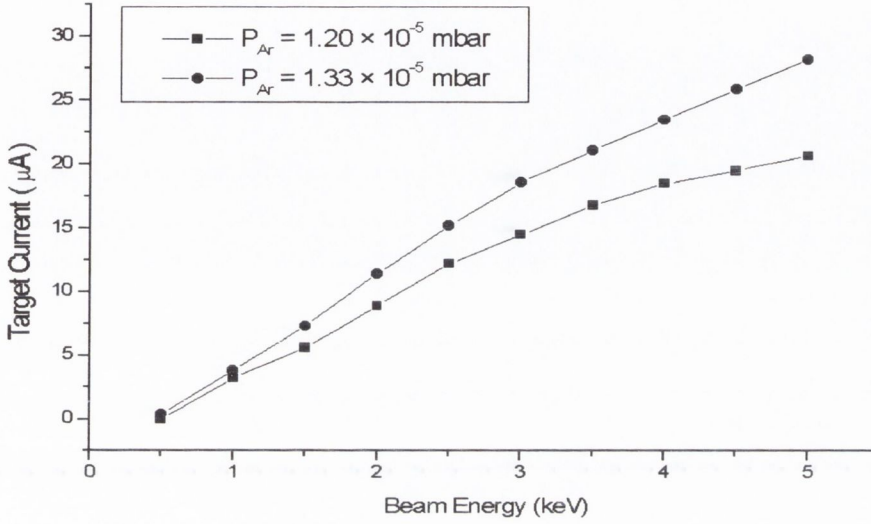


Figure 3.6: Ion gun target currents measured for various beam energies using two different argon partial pressures. The sample/gun working distance was 250 mm.

as:

$$\nu = \frac{4IYM}{e\pi D^2 \rho N_A} \quad [m.s^{-1}] \quad (3.15)$$

where I is the target current (A) and D is the sample diameter (m).

3.3 Sample analysis

3.3.1 The room-temperature STM

Comprehensive reviews of the theory and operating principles of scanning tunneling microscopy (STM) and spectroscopy (STS) are given in dedicated texts by Chen and Wiesendanger [11,98]. The fundamental theory of STM is modelled on the quantum-mechanical description of an electron with energy

E travelling in a 1D potential $U(z)$ of the form shown in figure 3.7(a). This electron is described by a wavefunction $\psi(z)$, which satisfies the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \psi(z) + U(z) \psi(z) = E \psi(z) \quad (3.16)$$

where m is the electron mass and $\hbar = h/2\pi$ (where h is Planck's constant). In the classically allowed region where $E > U(z)$, this equation has solutions of the form:

$$\psi(z) = \psi(0) e^{\pm i k z}, \quad k = \frac{\sqrt{2m(E - U)}}{\hbar} \quad (3.17)$$

where the electron can move in either the positive or negative sense of direction. In the classically forbidden *barrier* region where $E < U(z)$, the Schrödinger equation has the solution:

$$\psi(z) = \psi(0) e^{-\kappa z}, \quad \kappa = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (3.18)$$

The κ term describes the decay of the electron wavefunction within the barrier region. For a finite potential $U(z)$, there is a non-zero probability P of finding the electron at a position z inside the barrier region, which is given by:

$$P \propto |\psi(0)|^2 e^{-2\kappa z} \quad (3.19)$$

Consequently, if the width of the tunnel barrier is sufficiently narrow, there is a finite probability that the electron can tunnel through the barrier region.

In the tip-vacuum-sample configuration of an STM junction (figure 3.7(b)), the height of the tunnel barrier is determined by the *work function* ϕ of the tip and sample (assumed to be identical for convenience), which is the minimum energy required to remove an electron from the metal to vacuum. An electron at the tip or sample surface, with Fermi energy $E_F = -\phi$, will have the greatest opportunity to tunnel through the barrier, since by definition the *Fermi level* denotes the upper limit of electron occupancy in the

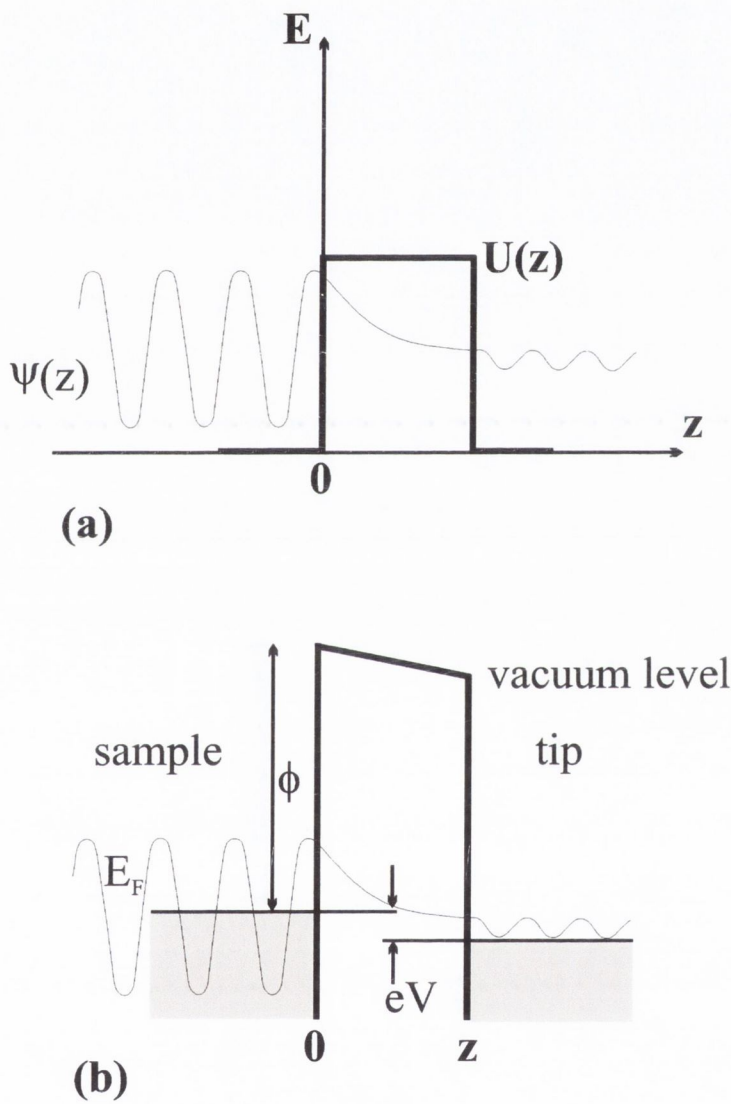


Figure 3.7: Schematic representations of (a) an electron described by the wavefunction $\psi(z)$ travelling in a one-dimensional potential $U(z)$ and (b) a STM junction under an applied bias V .

metal. In the absence of an externally applied bias, the electron can tunnel through the barrier in either direction so that there is no net tunnel current. By applying an external voltage V , electrons in the sample within the energy range $E_F - eV \leq E \leq E_F$ have an opportunity to tunnel through the barrier. If $eV \ll \phi$, then only electron states very near to the Fermi level are probed. The probability for an electron in the n th of these states to tunnel through a barrier of width W is given by:

$$P \propto |\psi_n(0)|^2 e^{-2\kappa W}, \quad \kappa = \frac{\sqrt{2m\phi}}{\hbar} \quad (3.20)$$

Taking all the possible states in the energy range $E_F - eV \leq E \leq E_F$ into account, the tunnel current is:

$$I_t \propto \sum_{E=E_F-eV}^{E_F} |\psi(0)|^2 e^{-2\kappa W} \quad (3.21)$$

This equation may be re-written in terms of the *local density of states* (LDOS) at the Fermi level of the sample surface $\rho_s(0, E_F)$:

$$I_t \propto V \rho_s(0, E_F) e^{-2\kappa W} \quad (3.22)$$

It is clear from this equation that: (1) the tunnel current is directly proportional to the bias applied across the junction, (2) it decays exponentially as the distance between the tip apex and the sample surface is increased and (3) the local density of states of the surface is sampled.

The significance of the probe-tip LDOS contribution is realised through a time-dependent perturbation model of metal-insulator-metal tunneling proposed by Bardeen [99]. Here, a *Transfer Hamiltonian* H_T is used to describe the transfer of a tunneling electron from a sample state ψ to a tip state χ . The tunnel current can be taken as a convolution of the sample LDOS ρ_s and the tip LDOS ρ_t .

$$I_t = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_s(E_F - eV + E) \rho_t(E_F - E) |M|^2 dE \quad (3.23)$$

I_t also includes a tunneling matrix element M , describing the amplitude of electron transfer across the tunnel barrier (through the overlap of the ψ and χ states). The integral describing M is evaluated over any surface lying within the barrier region.

$$M = \frac{\hbar}{2m} \int (\chi^* \frac{\partial \psi}{\partial z} - \psi \frac{\partial \chi^*}{\partial z}) dS \quad (3.24)$$

All STM images described in this thesis were obtained by scanning the tip across the surface in constant current mode. In this configuration the tip-sample separation is maintained at a constant value by means of a feedback-loop which controls a piezoelectric tube scanner holding the tip. The room-temperature microscope (RTSTM) used in this study was built by Dr. A. Quinn [83]. The STM head is constructed from machineable ceramic (Macor) and comprises a piezo tube scanner and a fine approach walker based upon the system developed by Dr. S.H. Pan at the University of Basel, Switzerland [100]. The sample is mounted on top of a polished quasi-cylindrical sapphire rod which is clamped between a set of six piezo stacks. These piezo stacks are arranged pairwise in a triangular fashion about the sapphire rod with one pair of stacks spring-loaded against it. The rod is moved towards or away from the tip in two steps: first the stacks shear sequentially so that the rod is clamped while each individual stack shears. Then they are allowed to relax simultaneously, dragging the rod in the direction opposite to the shear direction. A full description of this mechanism is discussed in [101,102]. This fine approach system is controlled using a home-built control unit [83].

The tube scanner is sectioned into four outer electrodes which carry the Z-X, Z+X, Z-Y and Z+Y voltages, while the inner electrode is grounded. The scanner has a dynamic range of ± 13000 Å in the z-direction and ± 20600 Å in the x- and y- directions. These ranges were calibrated on Cu(100) monatomic steps and HOPG atomic resolution images respectively. The STM head is

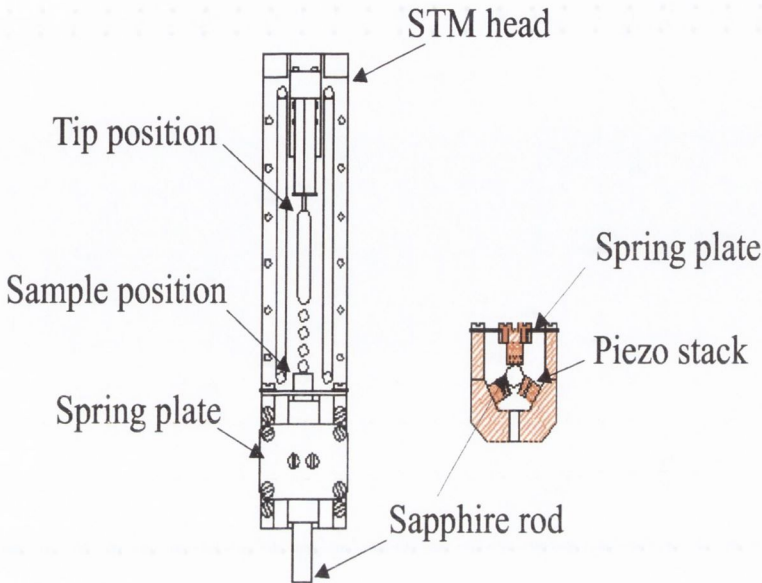


Figure 3.8: Schematic representation of a STM head similar to the RTSTM used. A front view and cross-section of the fine approach walker are shown.

isolated from vibrations by a two-stage spring system [83] which works in conjunction with the pneumatic dampers on the system frame.

The RTSTM chamber is also fitted with an electromagnet, designed and assembled by J. Naumann, to carry out magnetic STM experiments. This consists of two Permanorm 5000 poles with Kapton-insulated copper wire windings. Three thermocouples are fitted to monitor the heat output generated by the magnet. This magnet can be positioned so that the sample in the STM lies between the poles. An in-plane magnetic field of 90 mT is possible without significant overheating of the sample.

The STM controller used for these experiments is a TOPS II system by WA Technology [103]. The accompanying software provides some functions for data analysis, however data was also analysed using a MATLAB based

program *IMP*, which was developed by A. Quinn and J. Naumann⁴, and commercial software from NTMDT, Russia [104].

3.3.2 Four-grid LEED/AES optics

The RVLO 900 four-grid reverse view optics were manufactured by VG Microtech. Primarily used for low-energy electron diffraction (LEED), these optics can also be operated as a retarding-field analyser for Auger electron spectroscopy (AES). The optics are mounted on a O.D. 200 mm CF custom elbow which is tilted at an angle of 30° to the horizontal. The optics are surrounded by a mu-metal cylinder to provide shielding from stray magnetic fields. The sample sits in the transfer fork of a magnetic drive, which is grounded by a stainless steel braid to an OFHC copper block at the bottom of the LEED annexe. The sample is rotated in this drive so that its surface faces the electron gun. Scattered electrons are collected by the grids and screen located behind the gun.

LEED operation

A schematic illustration of the four-grid LEED is shown in figure 3.9. The grid nearest the sample M1 is earthed so that electrons scattered by the sample, initially travel in field-free space. A negative potential is applied to the two centre grids M2a and M2b to suppress inelastically scattered electrons, while elastically scattered electrons are accelerated towards the phosphorescent screen by its +5 keV potential. The fourth mesh M3 is also grounded to reduce the field penetration of the suppressing grids by the screen.

LEED patterns of the refractory metal surfaces were taken at energies between 40 and 200 eV, using an emission current of 0.5 mA, the target current

⁴With additional modifications by M. Kresnyak.

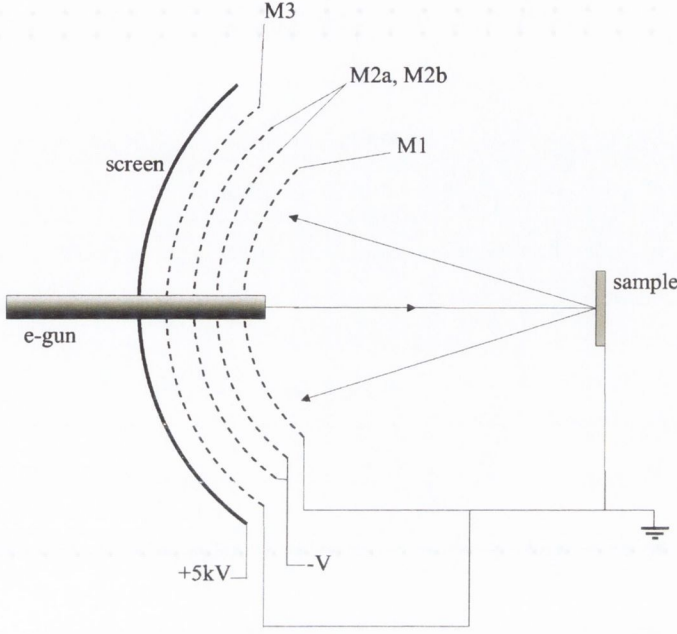


Figure 3.9: Schematic of four-grid optics operating in LEED mode (*c.f.* reference [105]).

could not be measured. LEED patterns were recorded by photographing the screen. The spot-separation in these photographs could be used to calculate the surface net parameters of the surfaces analysed [83].

For surface diffraction in a 2D system, the electron beam must conserve both its energy and the component of its momentum parallel to the surface.

$$\vec{k}_{\parallel}^2 + \vec{k}_{\perp}^2 = \vec{k}_{\parallel}'^2 + \vec{k}_{\perp}'^2, \quad \vec{k}_{\parallel}' = \vec{k}_{\parallel} + \vec{g}_{hl} \quad (3.25)$$

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

$$|\vec{g}_{hl}| = |\hbar \vec{a}^* + l \vec{b}^*| = |\vec{k}| \sin \alpha = \frac{\sqrt{2m_e E_{eV}}}{\hbar} \sin \alpha \quad (3.26)$$

where $\vec{a}^*$ and $\vec{b}^*$ are the reciprocal lattice *primitive net vectors*. These are related to the real space vectors $\vec{a}$ and $\vec{b}$ by [105]:

$$\vec{a} \cdot \vec{a}^* = \vec{b} \cdot \vec{b}^* = 2\pi \quad \vec{a} \cdot \vec{b}^* = \vec{b} \cdot \vec{a}^* = 0 \quad (3.27)$$

The reciprocal lattice vector $\vec{g}_{hl}$ lies in a direction that is orthogonal to the plane of the real space lattice that 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 spacing between atomic planes with these Miller indices is:

$$d_{hl} = \frac{2\pi}{|\vec{g}_{hl}|} = \frac{\mathbf{h}}{\sin\alpha\sqrt{2m_e E_{eV}}} \quad [\text{\AA}] \quad (3.28)$$

where $\mathbf{h}$ is Planck's constant. For a centred (or primitive) rectangular lattice the spacing of atomic rows is given by [35]:

$$\frac{1}{d_{hl}^2} = \frac{h^2}{|\vec{a}|^2} + \frac{l^2}{|\vec{b}|^2} \quad (3.29)$$

The angle α may be determined from the spot-separation d_r between indexed spots in the LEED pattern by using the geometry of the LEED screen, shown in figure 3.10. The actual spot-separation can be calculated from the distance d_{photo} measured in a photograph of the pattern using:

$$d_r = \frac{d_{photo} D_r}{D_{photo}} \quad (3.30)$$

where D_r is the actual screen diameter and D_{photo} is the screen diameter measured in the photograph.

For the bcc (110) surface the *primitive net cell* described by the primitive net vectors does not represent the full symmetry of the surface. A *conventional unit cell* is required, with lattice parameters a_0 and b_0 , that incorporates the full centred-rectangular structure of the surface. The distinction between the primitive and conventional cells is highlighted in figure 3.11 and

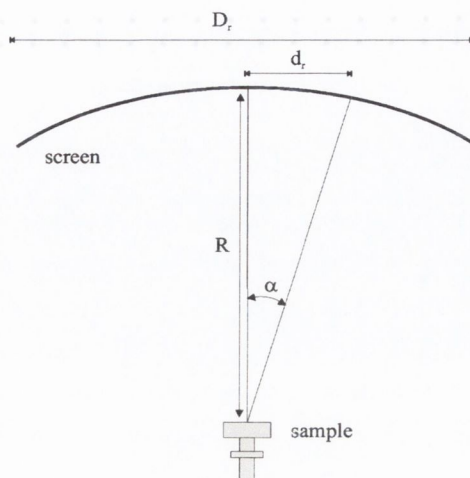


Figure 3.10: Schematic of the LEED screen geometry. The sample is placed at the focal point of the screen. The angle α can be determined from $\tan \alpha = d_r/R$. The distance d_r is the separation between the hk spot and the specular spot.

is discussed by Ashcroft and Mermin [106]. By convention the diffraction patterns of bcc (110) surfaces are indexed with respect to the conventional unit cell, leading to *missing* (10) and (01) beams [107,108]. Using this convention, the parameters a_o and b_o of the conventional surface net can be found.

AES operation

The LEED optics can be operated as a *retarding field analyser* (RFA) to perform Auger electron spectroscopy (AES). In this mode, the grids M1 and M3 are grounded, while a retarding potential is applied to the composite grid M2a + M2b. The screen is biased at +120 V to collect the electron signal.

The signal-to-noise ratio of the RFA is limited because it operates as a high-pass filter. Electrons reaching the screen will have an energy range between the minimum pass energy E_0 allowed by the retarding field and the

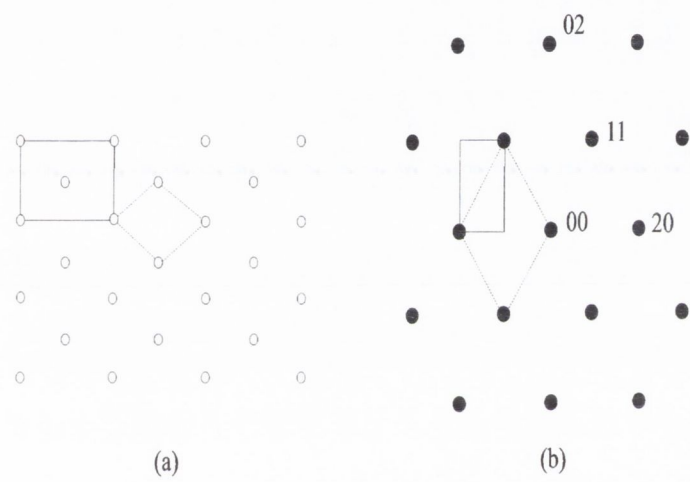


Figure 3.11: Illustration of the conventional (solid line) and primitive (dashed line) cells in (a) real space and (b) reciprocal space. The conventional unit cell highlights the centred-rectangular structure of the surface but forms a too small reciprocal lattice cell. Some of the diffraction spots are indexed according to convention, the 10 and 01 spots are absent.

primary beam energy E_p . The current arriving at the screen will be given by:

$$I_{scr} = \int_{E_0}^{E_p} N(E) dE \quad (3.31)$$

where $N(E)$ is the number of electrons of energy E which reach the screen. If an incremental increase $\Delta V = \Delta E/e$ is applied to the retarding potential, the difference in collector current will be:

$$\int_{E_0}^{E_0+\Delta E} N(E) dE \equiv N(E_0) \Delta E \quad (3.32)$$

In this way the signal $\int_{E_0}^{E_0+\Delta E} N(E) dE \equiv N(E_0) \Delta E$ can be detected. However, a large signal $N(E) \Delta E$ can only be obtained at the expense of resolution $\Delta E/E$, so that there is a trade-off between sensitivity and resolution.

If the retarding field is sinusoidally modulated ($V_0 + \Delta V \sin \omega t$), the collector current will then be given by a sum of harmonics [107]. The first harmonic has amplitude:

$$A_1 = \Delta E N(E_0) + \frac{\Delta E^3}{8} \frac{d^2 N(E_0)}{dE^2} + \dots \quad (3.33)$$

while the second harmonic has amplitude:

$$A_2 = \frac{\Delta E^2}{4} \frac{dN(E_0)}{dE} + \frac{\Delta E^4}{48} \frac{d^3 N(E_0)}{dE^3} + \dots \quad (3.34)$$

Lock-in detection can be used to measure either harmonic. For detection of the first harmonic, the resulting $N(E)$ spectrum will typically display the following features:

- a narrow, large *elastic peak* due to elastically back-scattered primary electrons (at 3-5 keV).
- at slightly lower energies, there will be a series of smaller *plasmon loss* peaks due to the interaction of electrons with (bulk and surface) plasmon excitations.

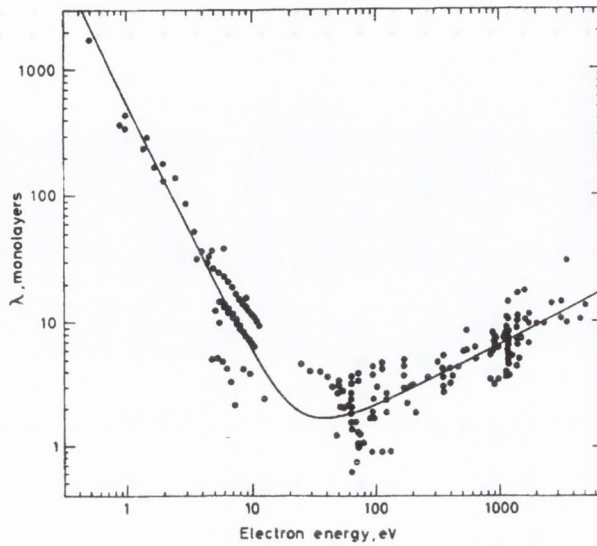


Figure 3.12: Attenuation lengths λ for emitted Auger electrons of various energies in a number of elemental solids. The attenuation length is related to the escape depth Λ by $\Lambda = \lambda \cos \theta$, where θ is the emission angle. Reproduced from [13].

- the signals due to Auger transitions occur in the 30-1500 eV energy range. The energies at which these peaks occur are independent of the primary beam energy. Auger electrons have an escape depth, which is dependent on their emission angle with respect to the surface normal and to their attenuation length λ within the target. The latter is dependent on the density of the target material and the kinetic energy of the escaping Auger electrons. The dependence of attenuation length on kinetic energy is shown in figure 3.12.
- *ionization* loss peaks also occur within this range. However, their energies depend upon the primary beam energy.
- at very low energies (≤ 20 eV) there will be a large signal due to the emission of *secondary electrons*, which rapidly tapers off at higher energies.

These features will be superimposed upon a continuous background due to

inelastically scattered primary electrons, which shows a broad maximum near the elastic peak. Usually, the second harmonic is detected as its amplitude is, in the first order, proportional to the differential signal $dN(E)/dE$. This is preferred as the differential spectrum allows weak signals to be extracted more readily from the background noise.

For the RVLO 900 LEED optics used here, the retarding potential could be swept from zero to 1 kV. A 2.375 kHz ac signal was superimposed on the retarding potential, so that the differential signal could be measured by lock-in detection of the second harmonic. The magnitude of this ac modulation could be varied from zero to 20 V_{pp} - typically a value around 10 V_{pp} was used. A primary beam energy of 2 keV was used.

This set-up was only used for qualitative analysis of the W(100) surface. The performance of the set-up was poor. Typically, the main tungsten Auger transitions (169 eV and 179 eV) could be detected, but it was difficult to separate any meaningful data from the background at higher energies. This may have been due to the low primary beam energy used. However, the problem could also have originated in the oscillator/preamplifier unit which provides the modulation and reference signal for lock-in detection. This unit also contains the pre-amplifier used to amplify and filter the detected signal. The pre-amplifier required tuning to the second harmonic of the oscillator to filter out the signal due to stray capacitances in the analyser grids and the connecting cables. The performance of the set-up may have been limited if the pre-amplifier was poorly tuned.

Finally, it was found that a significant amount of CO contamination could be produced over long periods of use due to electron-beam effects (*e.g. electron stimulated adsorption/desorption*). A similar problem was found using the cylindrical mirror analyser which is discussed in the next section.

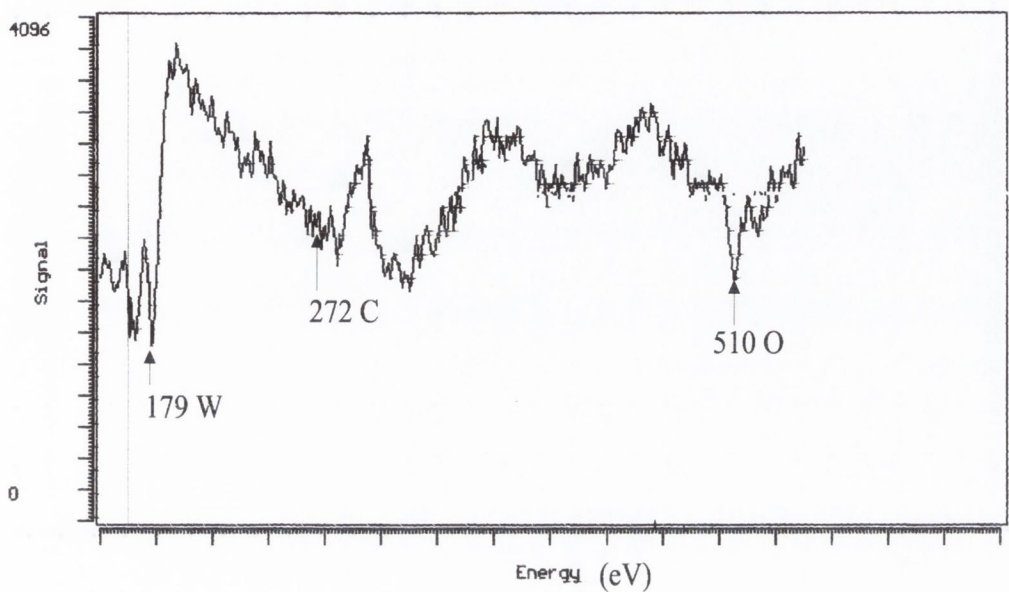


Figure 3.13: An Auger spectrum taken on the W(100) surface. The scan range was 150-550 eV, however, due to poor electronics the signal is only detected from 167 eV (marked by the dotted line). Peaks due to tungsten and oxygen are visible. The scan parameters are: beam energy 2 keV, filament current 2.3 A, emission current 0.71 mA and lock-in sensitivity 2 mV.

3.3.3 Cylindrical mirror analyser

A model 10-155A Physical Electronics cylindrical mirror analyser was used for AES analysis of both the W(100) and Mo(110) samples. The cylindrical mirror analyser (CMA) operates as an electrostatic deflection analyser. It consists of concentric inner (radius r_1) and outer (radius r_2) cylinders, with a coaxially mounted electron gun (figure 3.14). A primary electron beam is produced by thermionic emission from a hot filament (F1 and F2) and acceleration through a potential V2. The beam current can be varied by changing the extraction voltage V1 to vary the level of emission. The primary

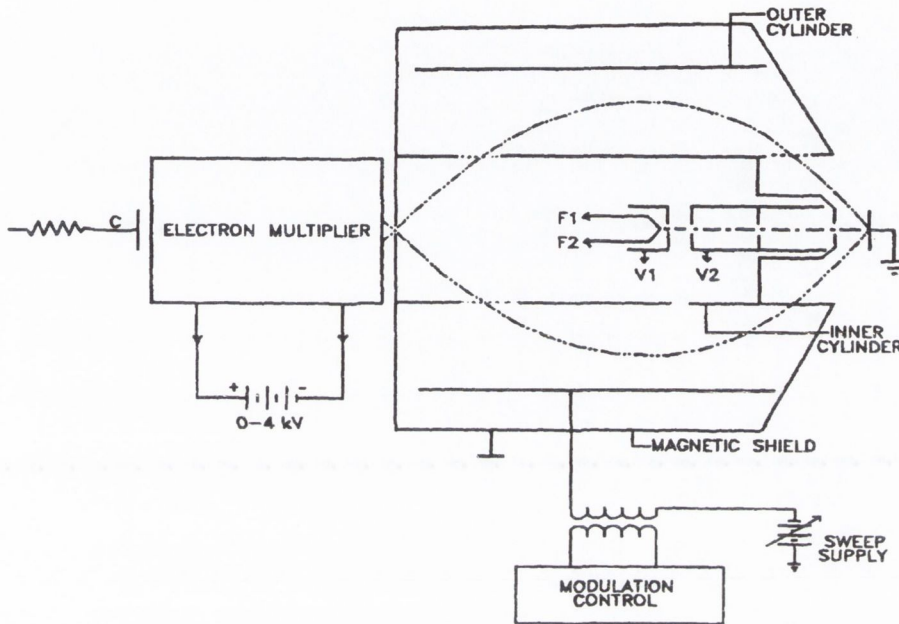


Figure 3.14: A schematic illustration of the layout of a cylindrical mirror analyser. Reproduced from [109].

beam could be focussed on the sample to produce a beam diameter of $100\ \mu\text{m}$.

Backscattered electrons enter the analyser through an annular aperture in the inner cylinder. This cylinder is grounded, while a deflecting potential is applied to the outer cylinder. The trajectory of electrons travelling in the resulting electrostatic field will be deflected by an amount which depends inversely upon their kinetic energy. Electrons with lower energies will be deflected to a greater extent than those with higher energies. The deflecting potential is chosen so that only electrons of a particular energy E_0 will have the correct trajectory to pass through the exit aperture at the opposite end of

inner cylinder. The analyser current will be given by the number of electrons $N(E_0)$ passing through the exit aperture. Between the exit aperture and the collector, an electron multiplier is used to amplify the analyser current to a level which can be detected by a lock-in amplifier. Sinusoidal modulation of the deflecting potential shifts the energy window for electron transmission above and below the value specified by the dc component. The first harmonic component of this signal, which can be measured using lock-in detection, gives the differential signal $dN(E)/dE$.

Because the primary beam is generated from hot filament source, the incident electrons will have a finite angular (and energy) spread. As a result, electrons with the same energy may be backscattered so that they enter the analyser at different angles. To avoid the resulting deterioration in resolution, the entrance aperture of the analyser is designed so that it accepts a conical annulus of electrons ($\sim \pm 6^\circ$ [107]) about a mean angle of $\alpha = 42.3^\circ$. The geometry of the analyser is such that at this angle, electrons with the same energy but different entrance angles are focussed onto the exit aperture. This arises because electrons entering the analyser at a steeper angle must travel a larger distance in the electrostatic field and are therefore deflected through a larger extent.

Because of this arrangement, the resolution of the CMA is fixed by the dimensions of the apertures and the mean electron path length inside the analyser, which is related to the inner cylinder radius r_1 . Since $\Delta E/E$ is constant, the transmission width ΔE widens as E increases, which means that more electrons can pass through. Moreover, the response of the analyser depends strongly on the working distance between the optics and the sample. As the sample moves closer to the entrance aperture, there is a shift in peak energies to higher values. This is simply because electrons of a given energy

enter the analyser at a steeper angle and require greater deflection to reach the exit aperture. The correct working distance is obtained by measuring an elastic peak of known energy, then moving the sample and focussing the primary beam until the analyser response is optimised.

Comparing the RFA and CMA, the RFA has a much larger solid angle over which electrons can be detected than the CMA. However, as it operates as a high-pass filter it has a poorer signal-to-noise ratio than the CMA, which only collects electrons within an energy window.

In the experimental set-up, the sample sits in a stainless steel insert, which is isolated from ground by a Macor block (figure 3.15). The latter is fixed to a double-sided O.D. 70 mm CF flange by three threaded stainless steel rods (~ 300 mm long). A coaxial cable connects the steel insert with a BNC feedthrough mounted on one side of the double-sided flange. The whole assembly is mounted on an x-y-z translator so that the sample may be positioned directly beneath the CMA optics.

A beam energy of 3 keV was used for all measurements, the filament and emission currents were 3.2 A and 1.4 mA respectively, giving a target current of $\sim 8 \mu\text{A}$. The deflecting potential was ramped by a Perkin-Elmer 11-500A AES control unit. A SR 850 DSP lock-in amplifier from Stanford Research Systems [110] was used to output a $0.5 V_{rms}$ sinusoidal signal of frequency 12 kHz. This signal was fed into the AES control and acted as a reference for the modulation of the deflecting potential. A peak-to-peak modulation of 2 eV was used in all experiments. The current passing through the exit aperture of the analyser was amplified using a Channeltron model 4839 electron multiplier [111], held at an accelerating potential of ~ 1 kV using a Perkin-Elmer 32-100 multiplier power supply. The first harmonic of the collector current was separated and converted to a voltage using the

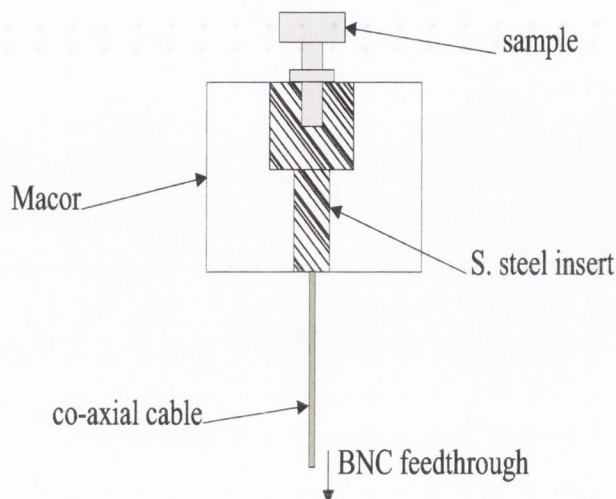


Figure 3.15: Schematic illustration of the sample stage used for AES analysis. The Macor block isolates the stainless steel insert and sample from ground. A co-axial cable connects the insert to a BNC feedthrough, which can be grounded directly or through an ammeter to measure the target current.

lock-in amplifier. A lock-in sensitivity of $100 \mu V$ was used to detect the Auger signal. Originally, this signal (y-axis) and a signal proportional to the dc component of the deflecting potential (x-axis) were used to run a Hewlett-Packard plotter. Later, these signals were fed through two digital multimeters to a GPIB PC interface card, where the data was acquired in *.dat format, using a programme written by D. Kashanin in the Lab Windows CVI environment. The latter method provides a much more accurate format for quantitative analysis. The scan speed was always set at $1 eV.s^{-1}$, with scan ranges of 0-750 eV, so that a single scan takes approximately $12\frac{1}{2}$ minutes.

Atomic concentrations are calculated in the manner described by Davis *et al.* [112] and McGuire [113]. The atomic concentration C_X of element X is given by:

$$C_X = \frac{I_X/S_X d_X}{\sum_{\alpha} (I_{\alpha}/S_{\alpha} d_{\alpha})} \quad (3.35)$$

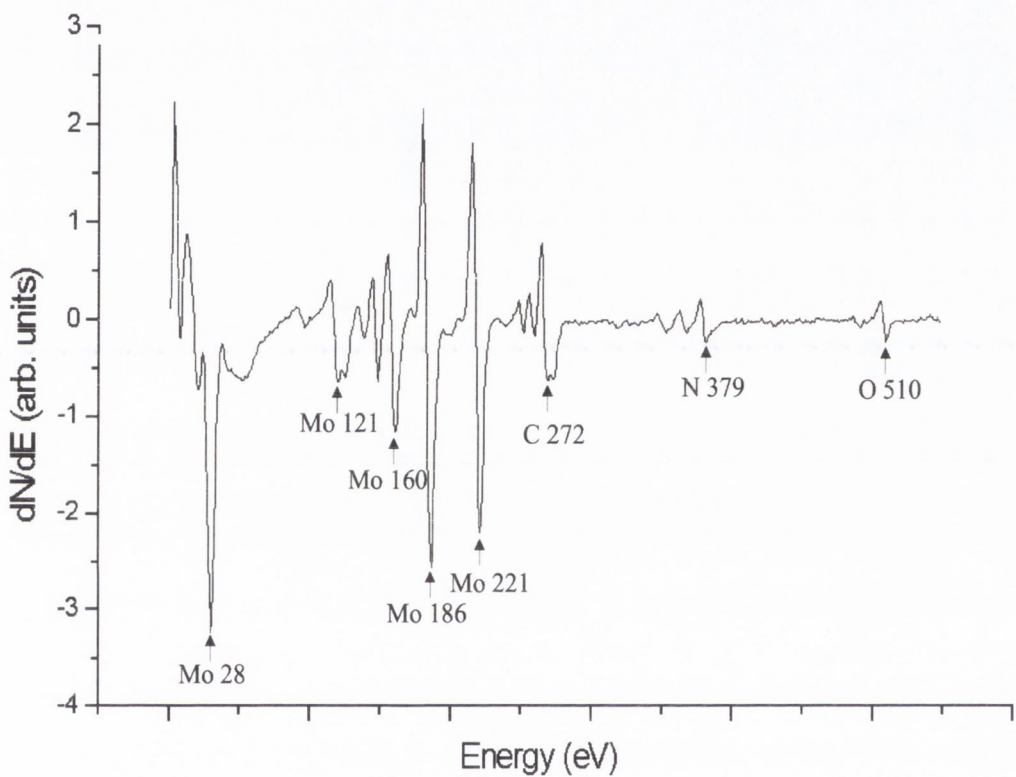


Figure 3.16: A sample scan of the Mo(110) surface, showing contamination from the AES set-up. Carbon, oxygen and nitrogen were the only contaminants detected. The main *LMM* Auger transition for sulphur at 152 eV is obscured by a molybdenum peak at 148 eV. It is assumed that this peak is also below the CMA detection limit when the carbon and oxygen peaks are not seen. Peak energies were read from a display on the 11-500A control unit.

where I_X is the peak-to-peak amplitude of the largest Auger transition measured for the element, S_X is a relative Auger sensitivity factor, taken from reference [112]. The main Auger transition peaks for pure elemental standards are marked in spectra also given in reference [112]. The summation is over one peak per element present on the surface. The scaling factor d_X is included so that concentrations may be determined from peaks measured under different conditions, this is given by:

$$d_X = L_X E_{M,X} I_{P,X} \quad (3.36)$$

where L_X is the lock-in sensitivity, $E_{M,X}$ is the modulation energy and $I_{P,X}$ is the primary beam current. When calculating concentrations using peak-to-peak values taken from the same spectrum, this scaling factor can be disregarded.

Outgassing effect

The set-up was typically out-gassed for 3-4 hours after bake-out, using a beam energy of 3 keV, filament current of 3 A and emission current ~ 0.4 mA. However, it was found that the set-up still caused rapid contamination of surfaces with carbon, oxygen and nitrogen during operation. It is assumed that this contamination was caused either by electron stimulated adsorption of molecules (H_2O , CO, N_2 , etc.) on the surface or some localised outgassing of the CMA caused by the hot filament.

The possibility that these contaminants arrived, unassisted by e-beam effects or otherwise, from the residual gas or the ion gauge was eliminated by measuring the contamination of surfaces which had been cleaned, then exposed to the residual gas in the chamber for periods up to six hours before Auger analysis. During some sessions the ion-gauge was switched on,

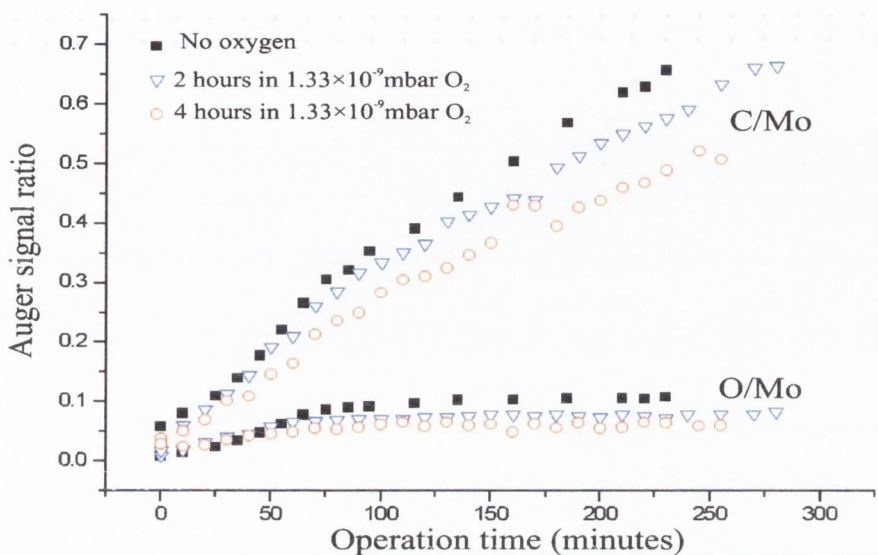


Figure 3.17: C/Mo and O/Mo Auger signal ratios as a function of the CMA operation time.

while during others it was turned off - the intention being to distinguish the contribution of the ion-gauge from the general background pressure of the chamber. In either case, the surface contamination was negligible with O/Mo and C/Mo ratios below 0.01 and 0.02 respectively, while no nitrogen peaks were observed.

Figure 3.17 plots the C/Mo and O/Mo Auger signal ratios for contamination of the clean Mo(110) surface as a function of operating time. Three sets of measurements are exhibited in this graph, the first is for the case where the CMA electron gun was outgassed in the usual fashion. The second and third sets show the result of outgassing the CMA electron gun in an oxygen atmosphere of partial pressure $P_{O_2} = 1 \times 10^{-9} \text{ mbar}$ for 2 and 4 hours respectively. The sample surface was cleaned and allowed to cool for 15-50 minutes before each set of measurements.

From figure 3.17, it is apparent that treating the CMA in oxygen lowers

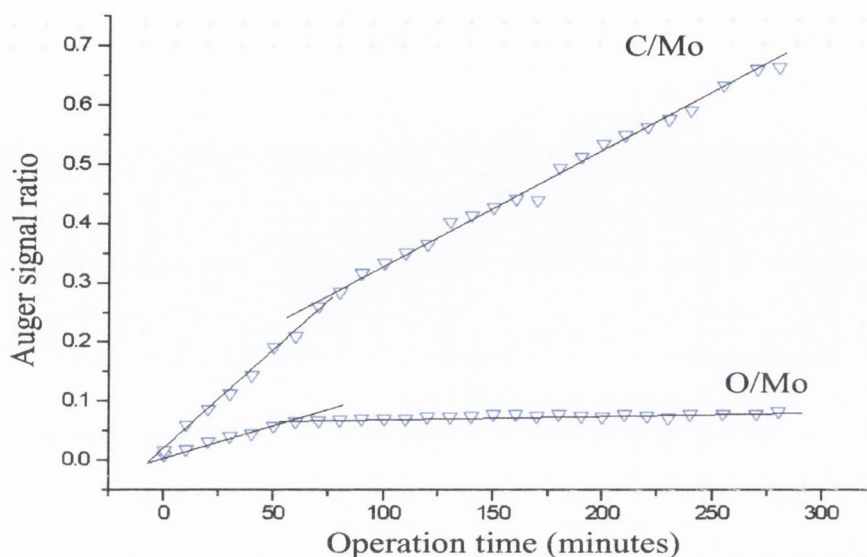


Figure 3.18: A C/Mo and O/Mo curve are reproduced from figure 3.17, highlighting the discontinuity in the C/Mo slope at the saturation of the O/Mo ratio.

both the carbon and oxygen contamination of the sample. There are some other interesting features to be noted in these results.

The O/Mo ratio tends to saturate at a value of 0.05-0.1 after approximately 1 hour, beyond which there is no further net adsorption of oxygen onto the surface. The saturation level decreases as the oxygen arrival rate is reduced. For each set of measurements the primary beam spot was fixed at one position on the surface, while Auger spectra were taken repeatedly. Subsequent measurements, taken on regions of the surface outside this initial beam position, gave O/Mo ratios much higher than the saturation value measured over repeated Auger spectra. This saturation is the possible result of an equilibrium between the oxygen adsorption process and some electron stimulated desorption (ESD) due to the primary beam. The adsorption sites adopted by the oxygen in the initial rise in the O/Mo ratio, may represent

the most strongly bound sites against ESD.

Overall, the contamination level and rate for carbon is much higher than that for oxygen, while also, the C/Mo ratio rises continuously over the time-span of all the measurements. This behaviour suggests that (a) carbon atoms can adopt less energetically favourable adsorption sites than oxygen, (b) the ESD rate for carbon may be lower than that for oxygen.

There is a break in the slope of the C/Mo curve (highlighted in figure 3.18) at around the same point as the O/Mo saturation. Like the O/Mo saturation level, the carbon concentration at which this occurs decreases as the carbon arrival rate is reduced, indicating some rate relation. The break in the C/Mo slope most likely corresponds to some critical coverage, at which most of the prime adsorption sites are taken. Beyond this point, the carbon adsorption rate is reduced. It may be that when carbon reaches the surface, it diffuses for some time (either as C, CO or some other species) during which it may become adsorbed at some site, or otherwise desorbs from the surface. With a reduced incident flux, the probability of desorption increases over that of adsorption near the critical coverage, so that the break point occurs at a lower carbon level. Outside the initial beam position the C/Mo level is much lower, while the O/Mo level is higher. This suggests that oxygen competes more effectively with carbon for the available adsorption sites, in the absence of continual ESD.

An alternative explanation for this observation is that the primary beam of energetic electrons is responsible for the *cracking* of carbon-containing molecules in the residual gas. This increases the carbon adsorption rate within the spot area of the beam. A similar process may also be at work to a lesser degree for oxygen-containing molecules. Outside the spot area, the cracking process does not occur so that the carbon adsorption rate can be lower than

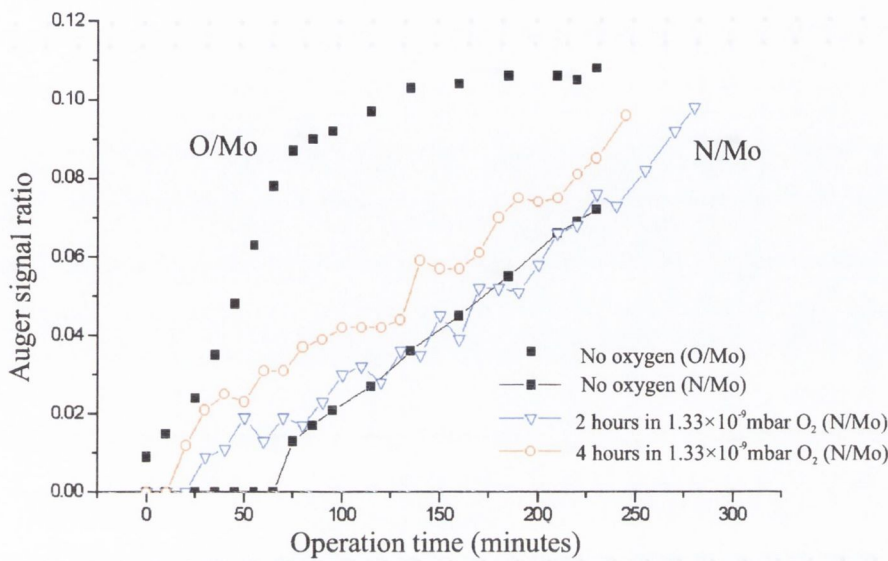


Figure 3.19: N/Mo signal ratios as a function of operating time. The O/Mo curve for the non oxygen-treated CMA filament from figure 3.17 is shown for reference. The other O/Mo curves are omitted for clarity. At longer operation times the N/Mo ratio crosses the saturation O/Mo level.

that for oxygen adsorption.

Figure 3.19 shows a graph depicting the N/Mo Auger signal ratio *vs.* operating time (one of the O/Mo plots from figure 3.17 is included for comparison). The nitrogen contamination rises without any distinct change of slope over the time-span of each set of measurements. However, both the level and the rate of rise are comparatively low, with the N/Mo level only crossing the O/Mo saturation level at the longest operation times.

Outgassing the CMA in oxygen appears to facilitate an increase in the nitrogen level, as well as the appearance of the N/Mo ratio at an earlier point in the measurement. This suggests that by lowering the concentrations of carbon and oxygen, N_2 molecules may compete more effectively for adsorption sites on the sample surface.

While the oxygen treatment lowers the overall contamination for both carbon and oxygen, it is evident that to achieve an acceptably low contamination level, the CMA filament should be outgassed for several hours with $P_{O_2} = 5 \times 10^{-9} \text{ mbar}$. Otherwise, the only meaningful results of Auger analysis will be obtained during the first scan.

3.4 STM tips

The importance of tip geometry and composition in STM are well established [11,98]. As a result, a large body of work has been published on the fabrication and characterisation of STM tips, highlighted in table 3.3. However, much of this material addresses the problem of making sharp tungsten tips (the standard tip in UHV STM applications), while the practice of fabricating tips of novel materials is less well developed.

The usual criteria for a good STM tip are: (1) an apex radius significantly lower than 100 nm, (2) a high aspect-ratio (the length/diameter ratio) near the tip apex to probe sharply contrasting contours, (3) a low aspect-ratio away from the tip apex to stabilise the tip against resonances and (4) no multiple tips. A variety of techniques have been developed to produce tips with different geometries. This is usually some variation on the electrolytic etching/polishing of a thin wire ($\phi 0.25\text{-}1 \text{ mm}$) with additional treatments to further sharpen and to remove residues from the electrolytic process. In the course of this work, tips of a variety of materials were prepared, with varying success. These are described in the following.

Tip material	Electrolytic etching	Additional features	Reference
W	1-4M NaOH, dcV		[114–125]
		Ar ⁺ ion-milling	[126–129]
		annealing/oxidation	[130–133]
		Ne ⁺ self-sputtering	[130, 134]
PtIr	CaCl ₂ /H ₂ O/conc. HCl, 25V ac	3kV Ar ⁺ ion-etching	[135]
Fe	75% H ₃ PO ₄ /saturated CrO ₃	floating on CHBr ₃	[119]
	10% HCl, I = 20-40mA	PTFE insulation	[136]
Re	62% H ₂ SO ₄ , 3V dc	H ₂ PO ₄ /H ₂ O drop-method	[137]
Pd	HCl/HNO ₃ , 2 stages	floating on CCl ₄	[138]
	HCl in glycerine, 10V ac	also NaCl, KCl and CaCl ₂	[139]
Ag	10%-35% NH ₃ /H ₂ O, 2-stage	electronic shut-off	[140]
Au	10%-50% CaCl ₂ , 30-40V ac		[139]
Rh	70% NaCl, 25V ac		[139]
MnPt	20% KCN		[141]
MnNi	5% HCl		[141]
	10% HCl, 1-2V dc	loop-technique	[142]
Cr	10% KOH		[141]
Au/W		W coated with 20nm Au	[143]
Fe/W		W coated with Fe	[96, 144]

Table 3.3: A sample list of fabrication techniques for STM tips of various metals, with appropriate references.

W tips

Tungsten tips were prepared by immersing a $10\text{ mm} \times \phi 0.5\text{ mm}$ wire (clamped into a holder at one end) to a depth of 5 mm in a beaker of 2 M NaOH . This acts as the anode during the electrolytic process, while a fully submerged stainless steel cylindrical foil acts as the cathode. Under an applied dc bias, preferential etching at the air/electrolyte interface occurs, with the oxidation of the anode to form soluble WO_4^{-2} anions which flow away from the active etching region. This process leads to a *necking-in* of the wire in the active etching region. This continues until the thinned region parts under the weight of the submerged portion which drops off. A number of groups have found that extremely fast shut-off of the electrolytic circuit at drop-off, requiring electronic shut-off control, is essential to produce very sharp tip apexes [114, 115, 140]. Consequently, an electronic shut-off control with a $\sim 9\text{ V}$ dc output was built by P. Flanagan and calibrated by C. Seoighe. This unit breaks the electrolytic circuit once a pre-set etching current, corresponding to the drop-off point, is reached. Additionally, the tip holder was fitted to a modified micrometer screw which allowed sensitive adjustment of the position of the etching region.

Tips prepared in this manner were covered in a layer of WO_3 oxide and residue from the electrolytic process. The tips were rinsed with propan-2-ol before insertion into vacuum. The oxide layer was removed and the tip further sharpened by ion-etching with Ar^+ ions. The parameters for this process are given in table 3.4.

Variations on this procedure usually involve confining the active etching region to a very small volume, these include:

- the *floating layer technique*, where a thin layer of electrolyte is floated on

Etching time (min.)	Ion energy (keV)	Target current (mA)
20	2	12-15
10	1	5-8
5	0.5	≤ 1

Table 3.4: Typical parameters for Ar^+ ion etching of W STM tips.

top of a denser, immiscible, non-conducting liquid. For tungsten etching with NaOH, this is usually CCl_4 [117, 119].

- the *loop technique*, where the electrolyte is held by surface tension in a small loop (or some similar geometry) which forms the counter-electrode [125]. A micro-positioner can be used to pierce the film with the wire. This method is awkward since the electrolyte must be repeatedly refreshed.
- *micro-polishing* is similar to the loop technique. A pre-made tip is moved in and out of a thin film of electrolyte to polish it to the desired sharpness. This set-up is controlled using a microscope and a micropositioner.
- *wire insulation*, where the submerged part of the W wire is covered with an insoluble, insulating layer *e.g.* PTFE tubing or wax. This physically confines the active etching region [118]. It also protects the dropped-off portion which can produce a sharper tip [121].
- in *reverse etching* a pre-made tip is immersed in such a way that its apex points upwards. An ac bias is used to polish the tip - a greater sharpness is achieved as the bubble flow in this configuration circulates the electrolyte along the tip shaft to the apex [123, 124].

More information on tip preparation techniques is given in reference [145].

PtIr tips

Platinum-iridium tips were prepared by mechanical cutting after the standard fashion. A pair of fine snips was used to simultaneously cut and pull a $\phi 0.25\text{ mm}$ wire at an acute angle. There is no oxide formation on the surface of these tips, so that they do not require ion-etching in vacuum. However, this method is not very reproducible and the tips produced are generally of lower quality than the electrolytically etched W tips. Additionally, since PtIr is a soft material, these tips are less resilient to minor crashes than their W counterparts.

MnNi tips

Antiferromagnetic (AF) tips have been proposed for magnetically-sensitive spin-polarised STM (SPSTM) studies [141, 146] (see also Wiesendanger [98] for a discussion of spin-polarised STM and STS), as they remove the problem of tip magnetostriction, while the magnetic order of the tip does not change with an externally applied magnetic field⁵. The family of ordered equiatomic binary alloys of manganese, MnMe where Me may be Pd, Pt, Au, Ir or Ni, are particularly attractive for this use. These alloys usually have high magnetic moments, are mechanically hard and have high Néel temperatures.

The binary phase diagram for MnNi is shown in figure 3.20, the AF phase exists in a region of a few atomic % around the equiatomic composition. It has a CuAu-I type face-centred tetragonal crystal structure with lattice constants $a_0 = 3.714\text{ \AA}$ and $c_0 = 3.524\text{ \AA}$. This structure evolves by a martensitic transition from the higher temperature CsCl type structure [148–150]. From

⁵Another work reverses the situation (to the same effect), by treating the case for an AF sample [147]. However, the AF tip approach is more flexible, allowing a wider range of samples to be studied.

neutron diffraction experiments [148, 149] the magnetic moments of the Mn atoms were determined to be $\mu_{Mn} = 4.0 \pm 0.1 \mu_B$, aligning antiparallel in planes normal to the crystallographic c-axis. The moments of the Ni atoms are small, $\mu_{Ni} \leq 0.6 \mu_B$. The Néel temperature is estimated to be 1140 K, this value is extrapolated from neutron diffraction data since it occurs above the martensitic transition [149].

A 12 g MnNi ingot was prepared by alloying equiatomic proportions of 99.9 % pure Mn and Ni in an arc-melter, under a clean argon atmosphere. The ingot was then annealed for 20 hours at 850 °C. X-ray powder diffraction (XRD) was carried out on a sample of the ingot to ensure that the lattice parameters were those of the CuAu-I type AF phase. Energy-dispersive X-ray analysis (EDX) was also performed on a sample, which confirmed an equiatomic composition to within a few atomic % [151]. Cylindrical rods with dimensions $\phi 0.5 \text{ mm} \times 13 \text{ mm}$ were prepared from the ingot by cutting with a low-speed diamond-wheel saw [152] and polishing with sandpaper in a high-speed drill.

After Shvets *et al.* [141], an aqueous solution of (10 % volume) saturated HCl was used as the electrolyte. Cathodes were made from stainless steel. Only dc voltages were used. It was immediately found that MnNi tips could not be prepared in the same manner as W tips. For W, preferential etching occurs at the air/electrolyte interface with *necking-in* of the wire as the electrolyte meniscus falls. For MnNi, etching occurs from the immersed end of the rod upwards. Therefore, it was necessary to physically confine the etching region along some portion of the rod to induce drop-off.

The first approach was to use the *loop technique*, using a $\phi 8 \text{ mm}$ loop of stainless steel wire. Typically a bias of 1-2 V was applied, the electronic shut-off control was not used. The upper portion of the rod was retained

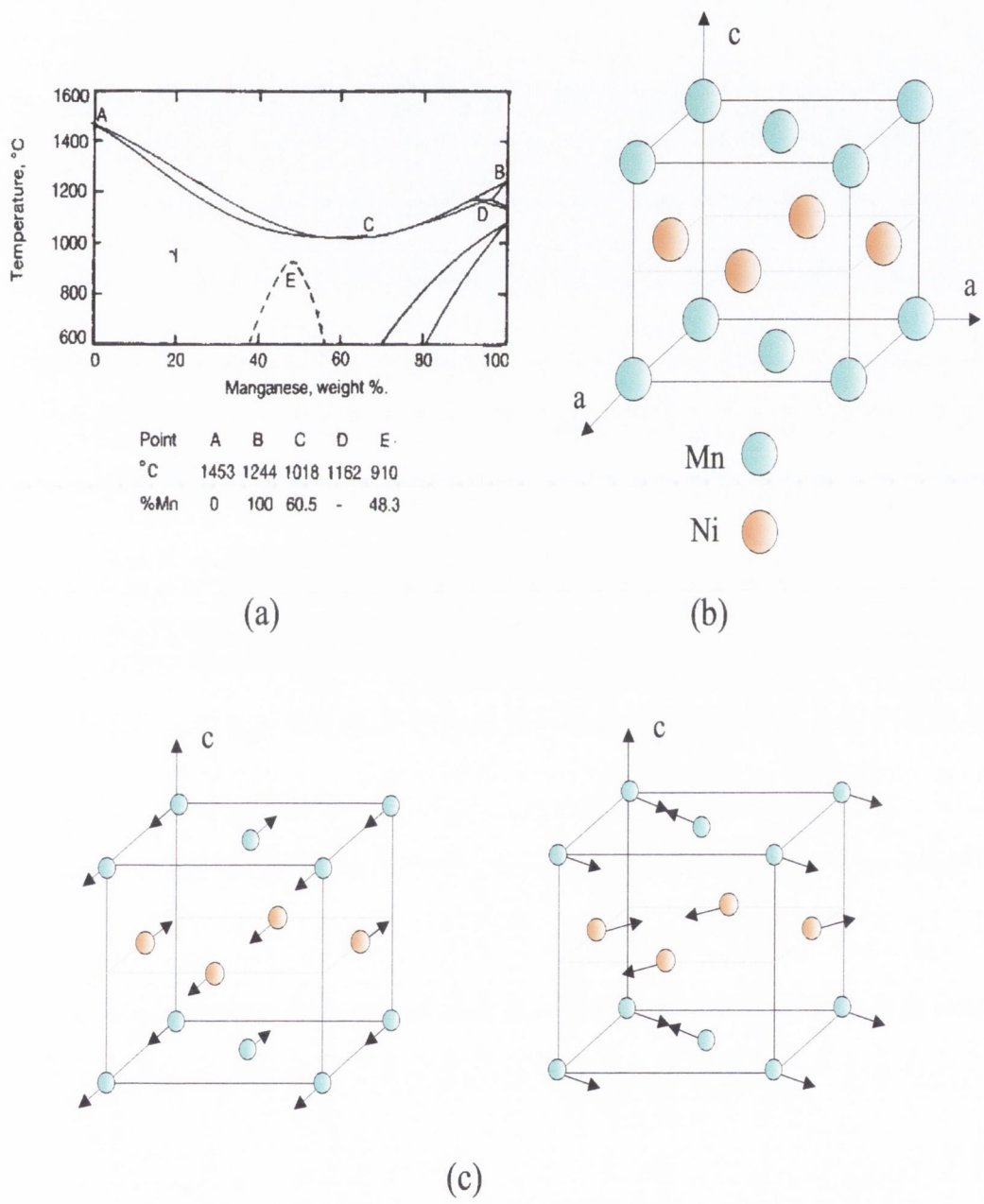


Figure 3.20: (a) Phase diagram for the Mn-Ni binary alloy system, (b) CuAu-I type face-centred tetragonal structure of equiatomic alloy, (c) possible AF ordering configurations for this alloy.

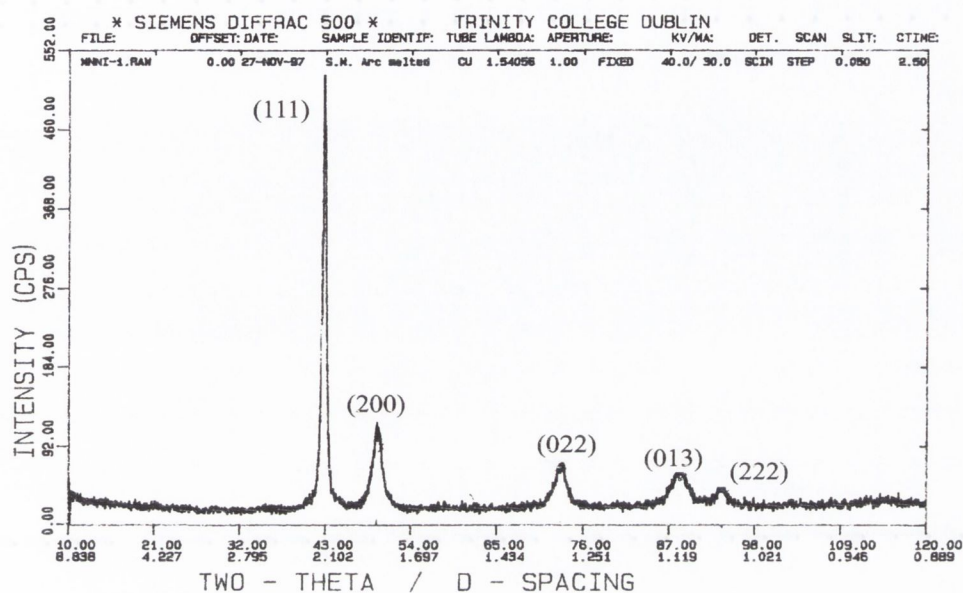


Figure 3.21: Powder-XRD spectrum of a sample taken from the MnNi ingot.

after drop-off and was immediately rinsed with distilled water and propan-2-ol. The tip-shape could be changed by varying the diameter of the loop and the size of the electrolyte droplet it held. The drawback of this technique was that the electrolyte needed continual refreshing, which became awkward near the drop-off point when there should be a minimal disturbance.

The *floating layer* technique was also used. Here, a 1-2 mm thick layer of HCl was floated on top of a thick layer of glycerol. Though glycerol is not completely immiscible with HCl, the two layers remain separate for much longer than the duration of the etching process. A stainless steel loop is again used as the cathode. The rod is thinned using a dc bias of 7 V, while a bias of 2 V is used to etch the rod until drop-off. A glass capillary is fixed beneath the lower portion of the MnNi rod to catch the dropped-off tip, which is generally sharper.

Tips prepared in this manner were ion-etched in vacuum using the same

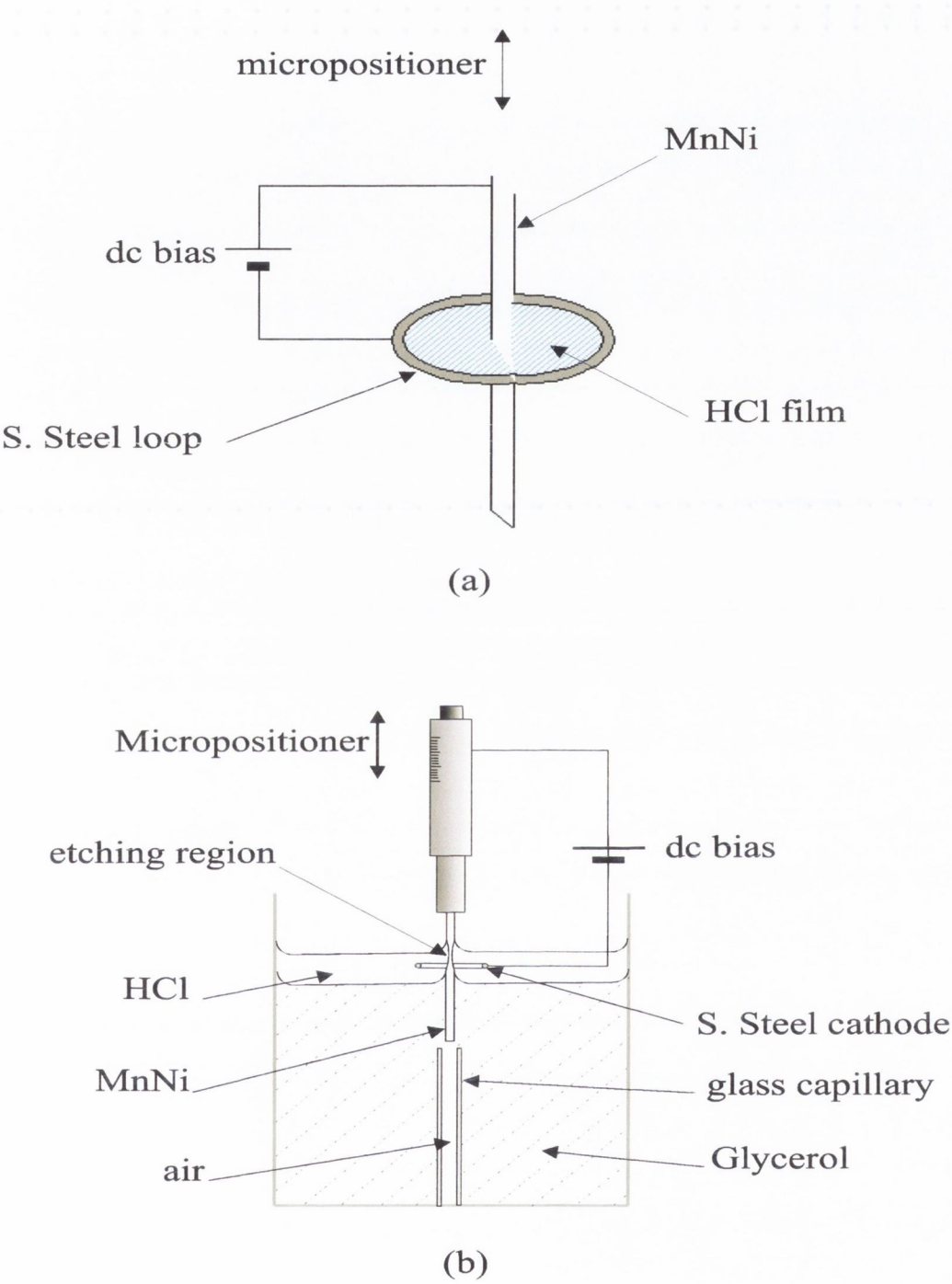


Figure 3.22: Schematic illustration of the (a) loop and (b) floating layer methods used to prepare MnNi tips.

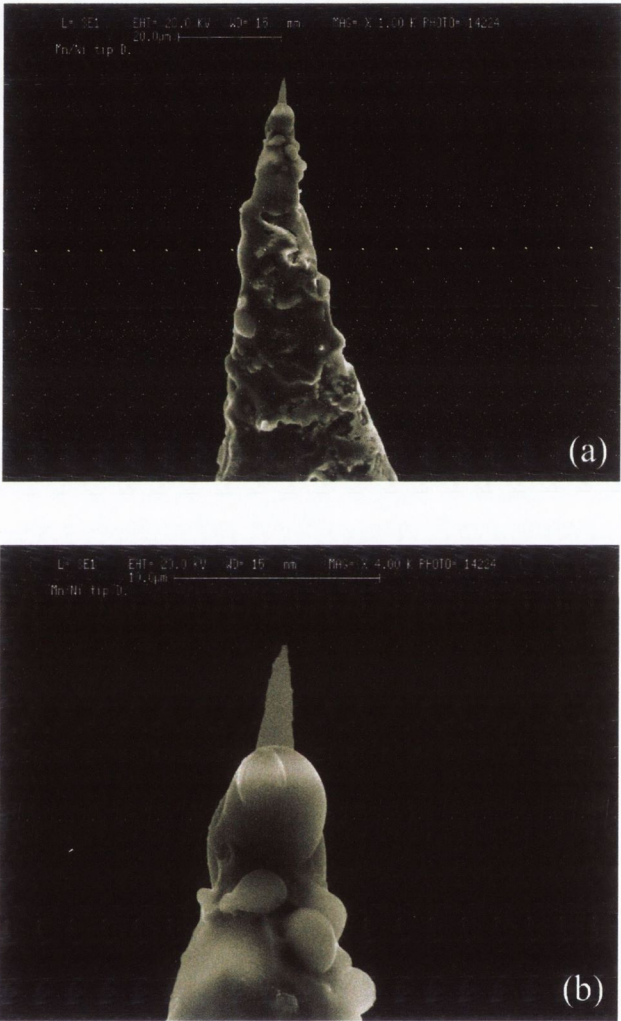


Figure 3.23: SEM images of a MnNi tip etched by the layer method with 2 V dc. Magnification (a) $\times 1000$, (b) $\times 4000$. The diameter of the tip apex is about 300nm.

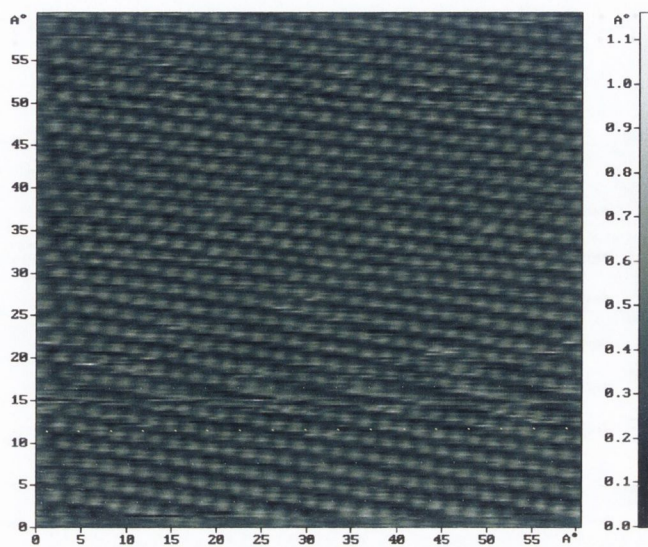


Figure 3.24: ($60 \times 60 \text{ \AA}^2$) STM image of atomically resolved HOPG, obtained with a MnNi tip prepared by the loop technique. There is a factor of two error in the z-scale. $V_{bias} = 100 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

parameters as those used for the W tips. Some excellent results were obtained using these tips, with atomic resolution images obtained on oxygen covered W(100) [142, 153], on $\text{Fe}_3\text{O}_4(100)$ [96] and on Fe islands on Mo(110) [9, 10].

Fe tips

Iron tips were prepared from 99.98 % pure $\phi 0.25 \text{ mm}$ Fe wire, using the *loop technique* described earlier. An aqueous solution of 10 % volume saturated HCl acid was used as the electrolyte, while the etching bias was typically 0.3-0.6 V dc. The tips were rinsed with distilled water and propan-2-ol, immediately after drop-off.

The tips were ion-etched in vacuum, using similar parameters to those used for W tips. They were used a few times in sessions on the magnetite (Fe_3O_4) surface [96]. However, they were easily blunted by minor tip crashes

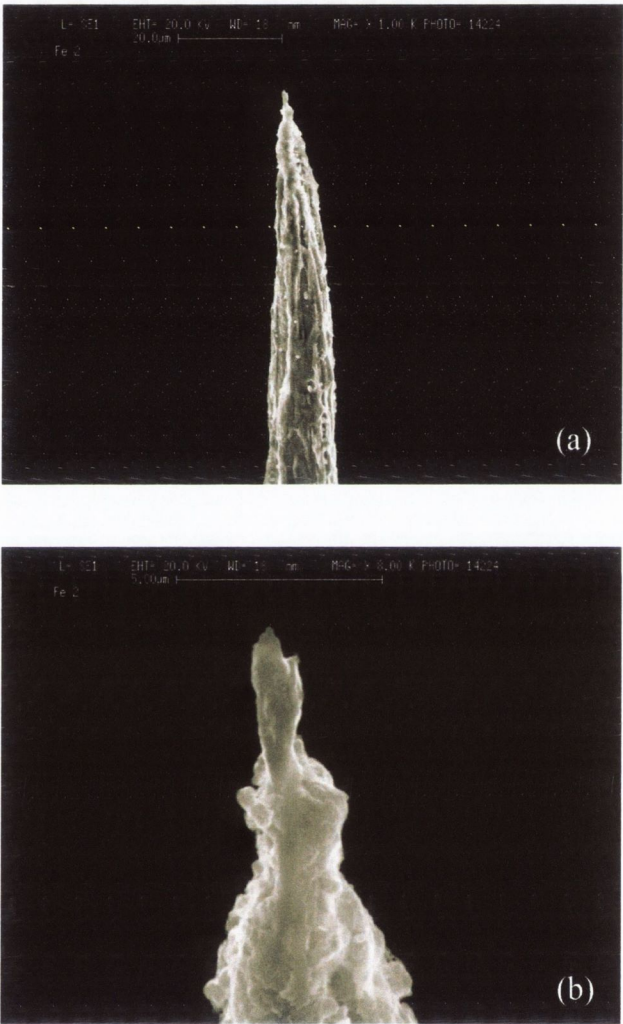


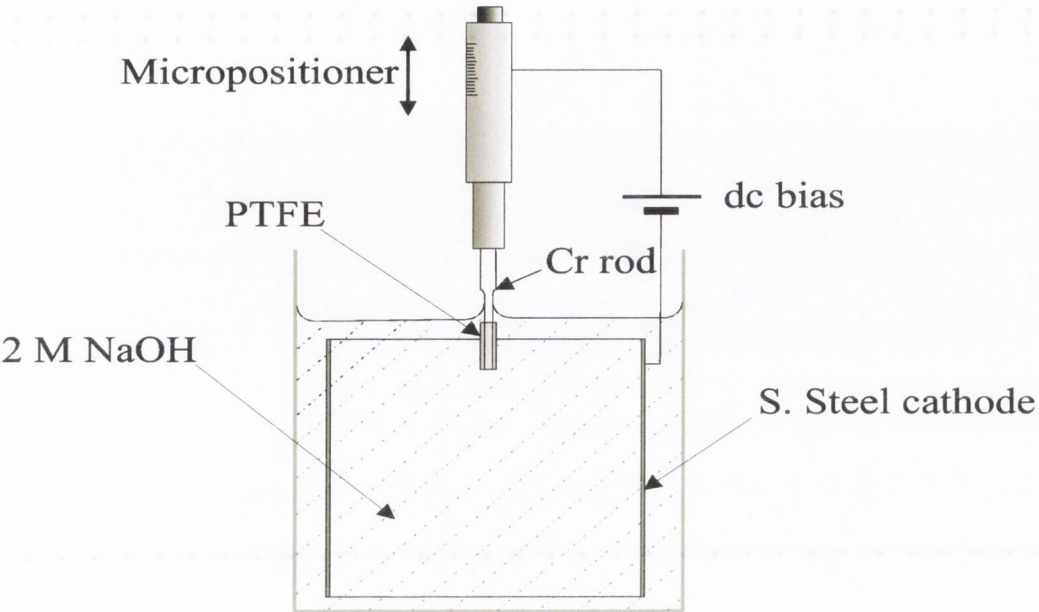
Figure 3.25: SEM images of an Fe tip etched by the loop method with 0.5 V dc. Magnification (a) $\times 1000$, (b) $\times 8000$.

and tip material tended to be deposited on the surface. Also, they were unsuitable for STM experiments in a variable magnetic field, due to their considerable magnetostriction [96].

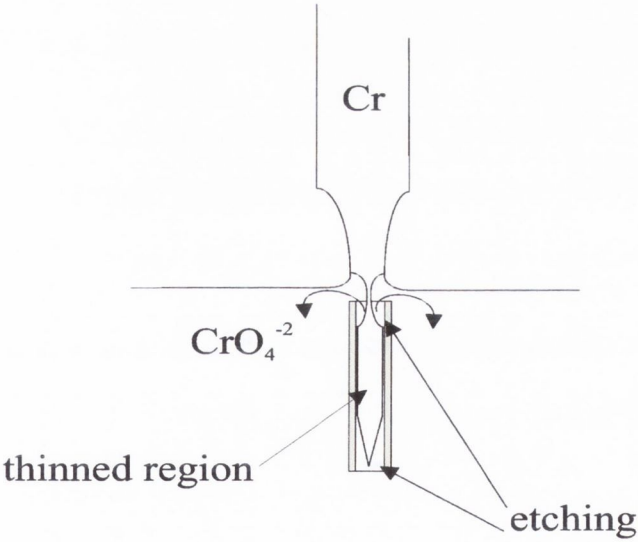
Cr tips

Cr tips were prepared from 99.5 % ingots, which were arc-melted, sliced and polished into $15\text{ mm} \times \phi 1\text{ mm}$ cylinders by Dr. I.V. Shvets. Etching of these rods was performed using the same set-up as that used for preparing W tips. First they were thinned along 10 mm of their lengths in 2 M NaOH with a dc bias of 4-5 V, until their diameter had been reduced below 0.5 mm. The rods were then washed and fitted with a 5 mm piece of PTFE tubing which encased their lower ends. Using the modified micrometer screw, the wire was submerged until the electrolyte covered the PTFE tube. The electrolytic cell was then connected to the electronic shut-off, which controlled etching until drop-off.

The dropped-off tips were always much sharper than the tips retained in the tip holder. The PTFE tube restricts electrolyte concentration in the active etching region at the tube entrance, leading to a slow, uniform etching rate. The dropped-off tips were retrieved and carefully removed from their PTFE cladding with a sharp needle. They were then glued into tip holders with a UHV-compatible conducting glue [154]. In vacuum, they were subjected to a light ion etch (1.5 keV for 10 minutes, 1 keV for 5 minutes and 0.5 keV for 5 minutes) to remove the oxide layer. These tips were used in a few sessions on the Mo(110) surface. A reasonable resolution was obtained, while they were more resilient to tip crashes than the PtIr or Fe tips.



(a)



(b)

Figure 3.26: (a) Etching set-up for Cr tips, (b) zoom-in to etching region. The PTFE tube restricts the etching process in the active etching region to produce tapered, sharp tips.

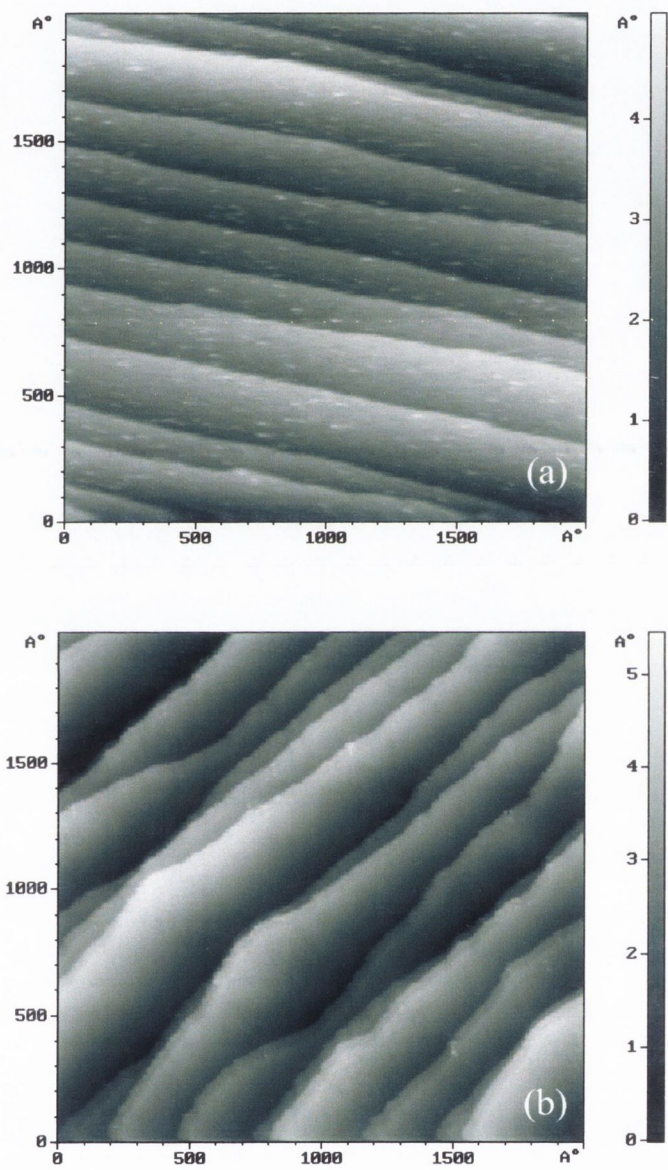


Figure 3.27: Comparison of two ($2000 \times 2000 \text{ \AA}^2$) STM images on the sputter-annealed Mo(110) surface, taken with (a) a mechanically cut PtIr tip and (b) an electrolytically etched Cr tip (both using $V_{bias} = 30 \text{ mV}$, $I_{tunnel} = 0.1 \text{ nA}$).

Chapter 4

Fe/Mo(110) epitaxial system

4.1 The Mo(110) surface

4.1.1 Sample preparation

The sample was prepared from a 4N purity single Mo crystal by Rene Koper of the Surface Preparation Laboratory, The Netherlands [155]. The surface was oriented to within 1° of the (110) crystal plane and finished by mechanical polishing to a surface roughness of $0.03\ \mu m$. The sample was fixed in a sample-holder with a Ta cap and inserted into the UHV system described previously (section 3.1.3). The procedure for cleaning the sample in UHV has been described in section 3.2.1. Initially, the surface was oxidised by annealing at $1300\ K \leq T \leq 1550\ K$ in an oxygen atmosphere of partial pressure $6.7 \times 10^{-7}\ mbar$ for 30 to 60 minutes. The sample was then flash-annealed to temperatures reaching $2400 \pm 200\ K$ for 15 to 20 seconds to remove the oxide layer. It was then left to cool for 5 to 10 minutes before the next flash, which allowed the chamber pressure to recover to the low $10^{-10}\ mbar$. This cycle was repeated several times, with flash times gradually shortened to a few

seconds, before the next oxidising cycle was begun. LEED and AES analysis were used to assess the cleanliness and structural order of the surface. After considerable repetition ($\sim$ seventy 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 at%. It should be noted that the main *LMM* Auger transition for sulphur at 152 eV is obscured by a molybdenum peak at 148 eV. While this means that the presence of sulphur contamination cannot be completely excluded, the cleaning procedure 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.

4.1.2 Oxygen on the Mo(110) surface

Figure 4.1 shows a typical Auger spectrum for the surface at this point. There is a comparatively high concentration of oxygen present at the surface, with an Auger signal ratio of $O/Mo = 0.26$ measured. Auger electrons with a kinetic energy of ~ 500 eV have an escape depth of approximately five atomic layers (figure 3.12). As a result, from Auger analysis alone, it is difficult to ascertain whether this oxygen is present as an ad-layer on top of the surface, or as bulk impurities diffused within the first few sub-surface layers.

Previous studies have indicated that annealing the Mo(110) surface to 2000 K is sufficient to remove any traces of adsorbed oxygen from the surface [156–158]. Here, the sample was repeatedly flash-annealed to temperatures reaching 2300 K with the result that a large oxygen peak persisted in Auger spectra taken on the surface. Upon further annealing to slightly higher temperatures (2400 ± 50 K) the O/Mo signal ratio dropped below

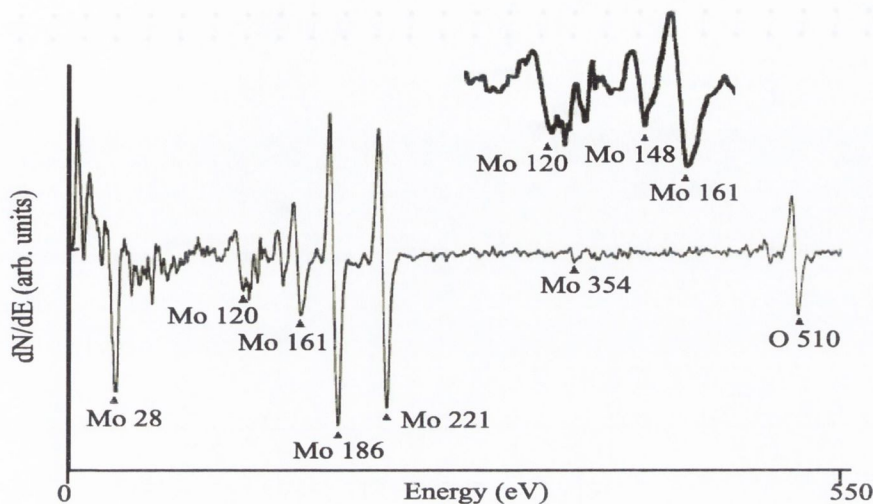


Figure 4.1: Auger spectrum of the oxidised Mo(110) surface from which the LEED pattern in figure 4.2 was taken. The O/Mo Auger signal ratio is 0.26. The insert enlarges the region where the sulphur 152 eV peak would be located.

0.03, indicating desorption of oxygen from the surface.

Figure 4.2 shows the LEED pattern recorded on this surface just after the Auger spectrum in figure 4.1 was taken. An identical superlattice was observed by J. Osing using the same cleaning procedure on a vicinal Mo(110) surface [10]. Using the matrix notation for superlattices at surfaces [105], this pattern can be described as¹:

$$Mo(110) - \begin{bmatrix} 4 & 3 \\ 3 & 4 \end{bmatrix} - O$$

A similar LEED pattern with sixth-order spots along the $[1\bar{1}0]$ direction,
¹This identification was made using the freeware program 'LEEDpat' made available by Prof. Dr. Klaus Hermann of the theory department, the Fritz-Haber Institute, Berlin [159].

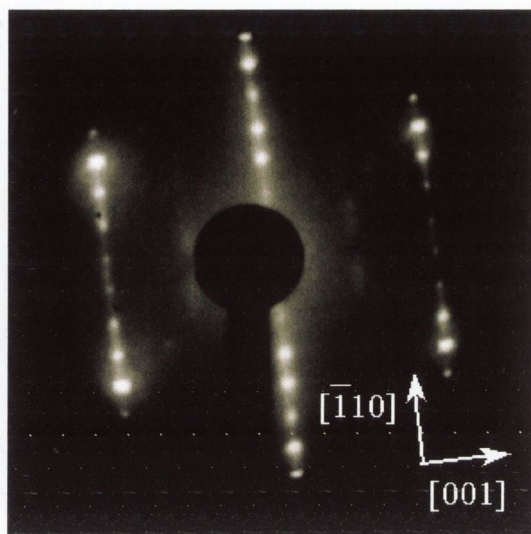


Figure 4.2: LEED pattern of an oxygen-induced superlattice formed on the Mo(110) surface. $E_{beam} = 60$ eV.

has been observed for high adatom coverages in studies of oxygen adsorption on the Mo(110) surface [156, 157, 160]. Bauer and Poppa [157] have asserted that adsorption occurs strictly on top of the Mo surface, without atom exchange between adsorbate and substrate, over the whole coverage range to one monolayer. This includes the coverage at which they observed sixth-order spots. Assuming that the pattern in figure 4.2 is also due to oxygen adsorbed on top of the Mo surface, a model of the surface superlattice may be constructed (shown in figure 4.3). The selection of quasi-threefold adsorption sites in this model is based on the findings of Colaianni *et al.* [161]. A coverage of $\theta_{model} = 0.86$ ML is required to produce this structure on the surface.

To verify this model, the O/Mo Auger signal ratio was calibrated as a function of oxygen coverage by measuring the ratio on a surface with a known coverage. The $p(2 \times 2)$ oxygen reconstructed surface is a natural calibration

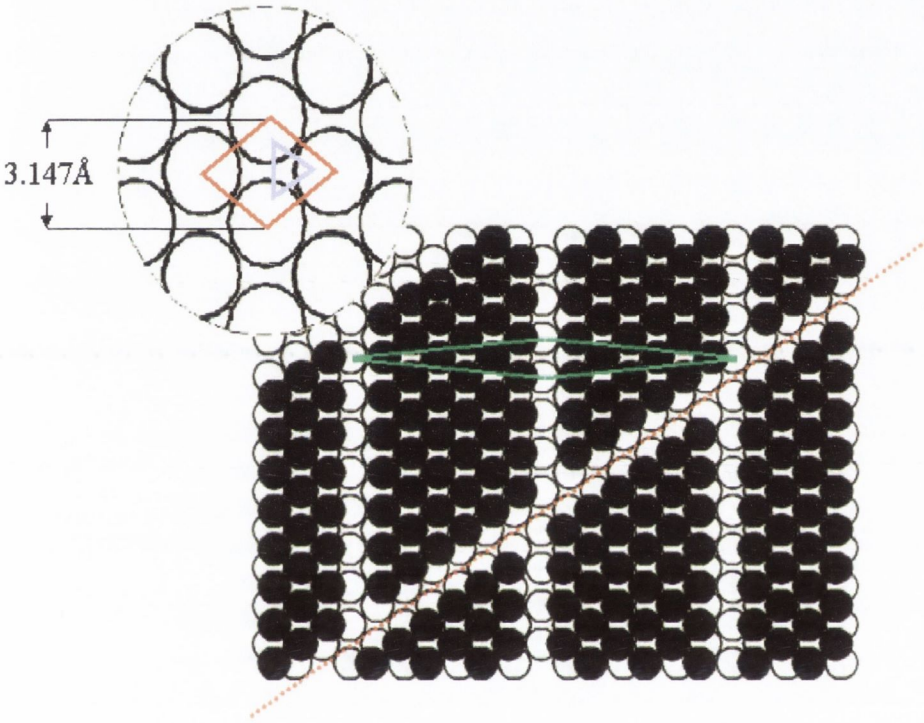


Figure 4.3: A model suggested for the superlattice formed by oxygen adsorption on top of the Mo(110) surface at a coverage of $\theta_{model} = 0.86 \text{ ML}$. Mo atoms are denoted by empty circles while oxygen atoms are filled. The superlattice primitive cell is highlighted in green, a domain boundary is indicated by the dashed line. The insert shows an enlargement of the substrate atomic arrangement including the primitive net cell and the quasi-threefold adsorption site, which is indicated by a triangle.

point as this structure forms at a coverage of 0.25 ML . To prepare this structure, a procedure similar to that used in reference [157] was adopted. The clean Mo(110) surface was dosed with 6.7×10^{-9} $mbar$ partial pressure O_2 at room temperature for three minutes. A sharp $p(2 \times 2)$ diffraction pattern was produced using this treatment, shown in figure 4.4. Auger analysis of this surface yielded an O/Mo ratio of 0.077 (or an oxygen concentration of 0.067). Equating this to a coverage of 0.25 ML means that the signal ratio of 0.26 measured in figure 4.1 must correspond to a coverage of $\theta_{meas.} = 0.84$ ML , which is in good agreement with the theoretical value for the suggested model.

In addition to the $p(2 \times 2)$ structure observed, dosing the surface for slightly longer periods (up to 6 minutes) produced the complex pattern shown in figure 4.5, which corresponds to a coverage of ~ 0.36 ML , while for low-coverages (dosing for 1 minute yields a coverage of ~ 0.01 ML) a $p(1 \times 1)$ LEED pattern with a bright background was observed.

Bauer and Poppa [157] have found that for O_2 adsorption on a number of Mo(110) surfaces, the sticking coefficient, $s(\theta)$ is approximately constant in the low-coverage regime to 0.25 ML . Taking this as the case, an estimate of the initial sticking coefficient, s_0 , for dissociative adsorption of molecular oxygen on this surface, can be made using the following treatment. The rate of arrival, R , of O_2 molecules at the surface is given by equation 2.27. A molecular arrival rate of $1.79 \times 10^{16} m^{-2}.s^{-1}$ was calculated for this experiment. The atomic arrival rate, $R_{arrival}$, is then taken as twice this value. The density of atoms required to stick to the surface to produce a coverage of 0.25 ML is $3.57 \times 10^{18} m^{-2}$. Allowing that $\theta = 0.25$ ML was reached after 3 minutes at 6.7×10^{-9} $mbar$ O_2 (or an exposure of 0.9 L), the adsorption rate, $R_{adsorption}$, is then $1.98 \times 10^{16} m^{-2}.s^{-1}$. The sticking coefficient can then



Figure 4.4: The $p(2 \times 2)$ LEED pattern due to 0.25 ML of oxygen adsorbed onto the Mo(110) surface. $E_{beam} = 57$ eV.

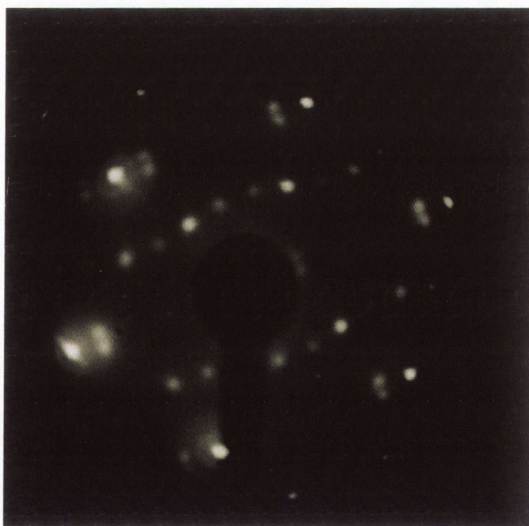


Figure 4.5: An example of the complex LEED pattern formed at coverages slightly above 0.25 ML . In this case the measured coverage was ~ 0.36 ML . $E_{beam} = 72$ eV.

Temp. (K)	$I_{emiss.}(mA)$	O/Mo	C/Mo
2128	310	0.24	0.17
2212	330	0.21	0.08
2275	370	0.22	0.00
2309	400	0.27	0.00
2389	418	≤ 0.03	0.00

Table 4.1: O/Mo and C/Mo Auger signal ratios after cleaning by flash-annealing, displayed as a function of anneal temperature and the emission current used. Carbon is removed from the surface at temperatures above 2275 K. Note that the relationship between the temperature reached and the emission current changes when a new filament is inserted into the e-beam heater. Temperatures were measured using an infra-red pyrometer.

be determined from the relation:

$$s(\theta) = \frac{R_{adsorption}}{R_{arrival}} \quad (4.1)$$

A value of $s_0 = 0.55$ was obtained for this surface, which has a miscut angle within $\pm 1^\circ$ of the (110) face. This result fits very well within the observations of Bauer and Poppa [157] who have measured the increase in s_0 as a function of increasing step density. In this study a value of $s_0 \approx 0.50$ was found for an almost flat Mo (110) surface with a miscut of better than $\pm 0.05^\circ$, while values of 0.65 and 0.75 were measured for surfaces with miscut angles of 5.62° and 11.40° respectively. The observed increase follows from the fact that surface defects such as steps and kinks provide higher coordination adsorption sites than would be found on an ideal flat terrace.

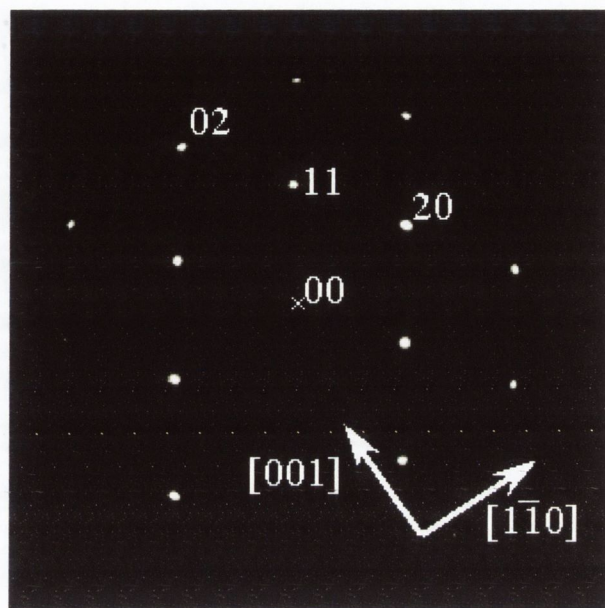


Figure 4.6: LEED pattern of the clean Mo(110) surface. $E_{beam} = 112 \text{ eV}$.

4.1.3 The clean surface

Auger data taken during the post-oxidation cleaning procedure is summarised in table 4.1. As indicated in the previous section, residual oxygen can be removed by 20 second flash-anneals to $2400 \pm 50 \text{ K}$, leaving a clean Mo surface². A typical LEED pattern obtained from the clean surface is shown in figure 4.6 with some of the beams indexed. The presence of sharp diffraction spots and a low background intensity suggests that the surface is well ordered. Following the approach outlined in section 3.3.2, a molybdenum lattice parameter of $a_{Mo} = 3.0 \pm 0.2 \text{ \AA}$ was determined from LEED patterns recorded at different energies.

Figure 4.7 shows a globally plane-fitted $2000 \times 2000 \text{ \AA}^2$ STM image of the surface taken 90 minutes after cleaning. The surface topography is

²At this point, the base pressure was usually regained within 20 to 30 seconds after flashing as the sample became free from contamination.

characterised by a 'staircase' arrangement of terraces of average width $d = 185 \pm 60 \text{ \AA}$, separated by monatomic steps (see figure 4.8 (a)). The average value of the step height is measured from histograms of locally plane fitted images, like the one shown in figure 4.8 (b). This histogram distributes the total pixel count of the image, N , as a function of the colour-scale height value of each pixel. As a result, terraces appear as peaks while the step height is determined from the separation between them. In this case, the measured step height is $h = 2.1 \text{ \AA}$, which is within 5.5 % of the value for the unrelaxed surface $(2.22 \text{ \AA})^3$. Taking these values for terrace width and step height and applying them to the simple geometrical expression:

$$\tan \alpha = \frac{h}{d} \quad (4.2)$$

yields a value for the miscut angle of $\sim 0.65^\circ$. Using a mark on the cap of the sample-holder as a reference, the direction of step-edges in STM images was correlated with LEED data. It was found that terraces were separated by $(\bar{1}01)$ steps where the step-edges on the surface run parallel to the $[1\bar{1}1]$ crystallographic direction.

With a finer scale images, it is possible to see that a small amount of contaminant material is still present on the surface. From figure 4.9 it can be seen that impurities decorate the step-down edges of the terraces, suggesting that at room temperature, these edges present a barrier to interlayer diffusion. The presence of such a diffusion barrier has significant consequences during non-equilibrium growth in a number of epitaxial systems and can, in fact, determine the growth mode obtained [162].

Figure 4.10 shows a zoom-in of two terraces separated by a step. Taken with a much lower tunneling bias than that used in figure 4.9, the resulting

³The discrepancy can be attributed to the error in the z-calibration of the piezo tube-scanner in the microscope [83].

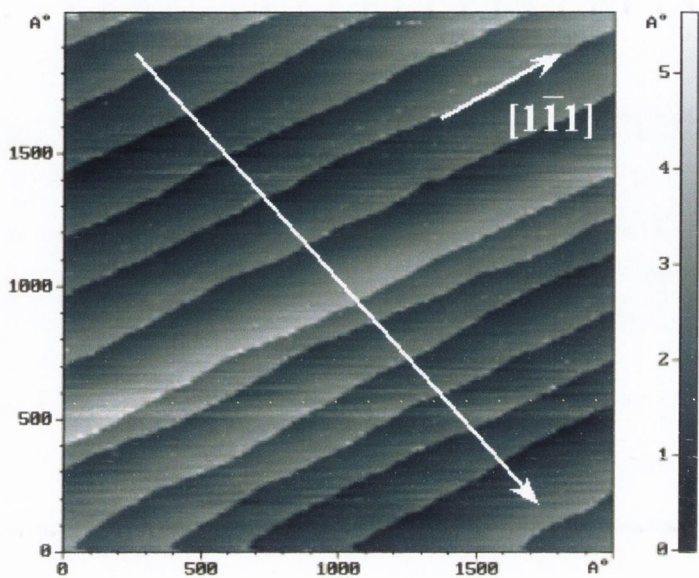


Figure 4.7: STM image of the clean Mo(110) surface with global plane fitting. MnNi tip. $V_{bias} = 100$ mV. $I_{tunnel} = 0.1$ nA. The arrow marks the location of the line profile taken in figure 4.8(a) after local plane fitting.

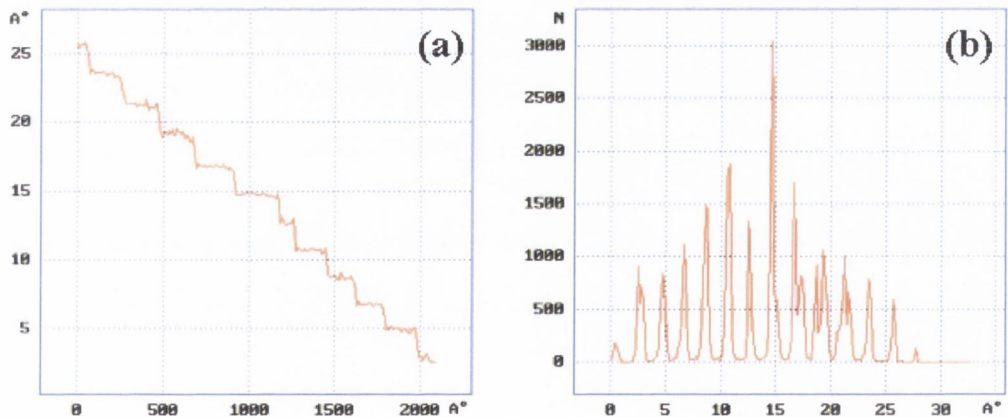


Figure 4.8: After local plane fitting to a terrace: (a) A line profile along the direction marked in figure 4.7 shows how the surface follows a 'staircase' topography. (b) A histogram of figure 4.7 shows that the step heights are monatomic, with an average value of $h = 2.08$ Å.

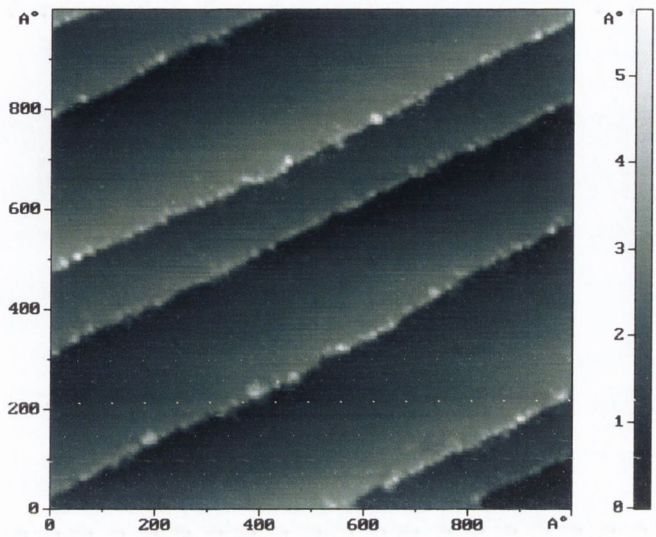


Figure 4.9: ($1000 \times 1000 \text{ Å}^2$) STM image of Mo terraces taken 195 minutes after cleaning. Impurities decorate the step-down edges of the terraces. MnNi tip. $V_{bias} = 200 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

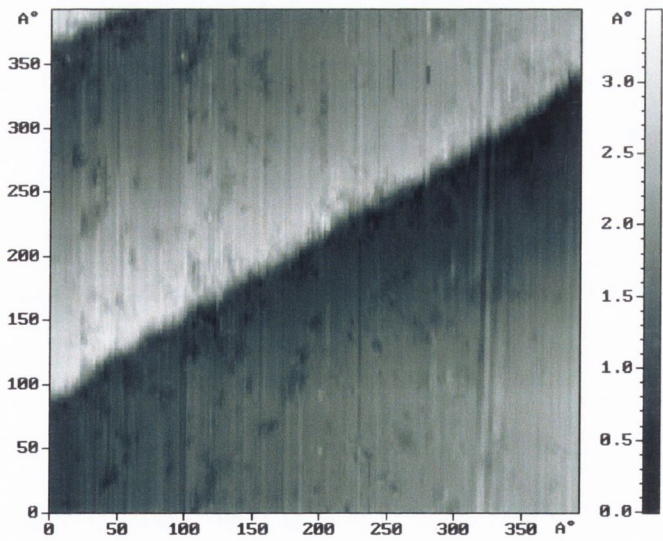


Figure 4.10: ($400 \times 400 \text{ Å}^2$) STM image of defects induced on the Mo terraces by the presence of impurities (most probably carbon and hydrogen). Taken 230 minutes after cleaning. MnNi tip. $V_{bias} = 10 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

increase in resolution makes it possible to discern numerous defects on the terraces. Oxygen and carbon peaks were not visible in AES spectra taken on this surface before the STM analysis was performed. A better example of these defects is shown in figure 4.11, taken on a separate occasion, approximately 260 minutes after cleaning the surface. A zoom-in on one of the terraces in this figure shows atomic corrugation on patches between these defects (see figure 4.12). The atomic corrugation along the $[1\bar{1}1]$ direction is less than $0.1 \text{ \AA}$, which places it at the detection limit of the set-up. The periodicity of this corrugation is of the correct magnitude for a $p(1 \times 1)$ surface. The depressions have a measured depth varying between 0.2 and $0.6 \text{ \AA}$. Some material also appears to protrude on top of the terrace. It is tentatively suggested that the depressions seen on the surface are the result of carbon or oxygen, as these are the most persistent impurities observed in Auger spectra of the surface⁴. Other possible agents for causing these defects are molecular hydrogen and water, which are both prevalent in the residual gas found in stainless steel UHV systems [9, 82].

As indicated by Osing [10], molecular hydrogen comprises the major part of the residual gas in the UHV system used during this study, with an estimated partial pressure of $P_{H_2} = 8 \times 10^{-11} \text{ mbar}$. This is to be expected as H_2 generally comprises the greater part of the residual gas in any stainless steel UHV system [164]. Chapell and Hayward [165], in a molecular beam study of hydrogen interaction with the Mo(110) surface at 300 K , have shown that beginning with an initial sticking coefficient of $s_0 = 0.35^5$, the sticking prob-

⁴The fact that adsorbates on a metal surface may not necessarily appear as bumps on the surface in STM has been highlighted in a review article by Van Hove *et. al* [163].

⁵The miscut angle of the crystal used for measurement of this value is unknown. A strong dependence of sticking probability upon step density is likely, as seen for H_2 adsorption on W(110) [166]. However, for the purposes of a rough estimate, this value is

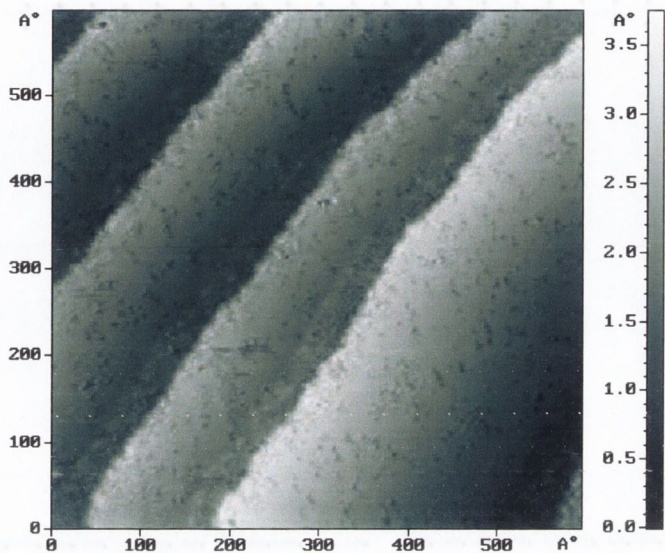


Figure 4.11: ($600 \times 600 \text{ \AA}^2$) A clearer example of defects formed on the Mo terraces by adsorbed contaminants. Taken 260 minutes after cleaning. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

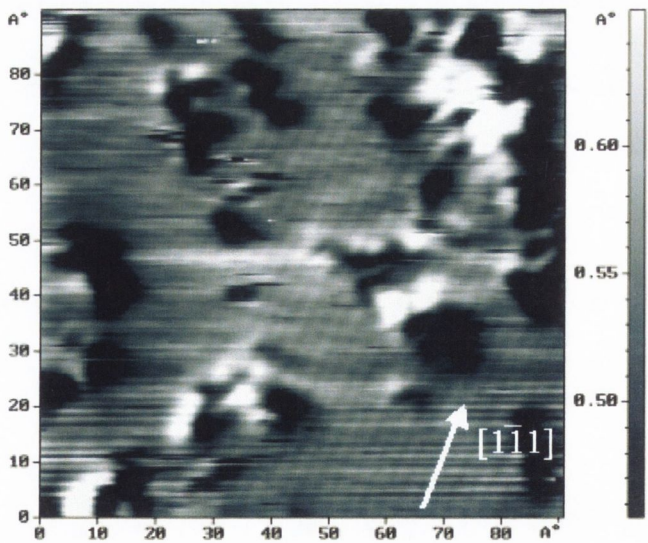


Figure 4.12: ($90 \times 90 \text{ \AA}^2$) A high-resolution image showing atomic corrugation in patches between defects on a Mo terrace. Taken 275 minutes after cleaning. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

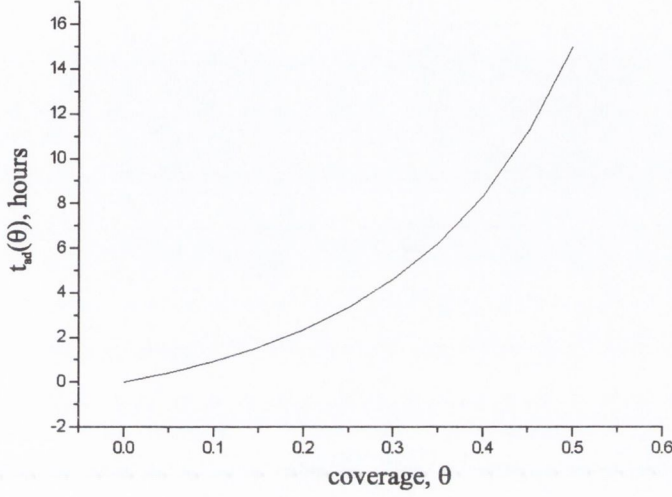


Figure 4.13: Plot of adsorption time $t_{ad}(\theta)$ for dissociative adsorption of H_2 on Mo(110) as a function of coverage, in the range $0 \leq \theta \leq 0.5$, assuming $s_0 = 0.35$ and $P_{H_2} = 6 \times 10^{-11}$ Torr.

ability, $s(\theta)$, decreases continuously with increasing coverage. The relationship between $s(\theta)$ and coverage, θ , for dissociative adsorption of a diatomic molecule without a precursor state is typically given by the Langmuir-type expression:

$$s(\theta) = s_0(1 - \theta)^2 \quad (4.3)$$

By rearranging equations 4.1 and 4.3 the following relation for the adsorption time can be arrived at:

$$t_{ad}(\theta) = \frac{\theta \times n_a}{3.6 \times 10^3 \times R_{arrival} \times s_0(1 - \theta)^2} \quad [\text{hours}] \quad (4.4)$$

where n_a is the total number of adsorption sites available and θ is the fractional coverage. Assuming a one-to-one correspondence between the surface
adequate.

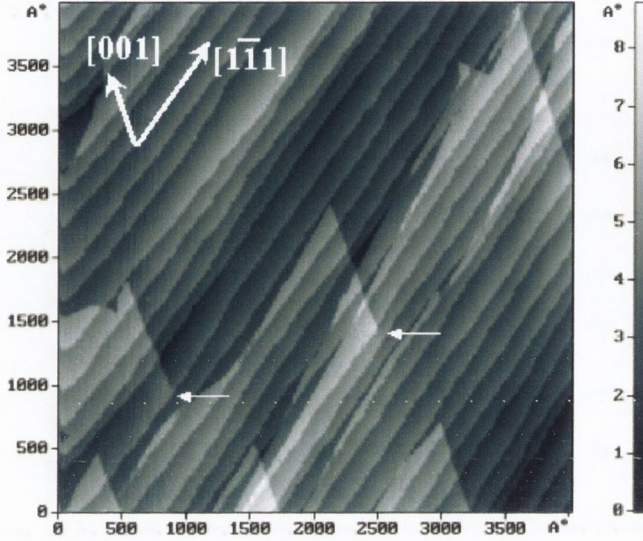


Figure 4.14: ($4000 \times 4000 \text{ \AA}^2$) Line defects observed in the deformed region. Originating from screw dislocations (marked with arrows), these additional steps propagate along the $[001]$ direction, abruptly change direction and propagate at an acute angle to the normal step direction. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

atoms and adsorbed hydrogen atoms, $n_a = 1.43 \times 10^{19} \text{ m}^{-2}$. Taking the values for s_0 and P_{H_2} given above, the value of $t_{ad}(\theta)$ in the coverage range $0.0 \leq \theta \leq 0.5$ is plotted in figure 4.13. An atomic hydrogen coverage of $\sim 0.3 \text{ ML}$ is estimated after 275 minutes, which is the time elapsed between cleaning the sample and taking the image in figure 4.12. Therefore, the observed atomic corrugation is more probably due to the Mo surface atoms, than to a $p(1 \times 1)$ atomic hydrogen layer.

4.1.4 Surface dislocations

During the high-temperature annealing process some localised plastic deformation of the sample occurred. This deformation was visible to the naked

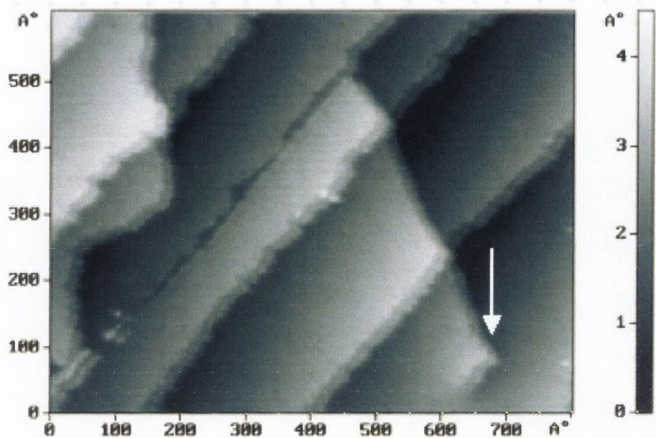


Figure 4.15: ($800 \times 600 \text{ Å}^2$) The starting point of a screw dislocation on the surface. The doubling of the step-edges is due to a multiple-tip effect. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

eye on part of the surface. It is most likely that some mechanical stress was exerted on the crystal when it was fixed into its holder. There may have been some additional stress induced upon annealing due to the slightly different thermal expansion coefficients of the crystal and its holder ($5.1 \times 10^{-6} \text{ K}^{-1}$ and $6.5 \times 10^{-6} \text{ K}^{-1}$ at 300 K for Mo and Ta respectively [167]). Annealing to near melting-point temperatures allowed the crystal to undergo slip [106] to alleviate the resulting mechanical strain. Fortunately, this deformation was restricted to a small area of the surface so that most of the surface remained intact and suitable for analysis.

STM analysis performed within the vicinity of this deformed region shows how the slip process is mediated by the formation of dislocations. The usual stepped surface is disrupted by numerous line defects, figure 4.14, which extend over many terrace spacings. These features, which appear as additional monatomic steps on the surface, originate from screw dislocations like the one shown in figure 4.15. In this figure it is evident that the dislocation initially

propagates along the $[1\bar{1}1]$ direction, parallel to the usual step direction. It is expected that in bcc metals, plastic deformation of the $\{110\}$ planes will occur along the $\langle 111 \rangle$ directions [168]. The Burgers vector associated with the dislocation [106, 169] is therefore likely to lie along either the $[111]$ or $[101]$ direction. This conclusion is based on a simplistic representation of the screw dislocation, illustrated in figures 4.16 and 4.17. While this model does not represent the real relaxation of the lattice around the defect, it is sufficient to determine the most probable direction of the resulting Burgers vector.

After following the $[1\bar{1}1]$ direction for a distance of approximately 80 Å the dislocation edge changes direction to travel along the $[001]$ direction, crossing several terraces before again changing direction (typically at a point on a terrace near to a step-up edge) to propagate at an acute angle ($\sim 5^\circ$) to the normal step direction. The extent to which the dislocation propagates along this direction is considerably larger than along the $[001]$ direction, extending beyond the limits of the largest area imaged ($4000 \times 4000 \text{ Å}^2$).

The time-evolution of the slip process in Mo(011) epitaxial films grown on sapphire substrates has been studied by low-energy electron microscopy [170]. In this study, it was observed that under certain conditions the dislocation system (comprising interfacial and screw dislocations) experienced a retarding effect in its lateral motion across the surface due to the surface steps encountered normal to its path. This effect was attributed to the interaction of the long-range elastic strain fields associated with each line defect - similar to the step-step interaction encountered on vicinal surfaces [26].

The presence of dislocation defects on a surface is liable to further complicate the kinetics of non-equilibrium growth on that surface. The diffusion and nucleation kinetics of adatoms arriving in the locality of these additional features can be affected, a dual result of the physical barrier due to the defect

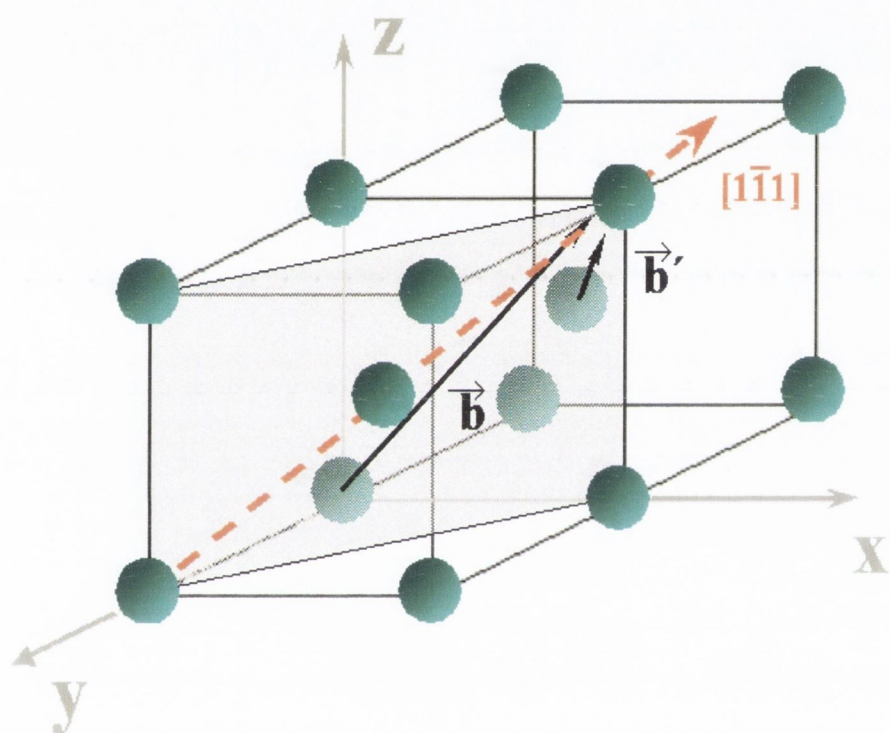


Figure 4.16: The Mo unit cell showing the (110) plane (shaded), the dashed arrow represents the $[1\bar{1}1]$ direction along which the dislocation first propagates. The two suggested Burgers vectors, $\vec{b}$ along the $[101]$ direction and $\vec{b}'$ along the $[111]$ direction, are indicated by the solid arrows.

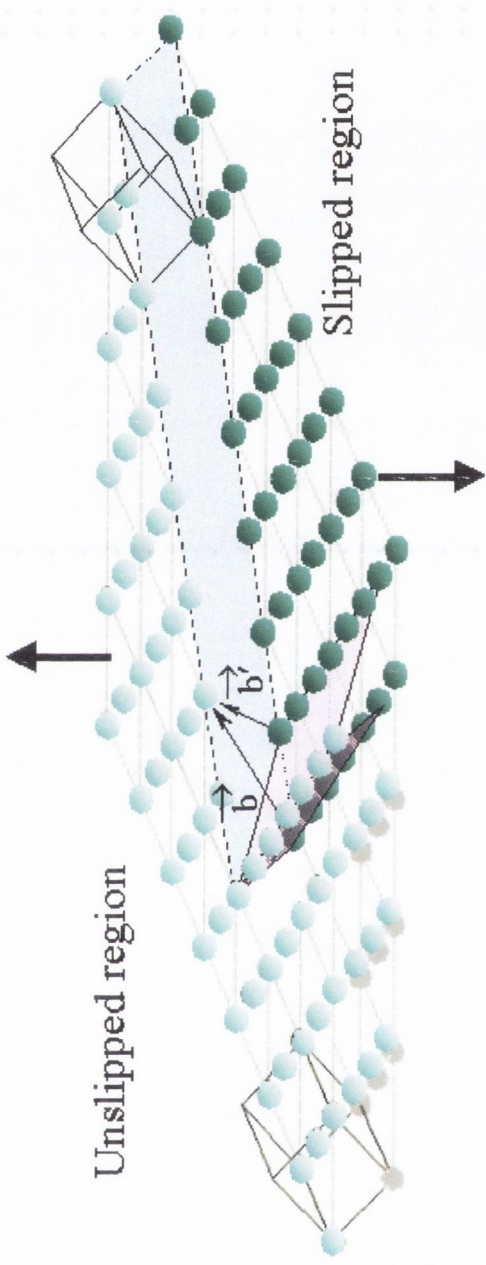


Figure 4.17: A schematic representation of the initial formation of a screw dislocation along the $[1\bar{1}1]$ direction. The additional monatomic $(\bar{1}01)$ step formed by the dislocation is shaded in blue. Both suggested Burgers vectors are marked along with the resulting planes of inclination between the slipped and unslipped regions. The directions of slip are marked by thick arrows, while the Mo crystal unit cell is also included for reference.

itself⁶ and the strain field produced around it. The most direct result is the increase in the number of higher-coordination binding sites made available. In homoepitaxy, adatoms usually prefer to bind to the step-edges of pre-existing incomplete layers rather than nucleate a new layer on a flat terrace. Consequently, the step formed by the emergence of a screw dislocation at a surface can enhance epitaxial growth by providing a continuously incomplete atomic plane to which additional adatoms can bond, resulting in a spiralling growth formation [171].

4.2 Fe growth near room-temperature

Table 4.2 summarises the deposition details for all films grown at near room temperatures, that were subsequently studied by STM. Following the procedure described in section 3.2.2, the Mo(110) surface was cleaned 20-45 minutes prior to deposition. Thermocouple readings from the sample stage indicate that the temperature of the sample remains slightly above 300K, estimated to lie in the range of $300 \leq T_{dep.} \leq 350 \text{ K}$ for all the depositions.

The fractional iron coverages θ_{Fe} for all films (including those where the misfit strain is relieved) are expressed in the pseudomorphic monolayer equivalent. Recognising that the packing density of a single pseudomorphically strained Fe layer on Mo(110) will be the same as that for the Mo(110) plane *i.e.* $n_{Mo} = 1.43 \times 10^{19} \text{ atoms.m}^{-2}$, the mass per unit area of a single pseudomorphically strained Fe layer will be $n_{Mo} \times m_{Fe} \text{ (kg.m}^{-2}\text{)}$, where $m_{Fe} = 9.27 \times 10^{-26} \text{ kg}$ is the mass of a single Fe atom. The mass of Fe per unit area arriving at the sample surface is determined by measuring the deposition time $t_{dep.}$ and the incident flux of Fe F_{Fe} in $\text{kg.s}^{-1}.\text{m}^{-2}$ measured

⁶*i.e.* the change in coordination experienced at the defect.

with the quartz crystal monitor. The fractional coverage is then calculated from:

$$\theta_{Fe} = \frac{F_{Fe} \times t_{dep.}}{n_{Mo} \times m_{Fe}} \quad (4.5)$$

4.2.1 AES and LEED

Figure 4.18 plots the surface concentrations of Mo and Fe for increasing deposition thicknesses. These values were calculated from Auger data taken after each STM session, using equation 3.35. As expected, the Mo surface concentration decreases as the surface is covered with a thickening layer of Fe.

Figure 4.19 displays the principal results of LEED analysis of these films. Like the AES analysis, the LEED analysis was usually performed after each STM session. At low coverages, LEED analysis typically yielded either a $p(2 \times 2)$ structure or a pattern of $p(3 \times 2) + p(2 \times 3)$ domains. AES analysis of freshly grown films, indicates the presence of sizeable carbon and oxygen fractional concentrations, $C_C = 0.03 - 0.09$ and $C_O = 0.015 - 0.03$ respectively, introduced during the film deposition. These contaminants probably originate from the Fe source rod. LEED analysis of these freshly grown films could give either $p(1 \times 1)$ or $p(2 \times 2)$ patterns, depending on the carbon and oxygen levels. The $p(3 \times 2)$ domain pattern appears to develop from the $p(2 \times 2)$ pattern, during long exposures to the residual gas in the UHV system. Table 4.3 summarises the carbon and oxygen contamination levels measured for the various structures observed.

One cannot assign the observed structures to either carbon or oxygen uniquely from LEED data alone, it is more practical to treat this as a co-adsorption system. However, one can note that the transition between the

Film	d_{Fe} Å	$\theta_{dep.}$ ML	t_{cool} min.	$T_{dep.}$ K	D ML.min. ⁻¹	P mbar	t_{STM} hrs.	t_{AES} hrs.
A	0.5	0.295	35	330	0.221	1.7×10^{-10}	2.7	11.7
B	1.5	0.885	100	-	0.59	3.7×10^{-10}	2.6	14.1
C	2	1.18	35	-	0.443	3.3×10^{-10}	2	9.1
D	2.5	1.475	25	340	0.506	2.7×10^{-10}	2.8	13.7
E	3	1.77	45	-	1.01	3.1×10^{-9}	1.75	5.1
F	4	2.36	40	-	0.708	3.3×10^{-10}	8.9	13.4
G	5	2.95	20	345 [†]	0.805	3.3×10^{-10}	1.2	5.8
H	8	4.72	45	-	0.322	3.3×10^{-10}	1.75	4.2

Table 4.2: Deposition details for each of the Fe films deposited at near room temperature. These are: (a) the deposited thickness d_{Fe} - read from the quartz crystal monitor (included for reference), (b) the equivalent monolayer coverage $\theta_{dep.}$, (c) the cooling period t_{cool} between cleaning the Mo surface and depositing the Fe film, (d) the sample temperature during deposition $T_{dep.}$ - read from the heating stage thermocouple († measured during a different deposition, but with the same cooling time), (e) the deposition rate D and (f) the chamber pressure P during deposition. The table also includes the period elapsed between film deposition and data acquisition using the STM and AES set-ups.

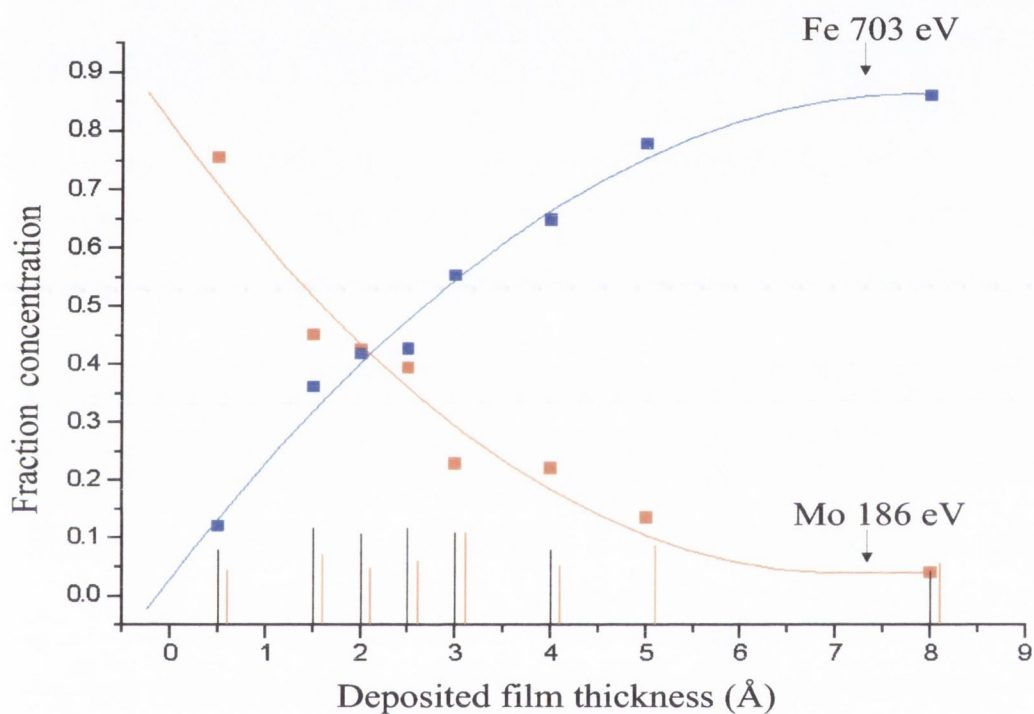


Figure 4.18: Line-fitted scatter plots showing the concentrations of Mo and Fe *vs.* deposited film thickness, for films grown at $300 \leq T_{dep.} \leq 350$ K. Carbon and oxygen contamination levels are represented by the columns at the base of the graph - the oxygen levels (red columns) are shifted along the x-axis for clarity.

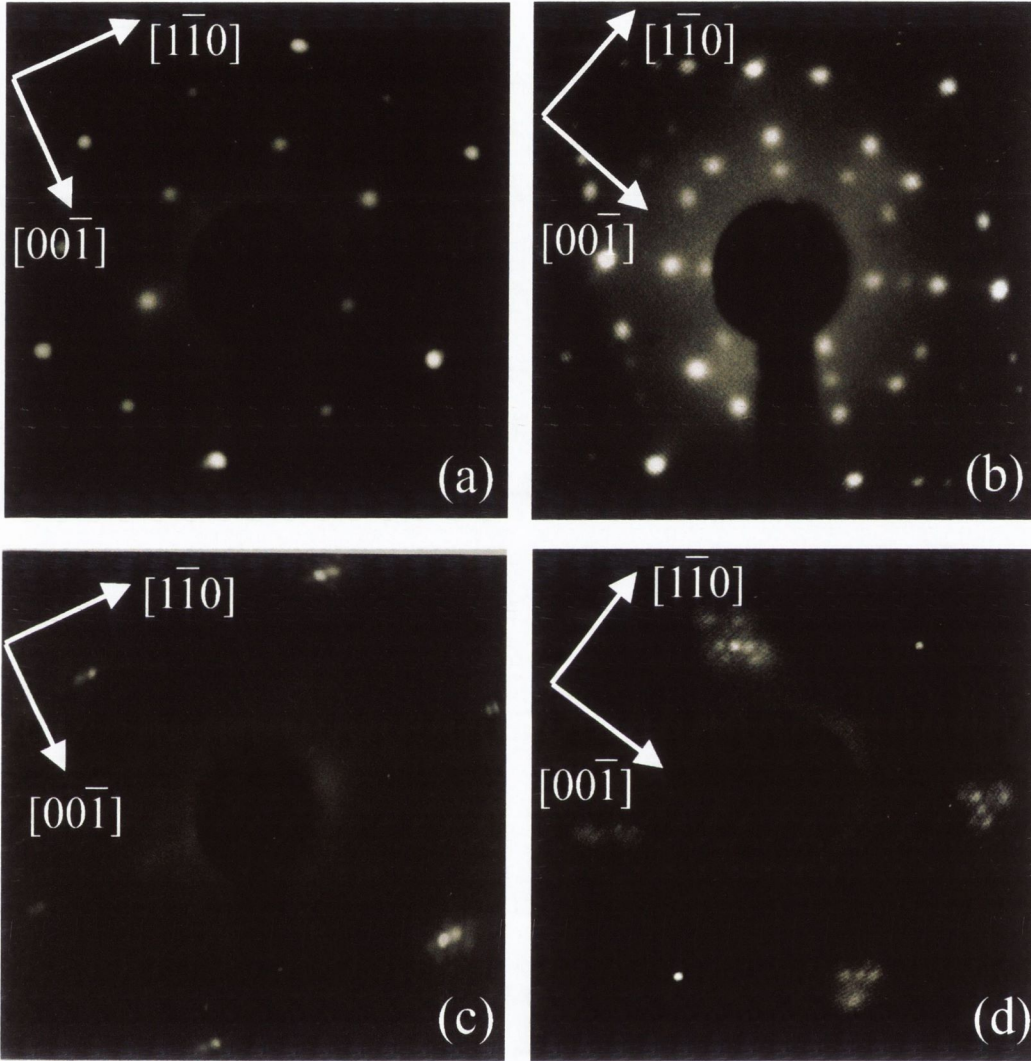


Figure 4.19: LEED patterns obtained from Fe films of varying coverages, grown near 300 K. The Fe coverage ranges in which each pattern was observed are assigned according to the corresponding deposition thickness. (a) $p(2 \times 2)$ - $0.3 \leq \theta_{dep.} \leq 1.2$ ML, $E_{beam} = 89$ eV, (b) $p(3 \times 2) + p(2 \times 3)$ domain pattern - $1.2 \leq \theta_{dep.} \leq 1.8$ ML, $E_{beam} = 93$ eV, (c) 2D lattice distortion - $\theta = 2.4$ ML, $E_{beam} = 37$ eV and (d) 2D lattice distortion - $\theta = 4.7$ ML, $E_{beam} = 123$ eV.

$p(1 \times 1)$ and $p(2 \times 2)$ structures corresponds to a more significant increase of 60-75 % in the carbon level, than the increase of 0-45 % in the oxygen level. On the other hand, the transition between the $p(2 \times 2)$ and $p(3 \times 2)$ structure corresponds to an increase in the oxygen level by about 40-50 %, while the carbon level remains roughly the same. The increase in contamination is most likely due to adsorption from the residual gas. It was found that exposure of the clean Mo surface to the residual gas (with and without the ion gauge activated) for up to 6.5 hours, or annealing the surface for up to 105 minutes at 690 K, did not increase either the carbon or oxygen fractional concentrations above 0.02. Therefore, the observed increase in contamination is ascribed exclusively to the presence of the Fe film.

One cannot also exclude the possible effects of contamination by molecular hydrogen or water. These have been observed to induce defect features including a (2×2) structure on pseudomorphically strained Fe layers, depending on the exposure time to the residual gas [9, 10]. It was found that the unrelieved misfit strain in the pseudomorphic Fe layers increased the getter ability of the films. This arises because the adsorption of atomic hydrogen onto the Fe(110) surface is predicted to reduce the bond strength of neighbouring Fe atoms by 70 % [172], thereby allowing surface relaxation. For island growth where strain relief is mediated by other processes, the getter ability of the film is reduced.

A similar effect may be expected for adsorption of carbon or oxygen onto strained Fe films. Both elements have much higher electronegativities than iron, meaning that upon adsorption they will form heteropolar bonds with the Fe(110) surface. This has been predicted theoretically for the case of oxygen adsorption on an Fe bilayer on W(001) [5]. The redistribution of electrons (particularly the d-character bonding electrons) away from the Fe layer may

Structure	Carbon level (%)	Oxygen level (%)
$p(1 \times 1)^\dagger$	0.03	0.04
$p(2 \times 2)$	0.08-0.12	0.03-0.07
$p(3 \times 2)$	0.09-0.12	0.06-0.11

Table 4.3: Contamination levels measured for the various LEED patterns observed on low-coverage Fe films grown near room temperature. $\dagger$ $p(1 \times 1)$ LEED pattern and AES data taken on a freshly grown film within 15 minutes of deposition. All other data were taken after STM analysis.

induce a compressive stress on the Fe layer which compensates for the tensile strain due to the misfit with the substrate.

The LEED patterns observed at higher coverages (figures 4.19 (c) and (d)) correspond to the transition between pseudomorphic LBL growth below two Fe monolayers, to the Stranski-Krastanov growth observed above this thickness. They are very similar to the results obtained for a coverage of $\theta \geq 2.43ML$ for the Fe/W(110) system [173]. The patterns observed in the latter study were correctly attributed to a strain-relieving 2D distortion or dislocation network which was subsequently resolved by STM [174]. This network is very similar to the one observed in this study at coverages of $1.8 \leq \theta_{dep.} \leq 4.7ML$ (*cf.* section 4.2.5). Notably, there is no evidence of any of the low coverage patterns superimposed on the patterns shown in figures 4.19 (c) and (d). This is a positive indication that where the dislocation network is pervasive, the formation of an ordered contaminant adlayer is inhibited.

Referring back to figure 4.18, the AES data taken on each film after STM analysis indicates that the overall contamination level remains roughly consistent over the whole thickness range. However, it should be pointed out

that the film roughness is much higher for the thicker films, which should increase their getter ability.

4.2.2 STM results - Sub-monolayer growth

Figure 4.20 shows the topography of film A, a deposited coverage of $\theta \simeq 0.3 \text{ ML}$ (determined from the deposition monitor) grown at 330 K with $D = 0.221 \text{ ML.min}^{-1}$. Using the IMP image processing software developed by Dr. A Quinn and J. Naumann, the Fe coverage could be determined from STM images, by measuring the area of an STM image covered by Fe. Fe growing from the substrate steps could be distinguished from the Mo substrate by a fractional step due to the difference in atomic spacings (normal to the surface) between Mo and Fe (*cf.* figure 4.21). The coverage measured from STM images of this film is $0.42 \pm 0.03 \text{ ML}$, which is about 40 % larger than the value determined from the quartz deposition monitor.

The morphology of this film is characteristic of a high adatom mobility without interlayer mass transport. Growth proceeds by a combination of the step-flow mechanism and 2D island growth. The contribution of the step-flow mechanism is greater, indicating that the deposited Fe adatoms are sufficiently mobile to reach the Mo step-up edge before nucleating clusters on the terrace. Adatoms reaching the step-down edge are reflected.

The density of terrace islands is low - of the total coverage, only $0.05 \pm 0.02 \text{ ML}$ is taken up as free-standing terrace islands. Both the local density and island area appear to scale with the terrace width - wider terraces have a higher number of islands with larger average diameters. It may be that during the early stages of growth, the nucleation density is more uniformly distributed across the surface. However, as growth progresses by the step-flow mechanism, islands on the narrower terraces are incorporated (an example

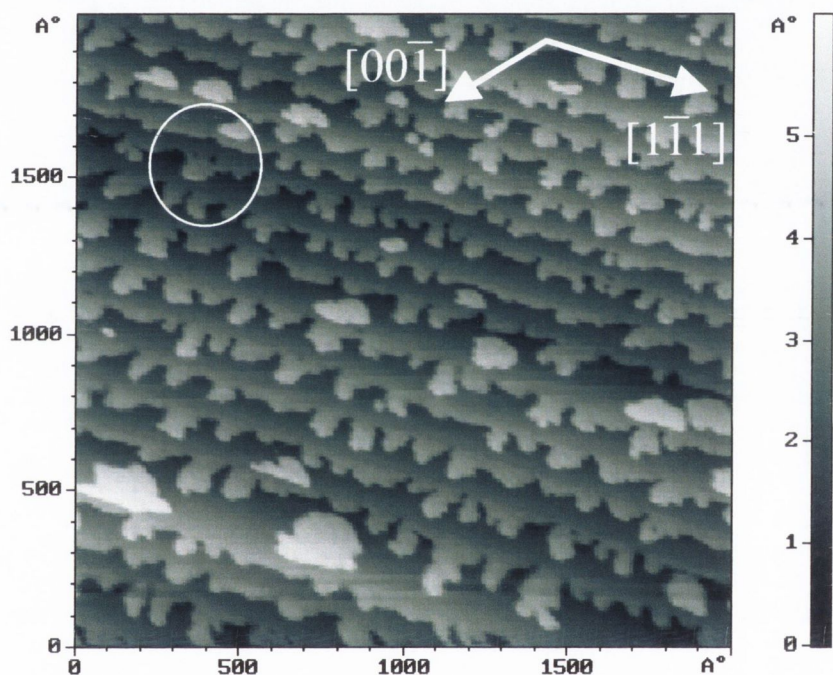


Figure 4.20: ($2000 \times 2000 \text{ \AA}^2$) STM image of film A, 0.295 ML Fe deposited at 330 K. An example of incorporation of a terrace island into the growing step-edge is circled. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

is highlighted in figure 4.20). On wider terraces islands have sufficient room to grow to large sizes, without being incorporated into the encroaching step-edge.

Island incorporation may also, in part, explain the roughness of the growing step-edge. Another factor which contributes to this roughness, is the preferential growth along the $[00\bar{1}]$ direction, typically encountered in bcc (110) growth systems [175, 176]. This has been attributed to anisotropic sticking probabilities at steps [177], as well as the local diffusion behaviour at the step-edges [176]. An advantage of the step-edge roughness is that it increases the number of Fe atoms at step-edge positions. This facilitates the reduction of the tensile strain in the film since Fe atoms at these positions can relax inwards to partially relieve the strain. A similar effect is observed for terrace islands in the Fe/Mo(110) and Fe/W(110) systems [94, 174].

In the STM study by Malzbender *et al.* [94], submonolayer growth was found to be predominantly mediated by island nucleation on terraces, with only a small step-flow contribution. In this study, forced layer-by-layer (LBL) growth was observed during submonolayer deposition on a surface with a terrace width of 100-1000 Å, using values of $D = 0.2 \text{ ML.min}^{-1}$ and $T = 300 \text{ K}$. The forced LBL growth was attributed to the reduced adatom mobility at the deposition flux used. Under similar conditions, Osing observed a high nucleation density of islands during submonolayer growth, with a mean diameter of 10-20 Å on a vicinal Mo(110) surface with an average terrace width of 25 Å [10]. This suggests that the average terrace width ($185 \pm 60 \text{ Å}$ for the surface used here) is not critical in deciding the growth mechanism at room temperature. Consequently, the predominant step-flow mechanism observed in this study is attributed to the higher adatom mobility caused by the slightly higher substrate temperature.

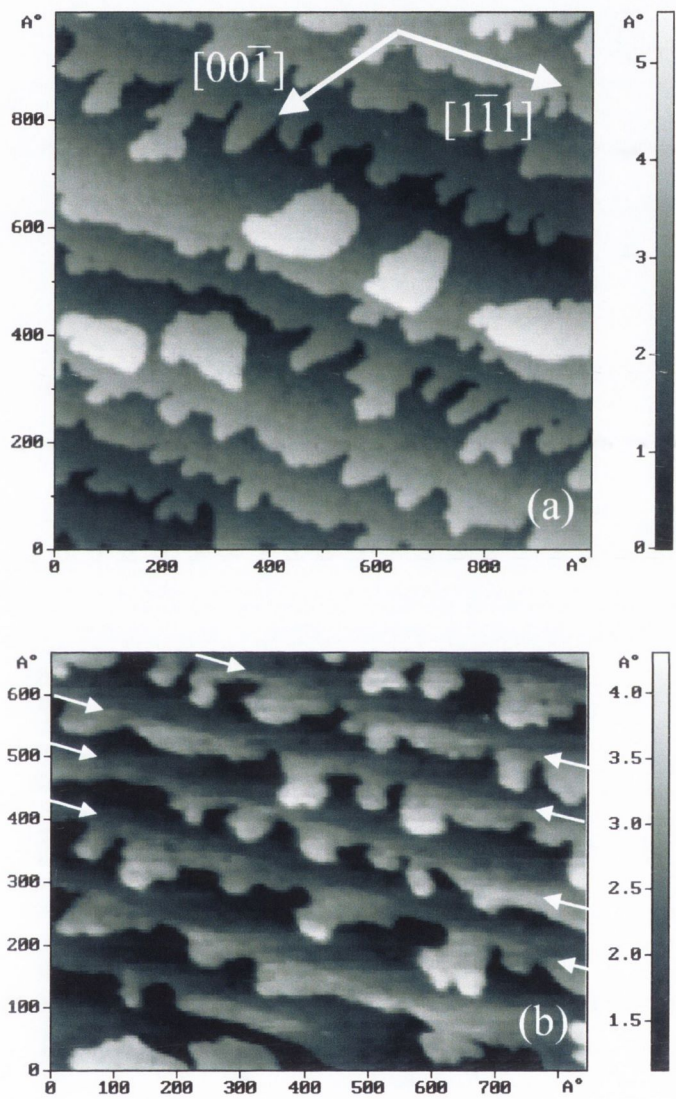


Figure 4.21: (a) Fe terrace islands tend to avoid crossing Mo step-down edges. (b) A contrast enhanced STM image showing the fractional step formed where Fe grows out from the Mo step-down edges. W tip. $V_{bias} = 30$ mV. $I_{tunnel} = 0.1$ nA.

The boundary at which the Mo step-down edge ends and the Fe layer begins is distinguished by a fractional step, shown in figure 4.21(b). This fractional step may be a topographic effect due to the differing lattice parameters of Mo and Fe (with the additional effect that the Fe layer is tetragonally distorted as it is stretched on the substrate lattice). Alternatively, the difference in the local density of states of both materials may be responsible for the contrast difference (*c.f.* section 3.3.1). This effect has also been observed by Malzbender *et al.* [94]. Another feature, demonstrated in figures 4.20 and 4.21(a), is that Fe terrace islands avoid crossing over the Mo-Fe fractional step to locally form an Fe bilayer. Instead the Fe islands form straight edges, which run along the Mo-Fe boundary. This is to be expected since the Fe ad-layer will prefer to wet the Mo surface due to the difference in their surface free energies ($\gamma_{Fe} = 2.55 \text{ J.m}^{-2}$, $\gamma_{Mo} = 2.95 \text{ J.m}^{-2}$ [94]). Where iron covers iron, the second Fe layer will not experience the same interface energy as the first layer, while there is also an increase in the strain energy associated with stretching Fe-Fe bonds to form a pseudomorphic layer.

4.2.3 Monolayer coverage

Figure 4.22 shows the morphology of film C - a deposited thickness of 2 Å, corresponding to a coverage of 1.2 *ML* - the actual coverage is $\sim 0.95 \text{ ML}$. The first pseudomorphic layer is almost completely closed before the second Fe layer begins to nucleate. The step-edges for the terraces in the width range of 50-150 Å are much rougher than those of wider terraces (150-300 Å). This reflects the fact that on narrow terraces, film growth is mediated by the anisotropic step-flow mechanism alone, where coalescence in the $[1\bar{1}0]$ direction (normal to the $[00\bar{1}]$ direction) is hindered. On wider terraces the process is a combination of step-flow and island growth. These islands are

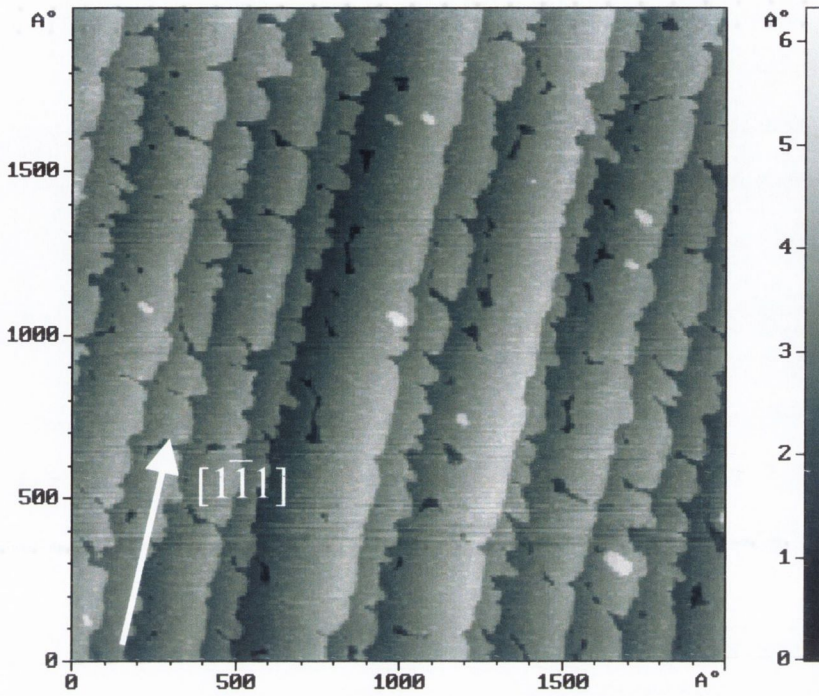


Figure 4.22: ($2000 \times 2000 \text{ \AA}^2$) STM image of film C, 1.2 ML Fe deposited at $\sim 330 \text{ K}$. There is almost complete closure of the first pseudomorphic layer before nucleation of the second begins. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

confined by the Mo step-down edge, so that they tend to grow parallel to the $[1\bar{1}1]$ direction until they coalesce with other islands, forming a smooth step-edge. Moreover, the density of voids in the first Fe layer is highest for the widest terraces, where coalescence between terrace islands and the growing step-edge has not been fully completed. The second layer nucleation density is very low ($\sim 4.4 \times 10^{14} \text{ m}^{-2}$), while the average island diameter is of the order of $50\text{-}70 \text{ \AA}$ ⁷.

There was no evidence of any misfit-induced lattice distortions or dislocations in any of the images taken of this or the previous film. It has been

⁷This is the diameter of a circular island of comparable area.

suggested that the first pseudomorphic Fe layer is stabilised against dislocations since it may be treated as an adsorbate which induces a compressive stress on the Mo surface [94], similar to that observed for submonolayer coverages in the Fe/W(110) system [8, 178, 179]. This compressive stress arises because the Fe adatoms remove some of the excess charge at the W surface which causes its intrinsic tensile stress [8]. This is thought to minimise the effective stress to zero on completion of the first monolayer.

4.2.4 The second pseudomorphic Fe layer

Films B and D were deposited with thicknesses of $1.5 \text{ \AA}$ and $2.5 \text{ \AA}$, corresponding to coverages of 0.89 and 1.48 *ML* respectively. The Auger data plotted in figure 4.18, show a continuous increase of the Fe surface concentration with increasing deposition thickness in the range containing these films. However, STM images taken of these films indicate that the coverage was locally much higher in the imaged regions. This most likely due to some misalignment of the sample stage relative to the evaporator aperture, resulting in a thicker coverage being deposited near the outer area of the sample surface. Since all the AES data were taken with the beam spot positioned at the centre of the sample, it did not detect the discrepancy.

The evidence is presented in figures 4.23 and 4.24, showing $2000 \times 2000 \text{ \AA}^2$ and $1000 \times 1000 \text{ \AA}^2$ STM images of film B respectively. A number of dislocation lines are visible on the incomplete Fe layer, which were not observed on either the 0.3 or 0.95 *ML* films. Previous studies of the Fe/W(110) and Fe/Mo(110) systems have found that dislocations only appear in the second Fe layer [94, 174]. As already discussed, the first monolayer is stabilised against the formation of dislocations. The presence of a closed pseudomorphic monolayer is also indicated by the presence of a number of $\sim 1.5 \text{ \AA}$ deep

voids on some of the terraces (circled in figure 4.24). These voids represent points where the first pseudomorphic Fe monolayer has not completely closed (*cf.* figure 4.22).

The growth mode of the second pseudomorphic layer is similar to that of the first pseudomorphic layer, with a mixture of step-flow and island growth. The anisotropic growth along the $[00\bar{1}]$ direction is more evident in these films. It should be noted that for the Fe/Mo(110) and Fe/W(110) systems, anisotropic growth does not typically appear until the second Fe layer [94, 174]. The first layer is characterised by dendritic-like island growth which maximises the number of adatoms at island-edge positions, where they can relieve the film strain.

For film B, the step-flow contribution is smaller than that observed for the monolayer films, while the density of terrace islands is higher ($\sim 1 \times 10^{11} \text{ cm}^{-2}$). This reflects the lower mobility of the Fe adatoms, caused by the lower substrate temperature (the substrate was cooled for 100 minutes) and the high local deposition rate $D = 1.05 \text{ ML.min}^{-1}$ (calculated using the measured coverage and the deposition time). By comparison, film D shows a lower density of terrace islands and a larger step-flow contribution - as deposition rate is lower $D = 0.61 \text{ ML.min}^{-1}$ and the temperature higher $T = 340 \text{ K}$.

The interesting feature of figure 4.23 is that nucleation of the third Fe layer occurs explicitly at dislocations in the second Fe layer. The nucleation density of third layer islands is higher in figure 4.23(b) than in figure 4.23(a), despite the fact that the latter has a lower deposition rate. This can be explained by the fact that the dislocations are formed because the relaxation of edge-atom positions only partly contributes to the relief of misfit strain in the film. The film that covers a larger surface area has a lower contribution

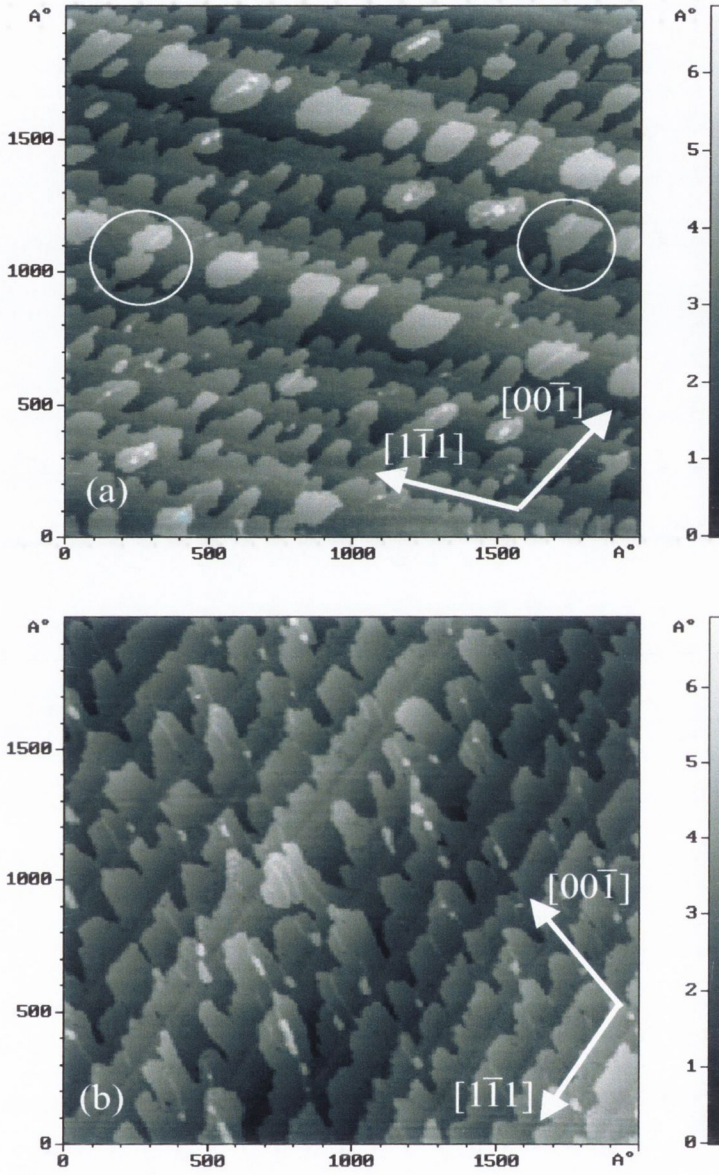


Figure 4.23: ($2000 \times 2000 \text{ \AA}^2$) STM images of films B and D. (a) Film B: 1.57 ML Fe grown near 300 K with a local $D = 1.05 \text{ ML.min}^{-1}$. The first Fe monolayer is completely closed, while the second and third layers have coverages of 0.565 and 0.005 ML respectively. Examples of island incorporation by the growing step-edge are circled. (b) Film D: 1.79 ML Fe grown at 340 K with a local $D = 0.61 \text{ ML.min}^{-1}$. The second and third layers have coverages of 0.77 ML and 0.02 ML respectively. W tip. $V_{bias} = 30\text{-}40 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

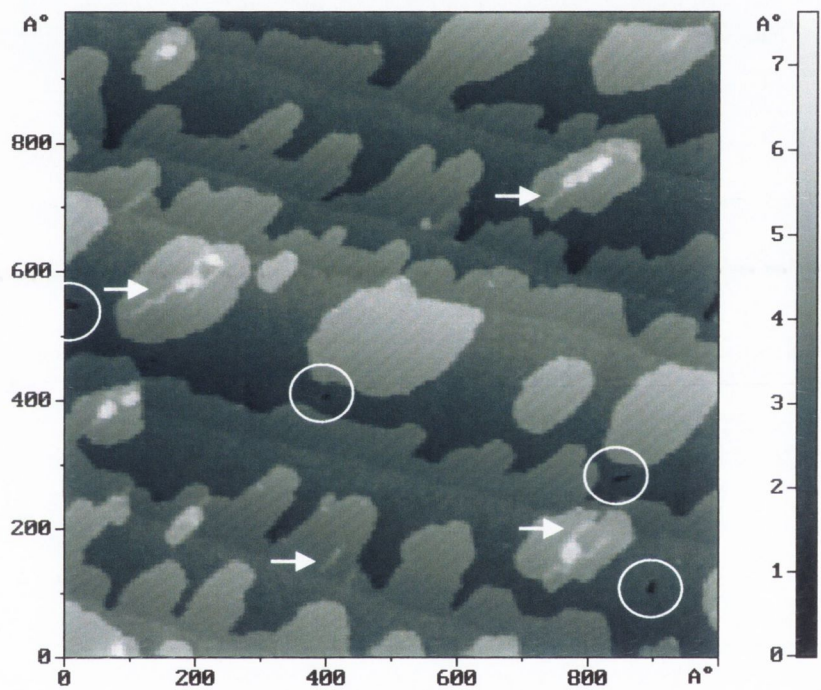


Figure 4.24: ($1000 \times 1000 \text{ \AA}^2$) STM image of film B showing dislocations on the second layer islands (arrows) and holes in the first pseudomorphic Fe layer (circled). The large-scale corrugation observed on the second Fe layer is attributed to an aliasing effect in the tunnel current acquisition. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

to strain relief by the edge-atom effect and therefore must accommodate a higher density of dislocations.

The strain field at the dislocation appears to increase the local binding energy for adatoms. Since the equilibrium lattice misfit between Fe(110) and Mo(110) is $m = -8.9\%$, the dislocations are formed by the insertion of extra atoms into the Fe layer. The increase in adatom binding energy may result from the associated local increase in coordination and electron distribution.

The dislocation lines propagate in the general $[00\bar{1}]$ direction, so that the film is initially relaxed along the $[1\bar{1}0]$ direction. A glancing incidence X-ray diffraction study of 0-200 ML films by Clemens *et al.* [168], found a significantly larger strain along the $[001]$ direction compared to the $[1\bar{1}0]$ direction. This was attributed to the fact that the Fe(110) film is stiffer along the latter direction, resulting in a higher energy cost to elastically strain the film along this direction. Therefore, any film relaxation is likely to begin along this direction first. Moreover, an extra row of atoms (parallel to the dislocation line *i.e.* the $[00\bar{1}]$ direction) can be accommodated more readily along the $[1\bar{1}0]$ direction as this has a lower packing density than the $[00\bar{1}]$ direction.

The dislocations have a typical corrugation of 0.5-0.9 Å, which is similar to the value found by Bethge *et al.* [174] for dislocation lines on Fe films grown at elevated temperatures. The dislocations generally appear to terminate at indentations in the growing step-edge and voids in the second Fe layer *i.e.* wherever the second Fe layer has not coalesced laterally along the $[1\bar{1}0]$ direction in a smooth manner. This suggests that the insertion of extra atoms is facilitated along the line of lateral coalescence between Fe islands (or the step-flow equivalent). In some cases, the dislocation will propagate across a step edge if there is a small overlap between successive Fe bilayers,

which suggest some correlation in the underlying pseudomorphic layer. Figure 4.25 shows the distribution of dislocation lengths for figure 4.23(b). The dislocations fall mostly in the range of 50-150 Å, while no dislocations are observed below a length of ~ 30 Å.

Figure 4.26 shows a high-resolution image of parallel dislocation lines separated by ~ 40 Å along the $[\bar{1}10]$ direction, which is one of the closest separations observed. The interatomic spacing along the $[\bar{1}10]$ direction between the dislocation lines is approximately 10 % lower than the value obtained on a film area that is free from dislocations⁸. The compensation of misfit strain by insertion of extra atoms may be accomplished in a number of ways, *e.g.* by the formation of a full edge dislocation or by buckling the film layer over the substrate, as shown in figure 4.27. In this case, the width of the distortion along the $[\bar{1}10]$ direction is 10-15 Å, which is roughly 2-3 times the periodicity along this direction. This indicates that extra atoms are inserted to form a full edge-type dislocation, causing a very localised lattice distortion.

Like the first pseudomorphic layer, there is a tendency for Fe layers on higher terraces not to overlap onto Fe growing from the following step-down edge. In the first layer, this is attributable to the higher free energy of adhesion onto the Mo substrate as well as the increase in strain energy associated with iron covering iron. For Fe layers growing on top of the completely closed first Fe layer, the latter term limits the overlap. Where a sizeable overlap does occur, the increase in strain energy is sufficient to necessitate the formation of a 2D dislocation network involving lattice distortions in both the $[00\bar{1}]$ and $[1\bar{1}0]$ directions. This effect is observed for both films B and D - examples are

⁸The same tip was used in both measurements, so that the error in x-y values due to variations in tip length [83] was assumed to be approximately the same

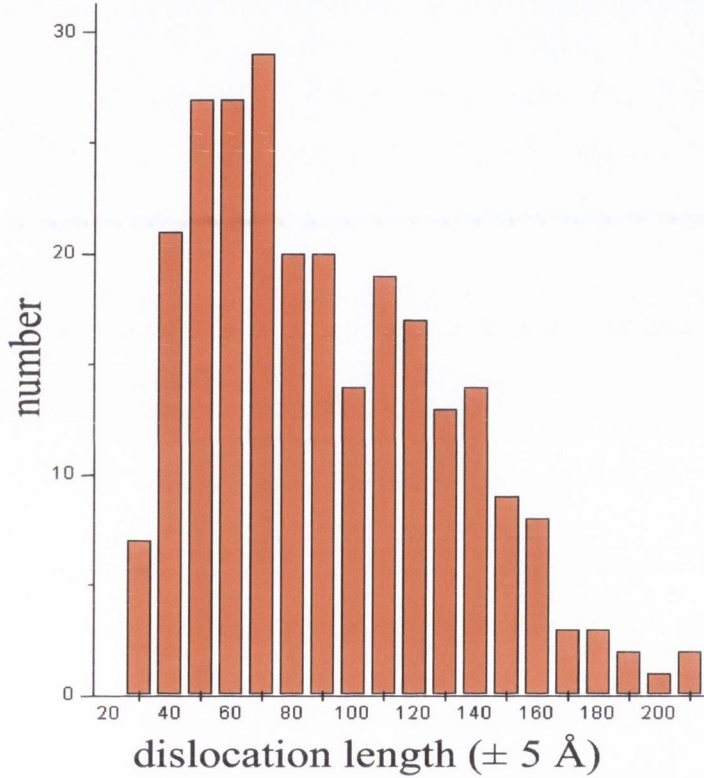


Figure 4.25: Histogram showing the distribution of dislocation lengths for figure 4.23(b).

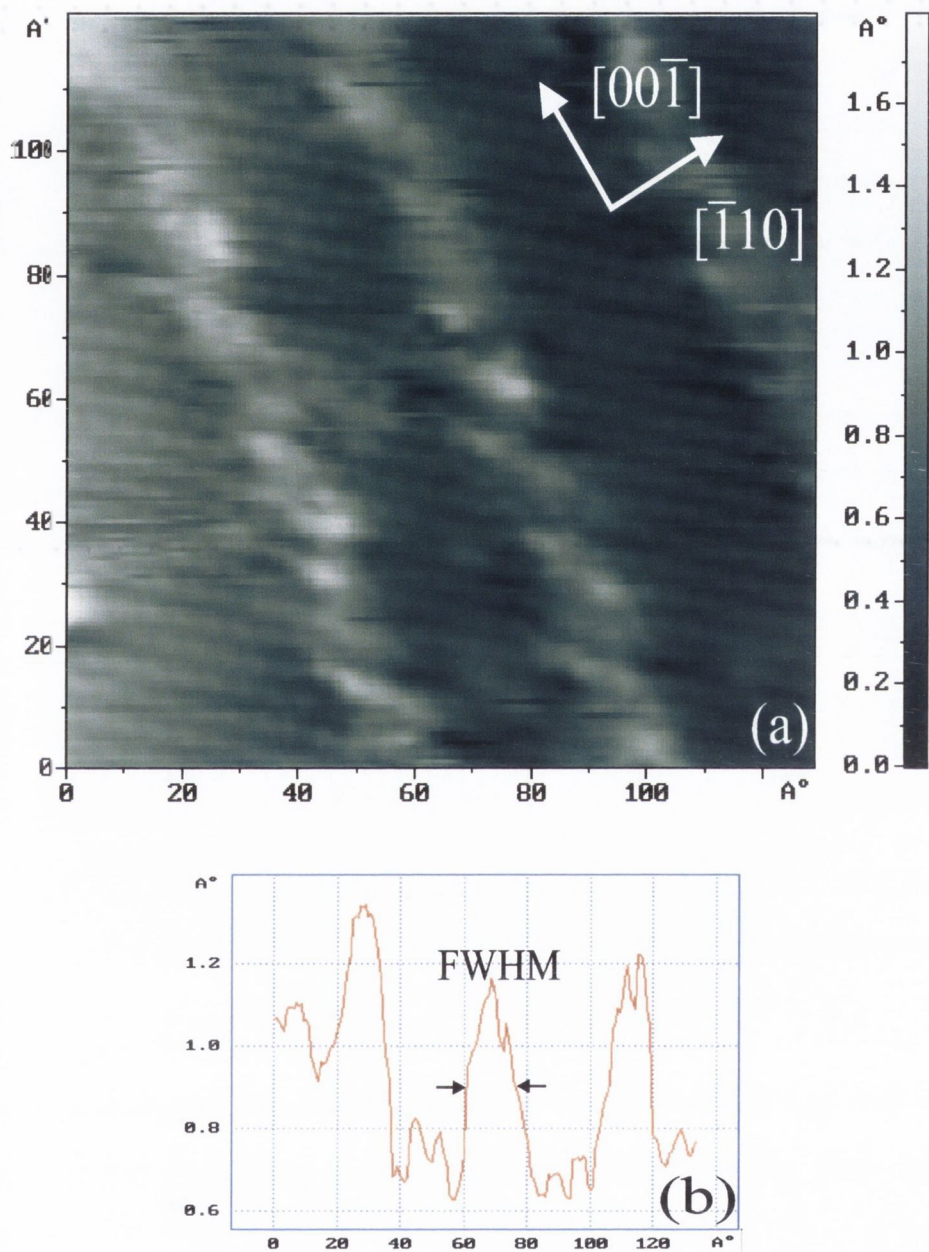


Figure 4.26: (a) ($1000 \times 1000 \text{ \AA}^2$) STM taken on film D, of parallel dislocations. The atomic corrugation is due to a $p(2 \times 2)$ surface mesh (cf. figures 4.30 and 4.29). W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$. (b) Line-profile along the $[\bar{1}10]$ direction showing the corrugation amplitude $0.4\text{--}0.6 \text{ \AA}$, full-width half-maximum (FWHM) $10\text{--}15 \text{ \AA}$ and separation $40\text{--}50 \text{ \AA}$ of the dislocations.

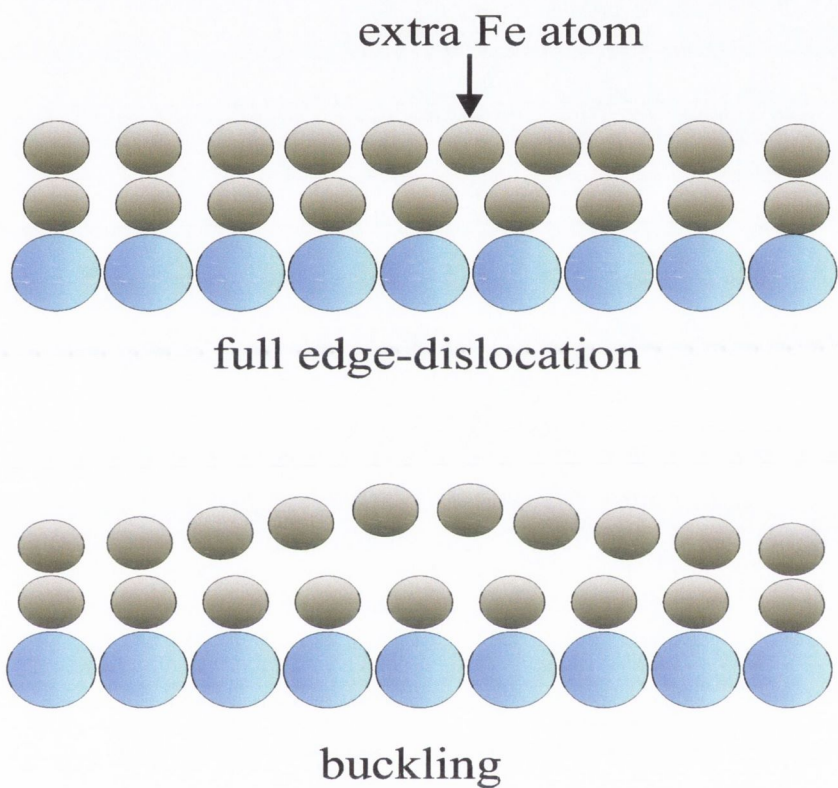


Figure 4.27: Two possibilities for relieving the Fe/Mo(110) misfit by inserting an extra Fe atom. The first pseudomorphic Fe layer is included. In this case, ten Fe atoms are fitted to every nine Mo atoms, after the proposal by Malzbender *et al.* [94] that this fully compensates for the -8.9 % lattice misfit. In fact this model yields a total misfit of 1.18 % (compressive strain), while a fit of eleven Fe atoms to every ten Mo atoms yields a misfit of only 0.18 %.

highlighted in figure 4.28. In some cases, 1D dislocations thread across the step-edge and propagate into the 2D distortion pattern. This network persists at higher coverages where the growth changes from the layer-by-layer to layer-plus-island mode. It will be discussed in more detail in the next section.

The large-scale corrugation (amplitude = $0.2 \text{ \AA}$, period = $\sim 20 \text{ \AA}$) observed in figure 4.24 is attributed to an *aliasing* effect rather than a tip resonance. The latter would be expected to appear continuously over the entire image. However, it appears exclusively on top of the second Fe layer. This corresponds to the preferential coverage of the second layer by an ordered $p(2 \times 2)$ carbon or oxygen adlayer, which distinguishes it from the apparently disordered contamination layer covering the first Fe layer (see figures 4.30 and 4.29). It is believed that the tip was so sharp as it scanned across the surface, that the contributions of individual atoms in the $p(2 \times 2)$ could be resolved. However, because the scan area was large, the sample rate (1 sample per $4 \text{ \AA}$) was too low to separate all these individual contributions, resulting in the superperiodic corrugation observed.

This $p(2 \times 2)$ adlayer structure is better resolved in figure 4.29. The periodicity and corrugation amplitudes along the main crystallographic axes are: $a_{[1\bar{1}1]} = 5.6 \pm 0.2 \text{ \AA}$ and $c_{[1\bar{1}1]} = 0.2 \pm 0.1 \text{ \AA}$, $a_{[00\bar{1}]} = 5.7 \pm 0.2 \text{ \AA}$ and $c_{[00\bar{1}]} = 0.4 \pm 0.1 \text{ \AA}$ and $a_{[1\bar{1}0]} = 9.4 \pm 0.2 \text{ \AA}$ and $c_{[1\bar{1}0]} = 0.3 \pm 0.1 \text{ \AA}$, for the $[1\bar{1}1]$, $[00\bar{1}]$ and $[1\bar{1}0]$ directions respectively. As one would expect, the corrugation amplitude is larger for the less densely packed crystallographic directions. The measured values for the lattice parameters along the $[00\bar{1}]$ and $[1\bar{1}0]$ directions give a surface net cell area that is $\sim 4 \%$ lower than the expected value. This discrepancy may be related to the 10 % error in the x-y calibration of the tube scanner, due to variations in tip length, as discussed by Quinn [83].

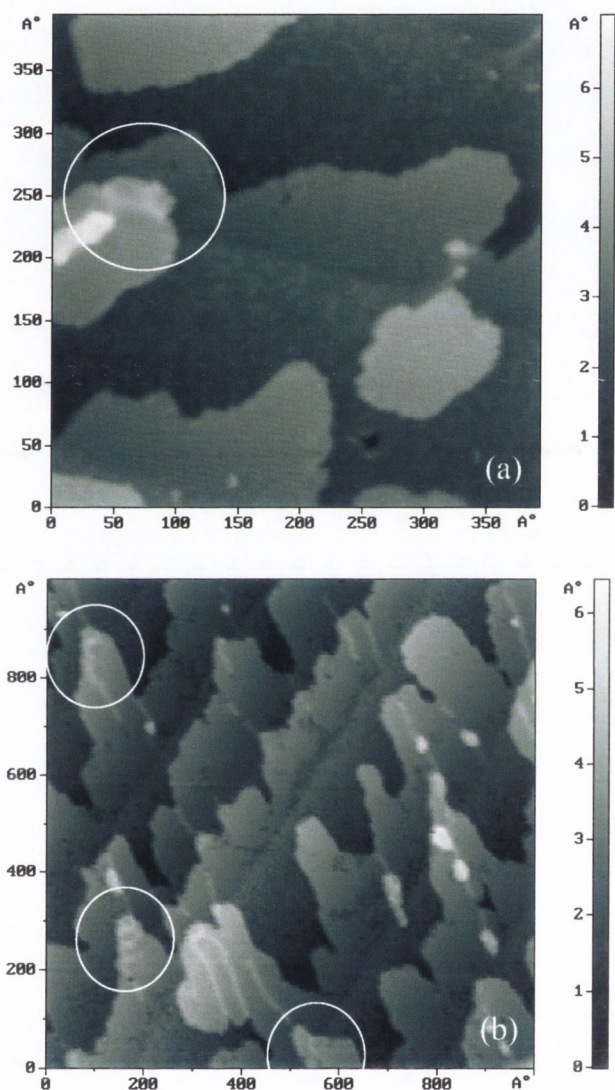


Figure 4.28: STM images of film B and D showing that where an Fe island crosses a substrate step to produce a local thickness of three layers, there is a transition from 1D dislocations to a 2D dislocation network (circled). W tip. $V_{bias} = 30\text{-}40$ mV. $I_{tunnel} = 0.1$ nA.

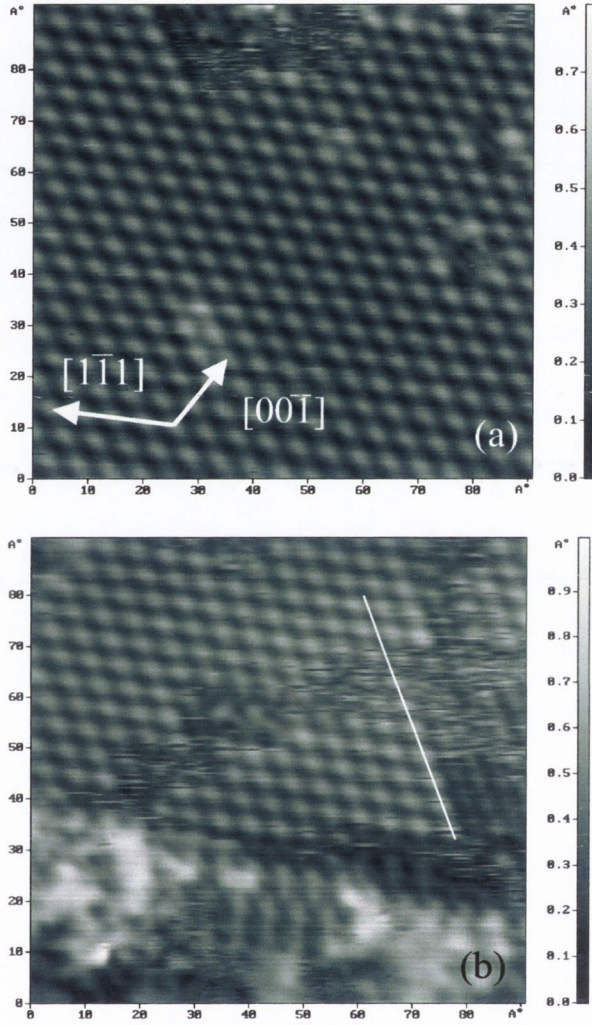


Figure 4.29: ($90 \times 90 \text{ Å}^2$) atomically resolved STM images, taken on film B, of the $p(2 \times 2)$ adlayer formed on the second Fe layer. An antiphase domain boundary is evident in (b), where the rows of atoms along the $[1\bar{1}\bar{1}]$ direction are shifted by an atomic spacing or half a superlattice spacing (line). The transition between the first and second Fe layers is also visible in (b). W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

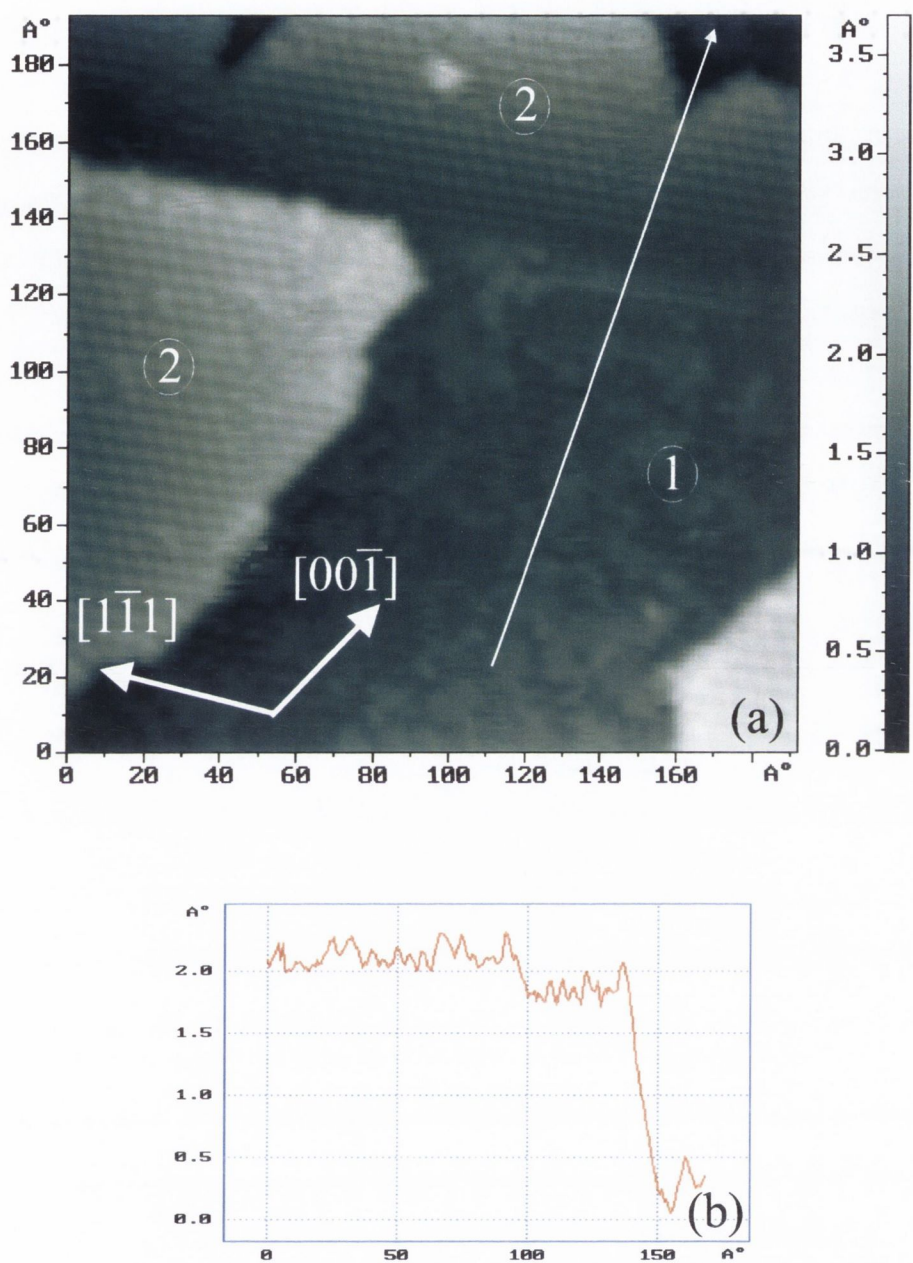


Figure 4.30: (a)(1000 × 1000 Å²) STM image of film B showing the transition between the first and second layers (marked) at the fractional step caused by the underlying Mo-Fe boundary. The contamination on the first Fe layer is relatively disordered compared to the $p(2 \times 2)$ adlayer on the second layer. W tip. $V_{bias} = 30$ mV. $I_{tunnel} = 0.1$ nA. (b) A line-profile along the direction marked in (a) for the locally plane-fitted image, shows the 0.2-0.3 Å high fractional step between the first and second layers at the original step-edge.

Figure 4.30 exhibits the difference in contamination on the first and second Fe layers. It is evident that the adsorption characteristics of the first and second layers differ significantly. It appears that there is selective adsorption of a single atomic species on the Fe bilayer, while the Fe monolayer is subject to co-adsorption of a variety of species. The latter conclusion is drawn from the fact that there appears to be some underlying order on the first Fe layer, which is disrupted by patches where there is no visible order. These disordered regions appear higher than the ordered regions. This underlying order may account for the $p(2 \times 2)$ LEED patterns observed on the submonolayer and monolayer coverage films.

The novel chemical activity of bimetallic systems has been a field of active research interest [4, 180–182]. The binding energy of simple gas probe molecules on pseudomorphic films can be significantly increased or decreased over the values obtained for the corresponding bulk metal surfaces. This property has been attributed to charge transfer between the film and substrate [183], modification of the film electronic structure through d-orbital hybridisation with the substrate [184, 185], as well as the effects of strain [4, 9, 186]. Strain arguments prove more favourable, as they can account for the novel adsorption properties of films several layers thick, while the charge transfer and hybridisation models are restricted to the locality of the film-substrate interface. The strain-related phenomena discussed in references [186] and [9], occur at multilayer thicknesses above a few *ML*. Because, in this case, the observed effect occurs within the first two pseudomorphic Fe layers, it would be ambitious to completely disregard charge transfer and/or hybridisation effects.

It is tentatively suggested, that the single atomic species forming the $p(2 \times 2)$ structure on the Fe bilayer, can be identified as oxygen. It has been

observed that oxygen can act as a surfactant for the homoepitaxial growth of Fe(001) [61], where it floats on top of the growing Fe. Additionally, the results of the AES contamination study of the clean Mo surface (*cf.* section 3.3.3) indicate that oxygen adsorption may be more site-selective than carbon. The oxygen concentration measured on the surface after each STM session lies within the value for which the $p(2 \times 2)$ -O structure was observed on the clean Mo surface (section 4.1.2).

The 0.2-0.3 Å high fractional step located at the position of a substrate step is also highlighted in figure 4.30. This is ascribed to the difference in the Fe and Mo interlayer spacings in the underlying layer (*cf.* section 4.2.2), though it may be attributable to a difference in the thickness of the contamination layer. There is no evidence in any of the STM images of a $p(3 \times 2)$ structure such as that indicated by the LEED analysis of these films.

4.2.5 Stranski-Krastanov growth regime

While the first and second Fe layers grow in a layer-by-layer (LBL) fashion, with a pseudomorphic first layer and partial relaxation of the second, subsequent layers are characterised by increasing roughness corresponding to a Stranski-Krastanov growth mode. This transition is driven by the increasing misfit strain energy. The results of STM analysis of higher coverage films grown near 300 K are summarised in figures 4.31 and 4.32. The films shown in these figures correspond to deposited thicknesses of 3 Å, 5 Å and 8 Å respectively. A trend towards increasingly anisotropic growth with higher coverage is evident in figure 4.31, with elongation of Fe islands along the $[00\bar{1}]$ direction most evident in the thickest film. Moreover, the average lateral width of islands along the $[1\bar{1}0]$ direction appears to decrease between images (b) and (c) of figure 4.32. It is likely that anisotropic growth in the

early layers of the film acts as a template for the growth of subsequent layers.

At the lowest coverage, the onset of the transition between LBL growth and the Stranski-Krastanov mode is evident. The second Fe layer is almost completely closed, while the third layer covers approximately 25 % of the film surface area. At about $3.6 \times 10^{16} \text{ m}^{-2}$, the nucleation density of this layer is much higher than that observed for depositions at lower coverages. This can be attributed to the high deposition rate $D = 1.01 \text{ ML.min}^{-1}$ used during the growth of this film. Previous studies of the Fe/Mo(110) system have observed that an increase in the deposition rate can force LBL growth to persist to higher coverages at a given deposition temperature [79,94]. This arises because a high deposition rate causes adatoms to nucleate rapidly after deposition, producing a high island density. Because the average area of these islands is small adatoms arriving on top can quickly reach the island edges and descend. The result is increased interlayer mass transport, which enhances LBL growth. In general, coalescence of the layer should occur at a lower average island area for a higher deposition rate.

The 2D dislocation network is visible on some of the larger 3 *ML* thick Fe islands. This network becomes prevalent at higher coverages, as illustrated in images (b) and (c) of figure 4.32. It is this network that is responsible for the satellite spots visible around the integral order Mo spots in figure 4.19(d). From this LEED pattern, the periodicity of the network along the $[00\bar{1}]$ and $[1\bar{1}0]$ directions was measured to be 36 Å and 64 Å respectively. The earliest appearance of satellite spots in a LEED pattern was observed for a 4 Å thick film.

This dislocation network is best resolved in images taken of a film F with a deposited thickness of 4 Å, shown in figure 4.33. A number of 1D dislocation lines are evident on the nearly closed second layer, while the 2D network is

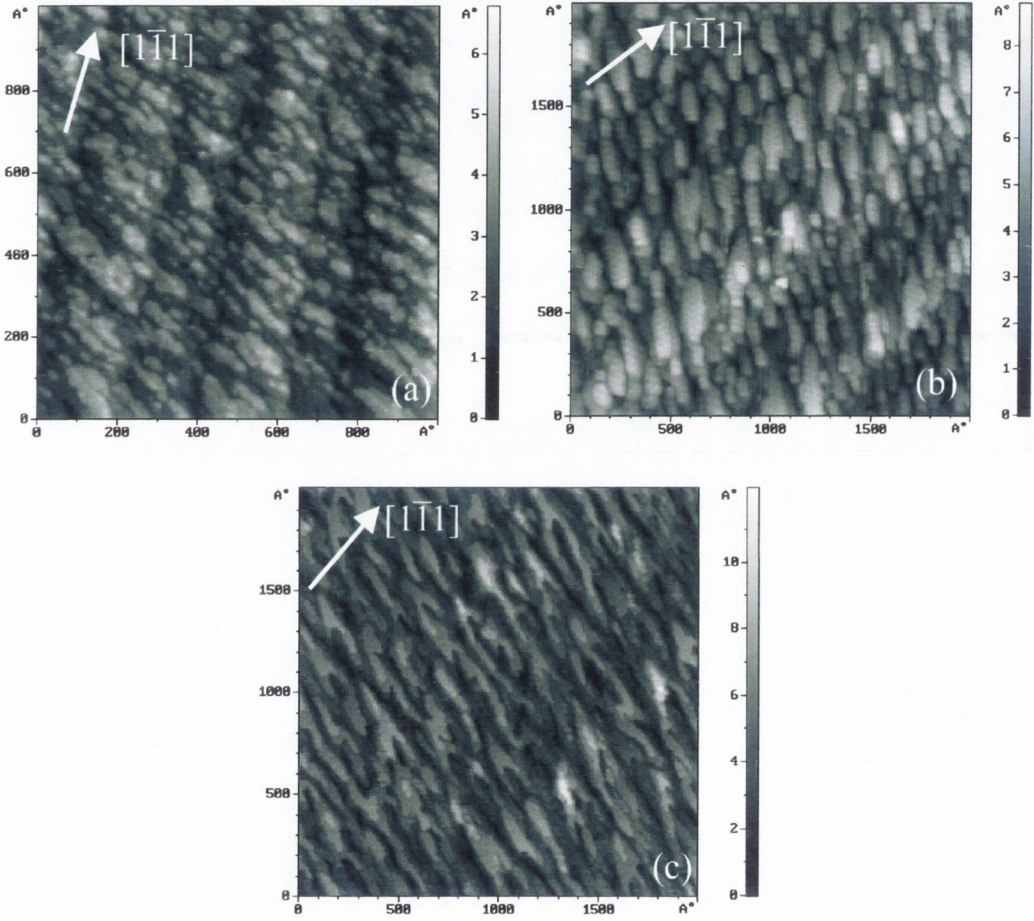


Figure 4.31: (a) ($1000 \times 1000 \text{ \AA}^2$) $\theta = 1.8 \text{ ML}$, $D = 1.01 \text{ ML.min}^{-1}$, $300 \leq T \leq 330 \text{ K}$, (b) ($2000 \times 2000 \text{ \AA}^2$) $\theta = 2.95 \text{ ML}$, $D = 0.81 \text{ ML.min}^{-1}$, $T = 345 \text{ K}$ and (c) ($2000 \times 2000 \text{ \AA}^2$) $\theta = 4.7 \text{ ML}$, $D = 0.32 \text{ ML.min}^{-1}$, $300 \leq T \leq 330 \text{ K}$. MnNi and W tips. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

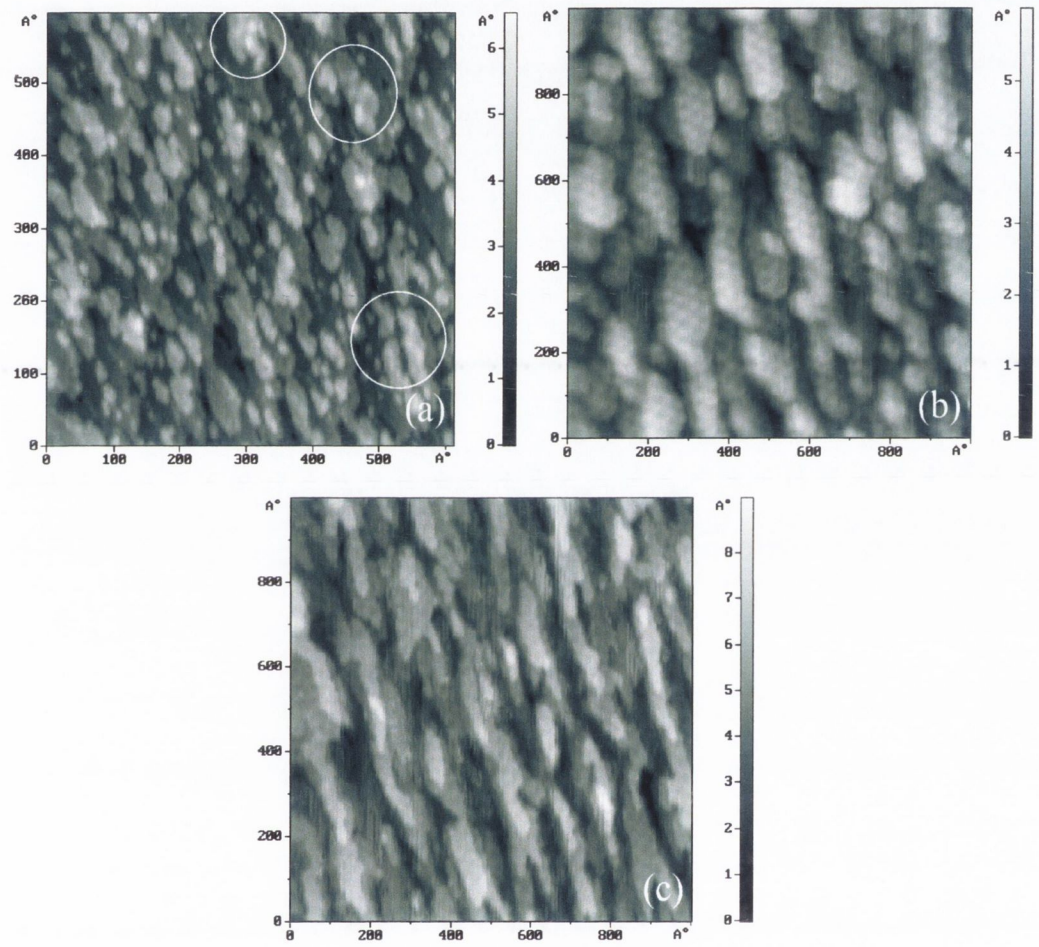


Figure 4.32: Zoom-in of the images shown in figure 4.31, showing the evolution of the 2D dislocation network with film coverage. (a) $(600 \times 600 \text{ \AA}^2)$ $\theta = 1.8 \text{ ML}$, (b) $(1000 \times 1000 \text{ \AA}^2)$ $\theta = 2.95 \text{ ML}$ and (c) $(1000 \times 1000 \text{ \AA}^2)$ $\theta = 4.7 \text{ ML}$. MnNi and W tips. $V_{bias} = 10\text{-}30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

evident on the third and fourth layers. The onset of the dislocation network as an Fe layer crosses a substrate step from a local thickness of 2 *ML* to one of 3 *ML* (like that seen in figure 4.28) is much more evident in this film. This can be used to trace the position of the underlying Mo terraces.

The exposed areas of the second layer of the film are covered with the $p(2 \times 2)$ adlayer structure observed at lower coverages. In agreement with the LEED data, this structure is not apparent on those areas of the film that are covered by the dislocation network. Figure 4.34 shows the adlayer structure and dislocation network appearing on separate layers of the film. The atomic resolution of the $p(2 \times 2)$ structure in this image allows an exact determination of the crystallographic orientation of the 2D network to be made.

Fringing of the edges of the film is evident in these images. These fringes have a periodicity of double the Mo lattice parameter and a corrugation of 0.2-0.26 Å. They may be related directly to the $p(2 \times 2)$ adlayer structure, however the effect was not evident on any other film. As the first STM images of this film were not taken until nearly nine hours after deposition, hydrogen or water adsorption may also be considered as a strong candidate for causing the effect. This possibility was suggested by Osing *et al.* [9] to account for a similar effect observed on 5 Å and 8 Å thick films grown at room temperature. A notable difference in this case is that the effect is observed at the edges of Fe islands where the dislocation network is prevalent. This observation conflicts with the interpretations of that study, which argued that the effect disappears on films that are relieved of misfit strain by the accommodation of dislocation networks.

The structure of the dislocation network is illustrated schematically in figure 4.35. Unlike in images 4.32 (a-c), where the network appears as a

series of bumps on the surface, here its quasi-hexagonal nature is apparent. This is probably due to the sharpness of the STM tip used, but may be caused by some physical difference in the extent of the strain relaxation. The network is formed by a regular array of dislocation lines that zig-zag along the general $[00\bar{1}]$ direction. From figure 4.34, the direction of the zig-zag lies slightly off ($\sim 10^\circ$) the $[1\bar{1}1]$ and $[\bar{1}\bar{1}\bar{1}]$ directions respectively.

These dislocation lines appear to overlap along the $[1\bar{1}0]$ to give regions of enhanced corrugation that are elongated along this direction ($\sim 14 \text{ \AA}$ long). These regions appear as the bumps in the images shown in figure 4.32 and are arranged in a centred-rectangular fashion analogous to the Mo(110) conventional cell. The corrugation amplitude was measured to be between $0.6 \text{ \AA}$ and $0.8 \text{ \AA}$ in both major crystallographic directions. The periodicity of the structure along the $[00\bar{1}]$ direction was measured to be $d_{[00\bar{1}]} = 36 \pm 2 \text{ \AA}$, while that along the $[1\bar{1}0]$ was approximately $d_{[1\bar{1}0]} = 59 \pm 2 \text{ \AA}$, giving a minimum lateral separation between the lines of $45 \pm 4 \text{ \AA}$. These values of $d_{[00\bar{1}]}$ and $d_{[1\bar{1}0]}$ are similar to those determined from the LEED pattern of film H ($8 \text{ \AA}$ thick) and correspond to roughly 11 and 10 Mo atomic spacings respectively.

4.3 Elevated temperature growth

The films listed in table 4.4 were grown using the procedure described in the last section, with the difference that the Mo sample was transferred shortly after cleaning (~ 5 minutes) to the pre-heated resistive heater. The temperature of the sample was allowed to stabilise for 20-30 minutes before deposition began. Typical values of 0.9 A and 3.5 V were used for the heater current and voltage respectively. The sample was allowed to cool for approximately

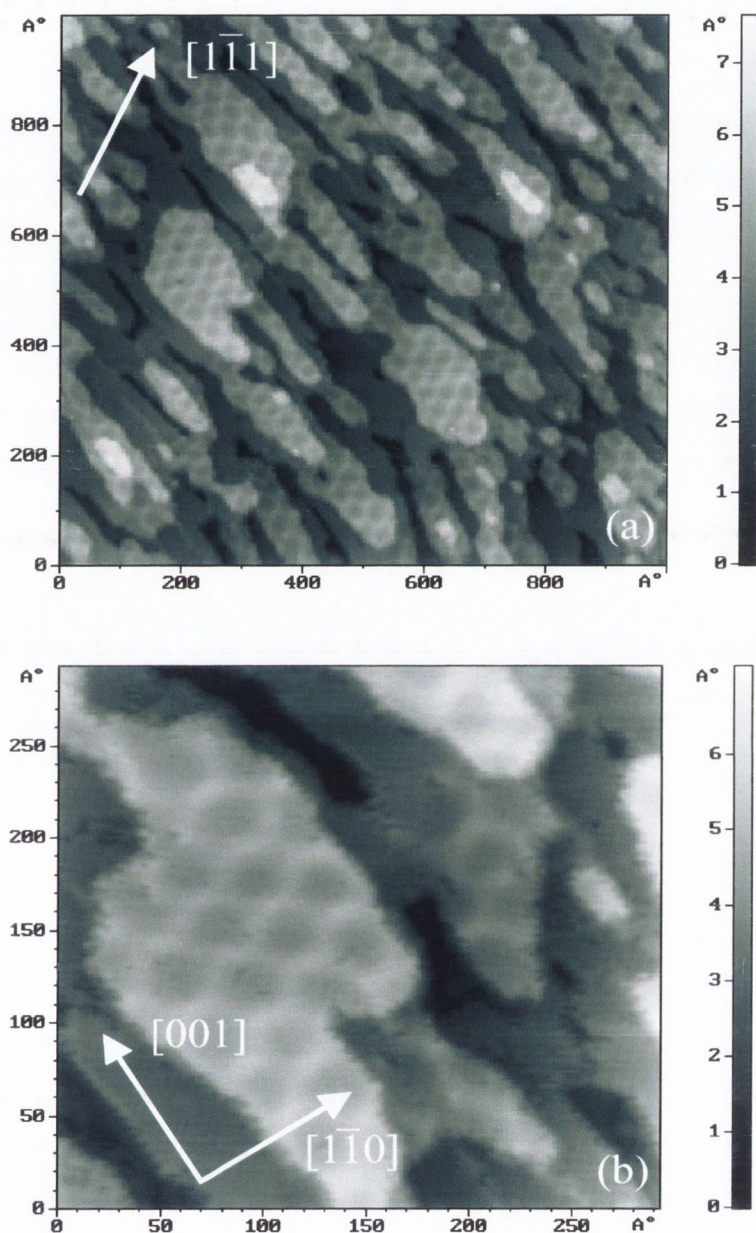


Figure 4.33: (a) ($1000 \times 1000 \text{ \AA}^2$) high resolution image of the 2D dislocation network formed on a $\theta = 2.4 \text{ ML}$ Fe film deposited with $D = 0.71 \text{ ML.min}^{-1}$ at $300 \leq T \leq 330 \text{ K}$. (b) ($300 \times 300 \text{ \AA}^2$) image of the same film showing the onset of the 2D dislocation network at a substrate step. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

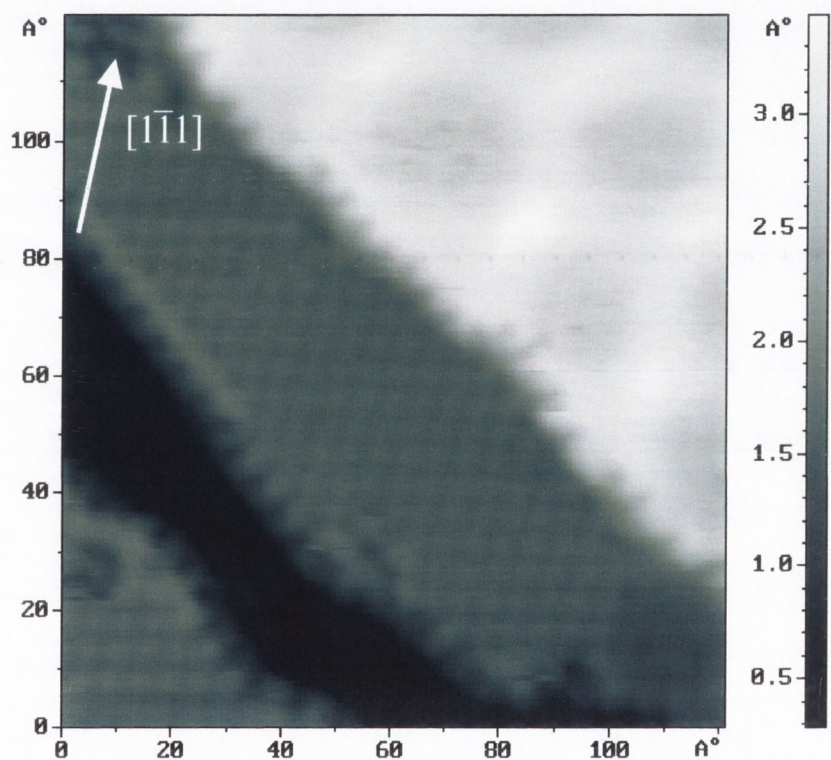


Figure 4.34: $(120 \times 120 \text{ \AA}^2)$ image showing the dislocation network and the adsorbate-induced $p(2 \times 2)$ structure on separate layers of the film. W tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

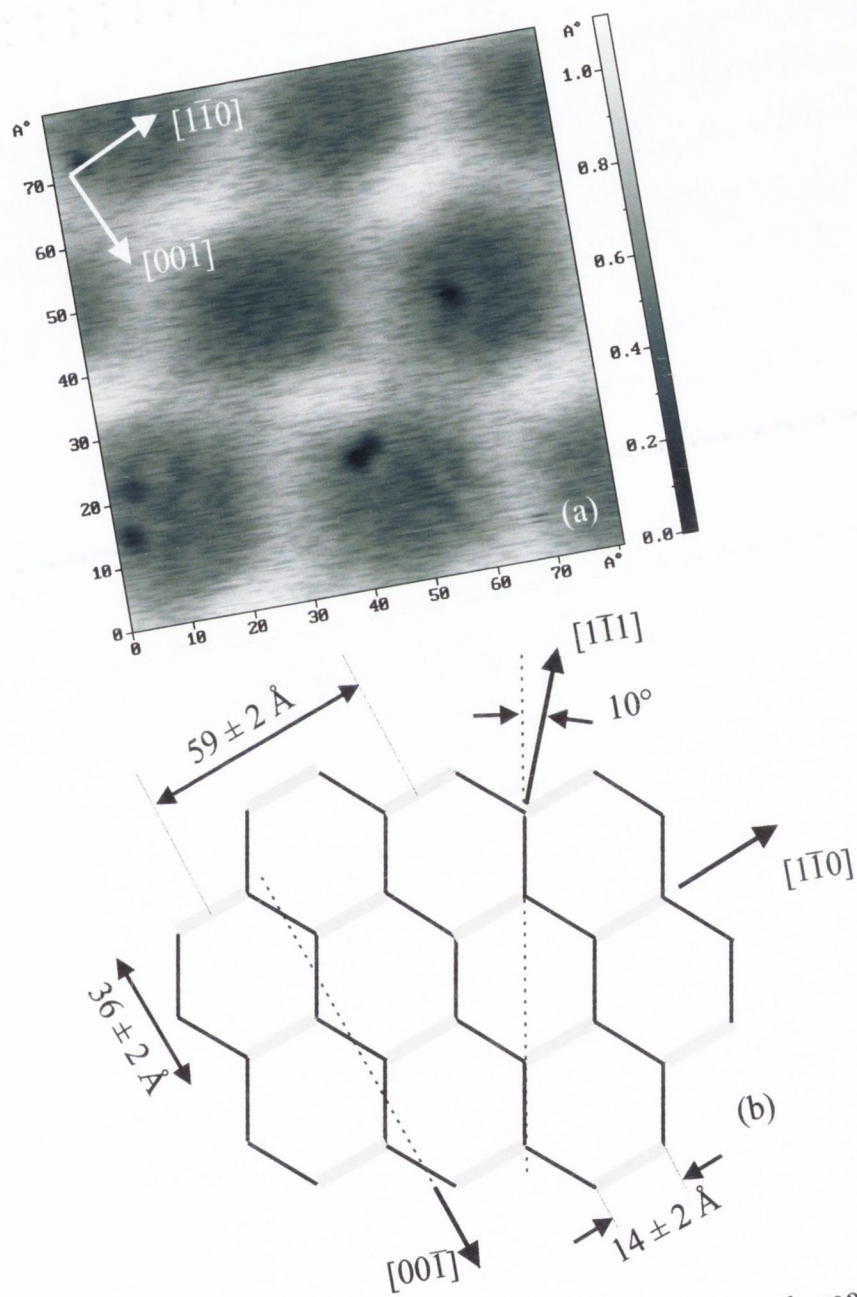


Figure 4.35: (a) $(80 \times 80 \text{ Å}^2)$ STM image and (b) schematic illustration highlighting the structure of the dislocation network.

Film	d_{Fe} Å	$\theta_{dep.}$ ML	t_{anneal} min.	$T_{dep.}$ K	D ML.min. ⁻¹	P mbar	t_{STM} hrs.	t_{AES} hrs.
A1	2	1.18	30	495	0.443	2.3×10^{-10}	7.9	10
B1	2.5	1.475	30	525	0.443	2.0×10^{-10}	1.4	4.8
C1	4	2.36	30	515	0.313	3.3×10^{-10}	2.1	7.8
D1	5	2.95	40	510	0.443	2.0×10^{-10}	1.3	5.3

Table 4.4: Deposition details for each of the Fe films deposited at elevated temperatures. The information listed is identical to that given in table 4.2, with the exception that t_{anneal} is the time allowed for the sample temperature to settle after cleaning. This replaces t_{cool} for the near room temperature films. The deposition temperatures are taken from the thermocouple attached to the Ta insert of the heater. It may be assumed that the actual temperature at the sample surface could be up to 50 K higher than this value as the thermocouple was not attached directly to the sample.

10-20 minutes after the deposition before insertion into the RTSTM so that thermal drift was reduced. The depositions were carried out at substrate temperatures well below the alloying temperature of 800 K [79].

4.3.1 LEED and AES

As indicated earlier, it is likely that the source of the film contamination are the residual bulk impurities present in the Fe source rod. LEED analysis of the low coverage films A1 and B1 gave a sharp $p(2 \times 2)$ pattern. Figure 4.36 shows the LEED pattern obtained on film C1 - with a deposited thickness of 4 Å. The satellite spots due to the dislocation network are much sharper than those obtained for the near-RT films. The satellite spots shift their position from around the 20, 02 *etc.* to the next set of integral order spots (*i.e.* 40,

04 *etc.*) when the primary electron beam energy is increased from 111 eV to 165 eV. Compared to figure 4.19 (c), taken for a film of the same deposited thickness, a higher degree of strain relaxation is observed at lower coverages for films grown at elevated temperatures, in agreement with the fact that strain-relaxation is a thermally activated process. A LEED pattern giving separate integral order spots for both the Mo and Fe bulk lattices was not observed - *cf.* Osing [10] who observed such a pattern for an 8 Å thick Fe film grown on a vicinal Mo(110) surface at 770 K. This indicates that none of the films grown were fully relaxed to the bulk Fe(110) state. The periodicity of the network was measured from LEED patterns of film C1 to be 55 ± 4 Å along the $[1\bar{1}0]$ direction and 36 ± 2 Å along the $[00\bar{1}]$ direction. These periodicities correspond to 12.4 and 11.4 Mo atomic spacings respectively. A (12×12) LEED pattern has been reported by He *et al.* for an Fe film with $\theta = 1.3$ ML grown at 115 K and annealed to 540 K [158].

4.3.2 STM results

As shown in figure 4.37, the initial growth of the second Fe layer is dominated by the step-flow mechanism. This indicates that the step-down edges of the substrate and first pseudomorphic layer are reflective to adatom diffusion. At these higher substrate temperatures the anisotropic growth observed for growth near room temperature is reduced, resulting in much smoother step-edges than those observed for near-RT growth. The second Fe layer appears as monolayer stripes running along the step-down edges of the first pseudomorphic layer - the fractional step between these layers is visible in both images. For film A1, the width of these Fe stripes is 30-70 Å, while for film B1 the width lies between 60-190 Å. In the latter case, dislocation lines are visible on some of the second layer stripes, which run along the $[00\bar{1}]$ direc-

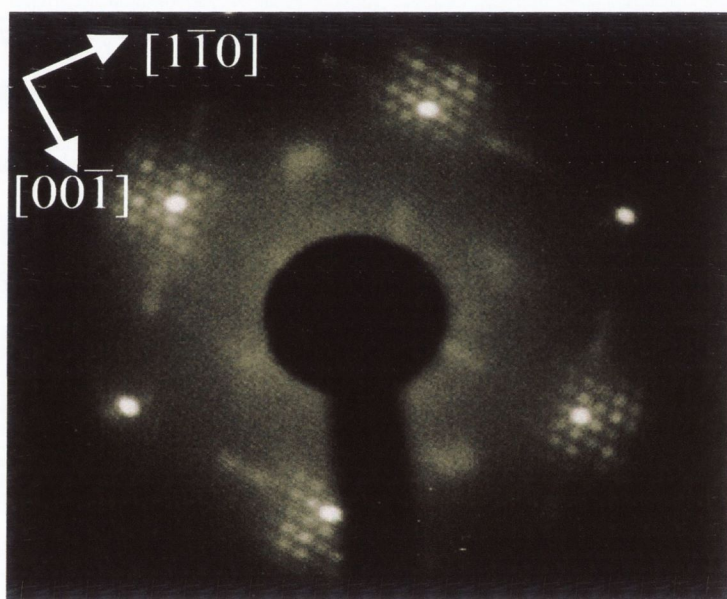


Figure 4.36: A LEED pattern of film C1, 2.4 *ML* Fe grown at 515 *K*. The satellite spots due to a 2D dislocation network are clearly visible. A streaked $p(2 \times 2)$ pattern is faintly visible. $E_{\text{beam}} = 111 \text{ eV}$.

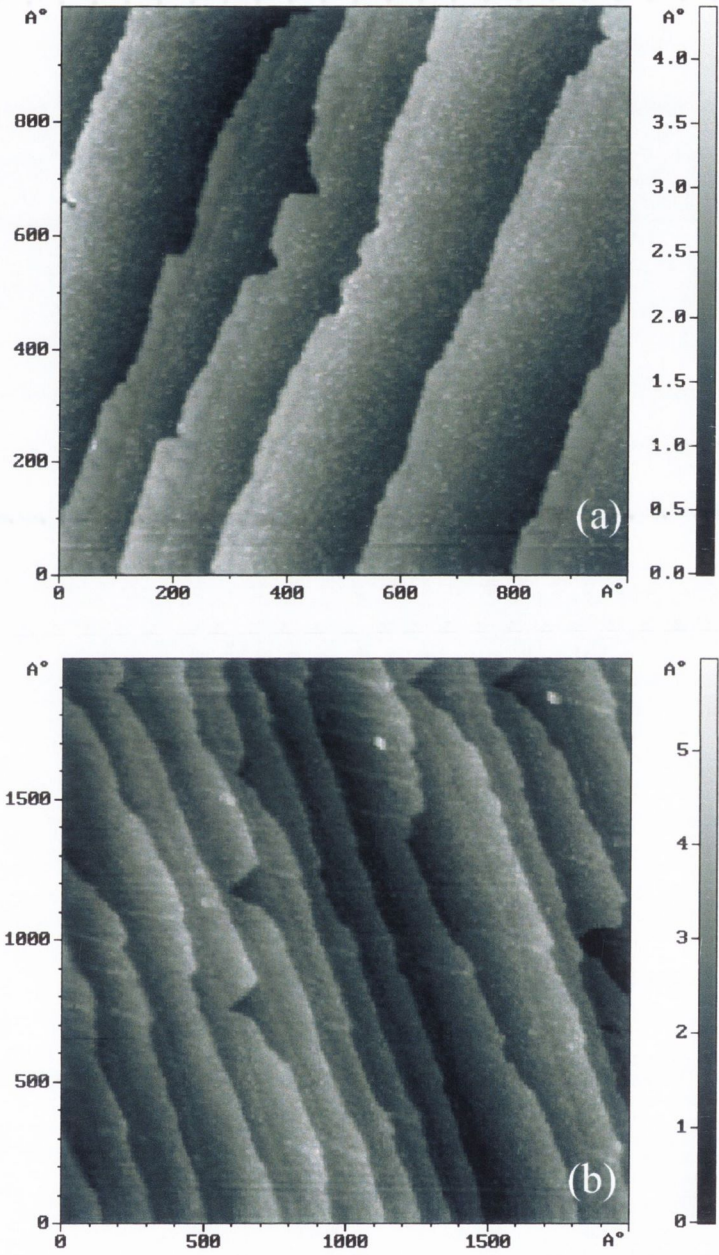


Figure 4.37: (a) ($1000 \times 1000 \text{ \AA}^2$) image of film A1 - 1.2 ML deposited at 495 K, (b) ($2000 \times 2000 \text{ \AA}^2$) image of film B1 - 1.48 ML deposited at 525 K. The actual coverages measured from the STM images are 1.21 and 1.57 ML respectively. W and PtIr tips. $V_{bias} = 30\text{-}60 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

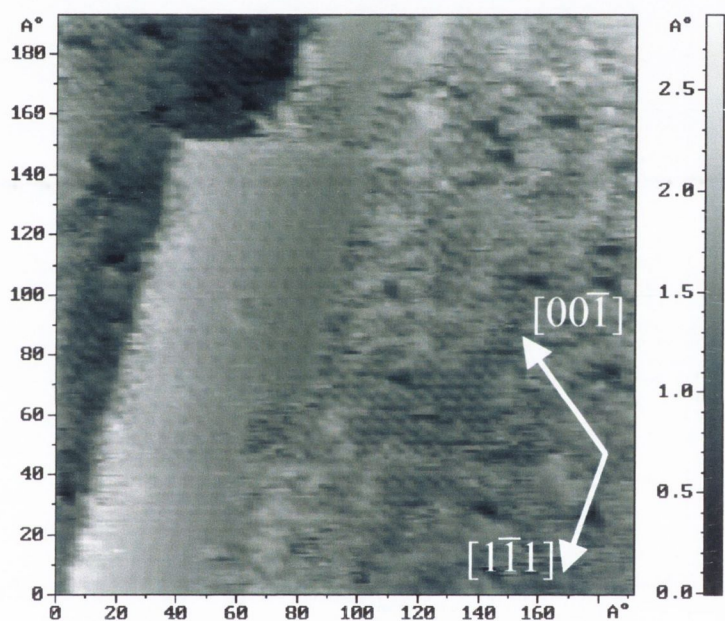


Figure 4.38: $(200 \times 200 \text{ \AA}^2)$ STM image of film A1, showing the $p(2 \times 2)$ structure formed on both the first and second Fe layers. W tip. $V_{bias} = 30$ mV. $I_{tunnel} = 0.1$ nA.

tion. These dislocations only appear on stripes which have a lateral width above $\sim 100 \text{ \AA}$. It is evident that despite the high adatom mobility, these dislocations provide very attractive sites for island nucleation as a couple of Fe islands can be seen to have nucleated at dislocations in figure 4.37(b).

For films grown near room temperature, dislocations with lengths well below $100 \text{ \AA}$ have been observed (*cf.* figure 4.25). As indicated earlier, dislocation formation appears to be facilitated near the voids and indents in the second Fe layer caused by coalescence. As Fe stripes grown at lower temperatures contain more of these defects, dislocation lines with a wider length distribution may be allowed.

The contamination behaviour of the first and second Fe layers grown at elevated temperatures does not appear to change much from that observed on films grown near 300 K . Figure 4.38 shows a zoom-in of one Fe stripe on film A1. A $p(2 \times 2)$ structure is clearly resolved on both the first and second Fe layers, though the structure on the first layer is much more disordered. It is assumed that the origin of this structure is the same as for the near-RT examples.

There is a significant transformation in the morphology of the film as the deposited thickness is increased from 1.5 to 2.4 ML . Figure 4.39 displays large-area STM images of films C1 and D1, grown at $510\text{--}515 \text{ K}$ with deposited coverages of 2.4 and 2.95 ML respectively. The Fe has agglomerated into large, well separated islands, which propagate across as many as six terraces. There is a tendency for many of these islands to grow along the general $[00\bar{1}]$ direction - some of the elongated islands in figure 4.39 (a) have lateral aspect ratios from $3:1$ to $6:1$. The islands on film C1 appear to approach the equilibrium shape to a larger extent than islands on film D1. This may be an effect of the slightly higher deposition rate used for the

latter, since the deposition temperature and chamber pressure were similar. While spreading across a few terraces, these islands minimise their surface free energy by maintaining a flat (110) surface that is unbroken by steps. This results in a wedge-shaped structure highlighted in figures 4.40 and 4.41. The local island thickness increases from an initial thickness of 2-3 *ML*, by a further monolayer for each substrate step-edge crossed. This phenomenon has been observed previously for both the Fe/W(110) and Fe/Mo(110) systems [9, 94, 174, 187].

Details of the island density, average area, total surface area and volume occupied by these islands for films C1 and D1 are listed in table 4.5. These estimates were taken from quantitative analysis of STM images for each film (using IMP software *cf.* section 3.3.1) - for film D1 the values are overestimated as a result of the multiple-tip effect present in the STM images. The analysis is performed by globally plane-fitting an STM image so that the region between the islands appears flat. The islands then appear as shown in figure 4.42 (a). A histogram of pixel count *vs.* height is then plotted for this image, figure 4.42 (b). The area under the graph which corresponds to the 3D islands can be used to calculate the total area and volume that they occupy.

From table 4.5, each film appears to be missing an amount of Fe equivalent to 0.25 and 0.5 pseudomorphic monolayers respectively. In the case of film D1, it can be assumed that the volume of Fe present is significantly overestimated due to multiple tip effects. Similar to observations by Osing and Shvets [187], it is concluded that this missing material is spread out between the Fe islands as a partial pseudomorphic monolayer. The growth is therefore considered to be of a Stranski-Krastanov (SK) nature. It appears that upon deposition of subsequent Fe layers, the second layer which initially

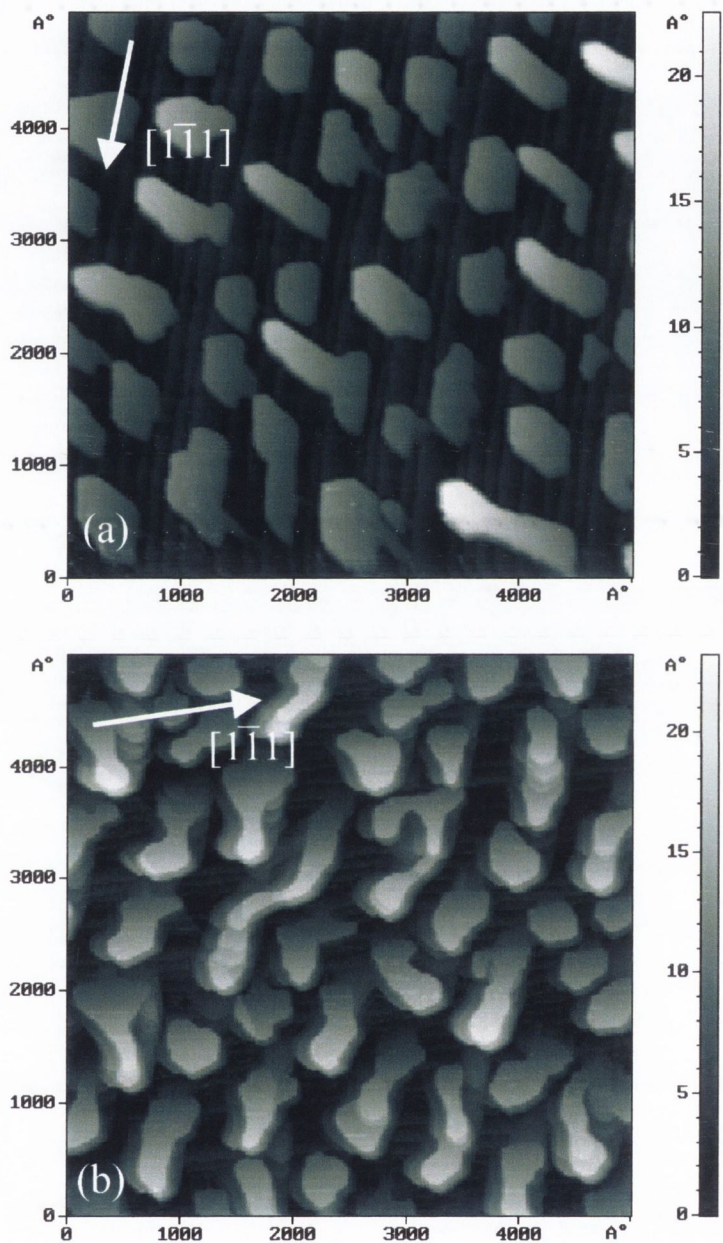


Figure 4.39: ($5000 \times 5000 \text{ \AA}^2$) STM images of films (a) C1 and (b) D1. A multiple tip effect is evident in image (b), which was imaged with a W tip, while image (a) was taken using a PtIr tip. $V_{bias} = 30\text{-}50 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

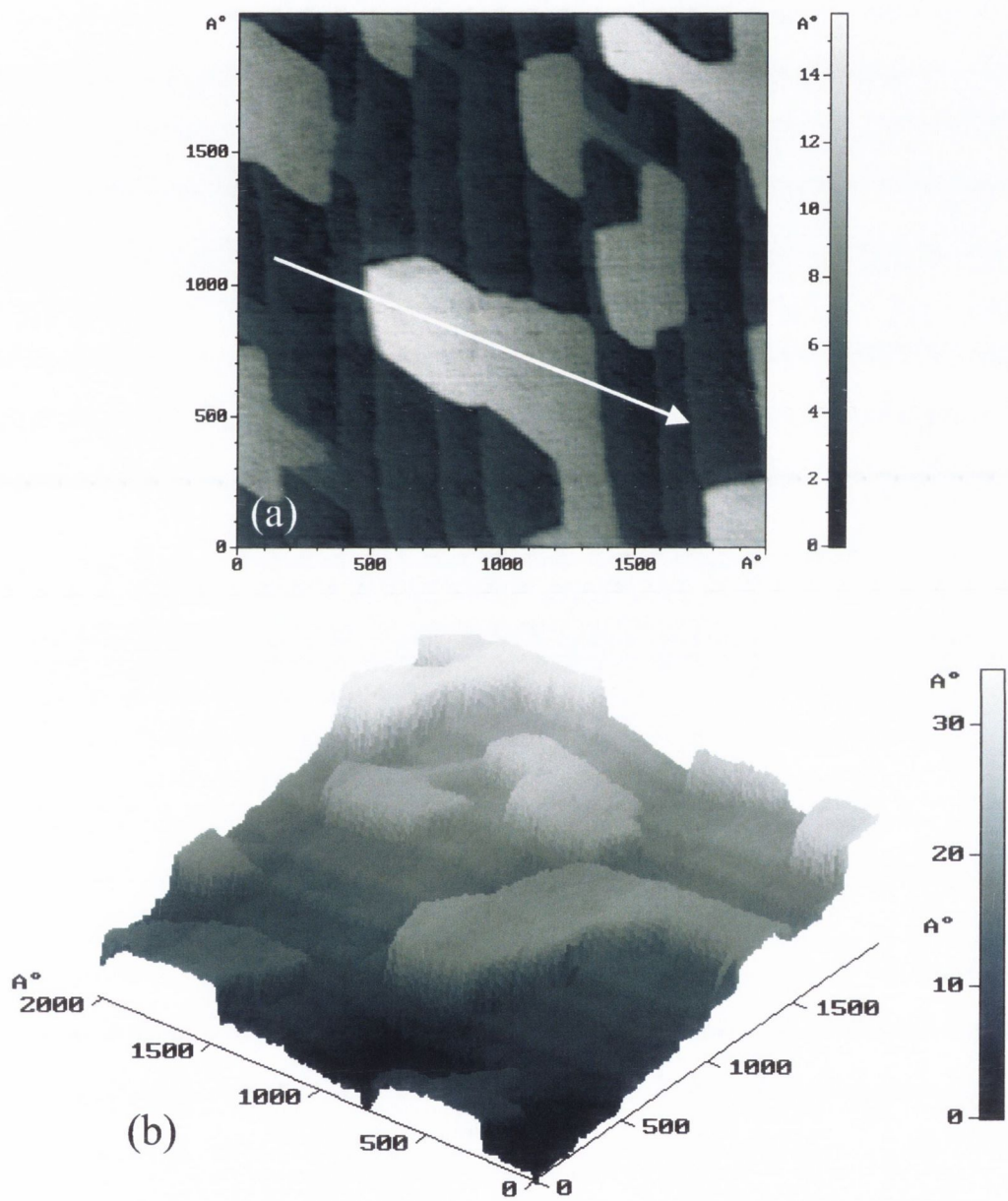


Figure 4.40: (a) ($5000 \times 5000 \text{ \AA}^2$) Globally plane-fitted STM image of an area covered by Fe islands, (b) 3D view of the same image after local plane fitting to the central island.

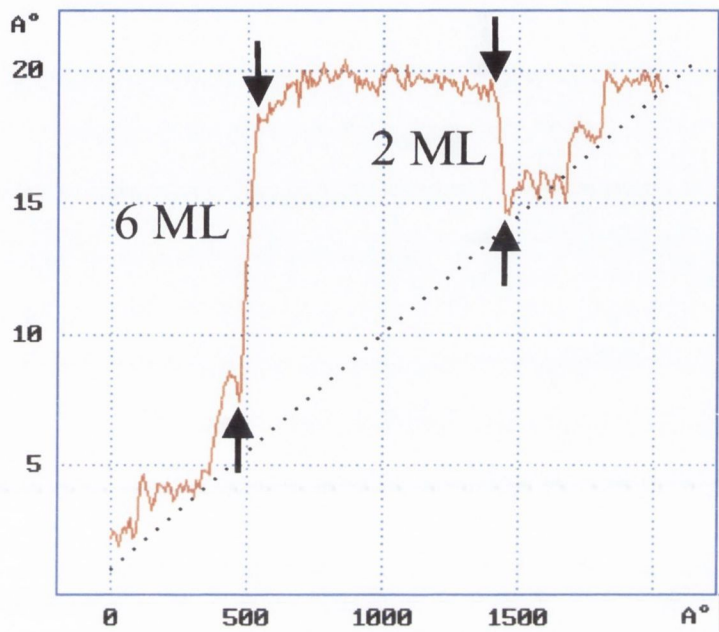


Figure 4.41: Line-profile along the direction marked in figure 4.40 (a) after local plane fitting. The wedge-shape of the Fe island is apparent against the staircase arrangement of the substrate steps.

Film	island density	average island diameter	total area covered	Fe coverage	missing volume
	m^{-2}	$\text{\AA}$	%	ML	%
C1	1.89×10^{14}	490 ± 40	35	2.1 ± 0.1	11
D1	2.06×10^{14}	500 ± 100	50	2.5 ± 0.3	15

Table 4.5: Results of histogram analysis of films C1 and D1. The average island diameter corresponds to that of a circular islands of equivalent area. The Fe coverage is given as the equivalent pseudomorphic monolayer coverage.

grows almost pseudomorphically by the step-flow mechanism, is incorporated into the 3D islands. The first layer appears to be stable against this form of ripening, which is likely due to its high free energy of adhesion to the Mo surface.

Malzbender *et al.* [94] have observed SK growth for films deposited at $D = 0.2 \text{ ML.min}^{-1}$ on 100-1000 Å wide Mo(110) terraces at 600 K. In an AES, LEED and thermal desorption (TPD) study of the Fe/Mo(110) system by Tikhov and Bauer [79], it was observed that the Mo (Fe) Auger signal increased (decreased) for all coverages except the first Fe layer, upon annealing of films grown at 300 K. This was attributed to Fe agglomeration which did not occur in the first Fe layer. It was also noted that alloying of the system occurred at about 800 K, while Fe desorption occurred between 1120 and 1170 K depending on the coverage - the first monolayer being most stable. From these data the SK mode was predicted for the system below the alloying temperature. Osing [10] observed that by reducing the deposition temperature from 750 K to 640 K and increasing the deposition rate from 0.3 ML.min^{-1} to 0.5 ML.min^{-1} for films of roughly similar coverage (4-5 Å thickness), there appeared to be a transition from Stranski-Krastanov growth to Volmer-Weber (pure island) growth. This work was performed on a vicinal surface with an average terrace width of 25 Å and step-edges running normal to the $[1\bar{1}\bar{1}]$ direction. The higher step density and different miscut orientation make a direct comparison to the results here ambiguous. However, this result suggests that the formation of the first pseudomorphic layer can be very sensitive to the adatom mobility.

A 2D dislocation network is evident on these islands (it is not well resolved on film C1), as shown in figure 4.43. The corrugation amplitude was 0.4-0.6 Å along both the $[00\bar{1}]$ and $[1\bar{1}0]$ directions, while the periodicities along

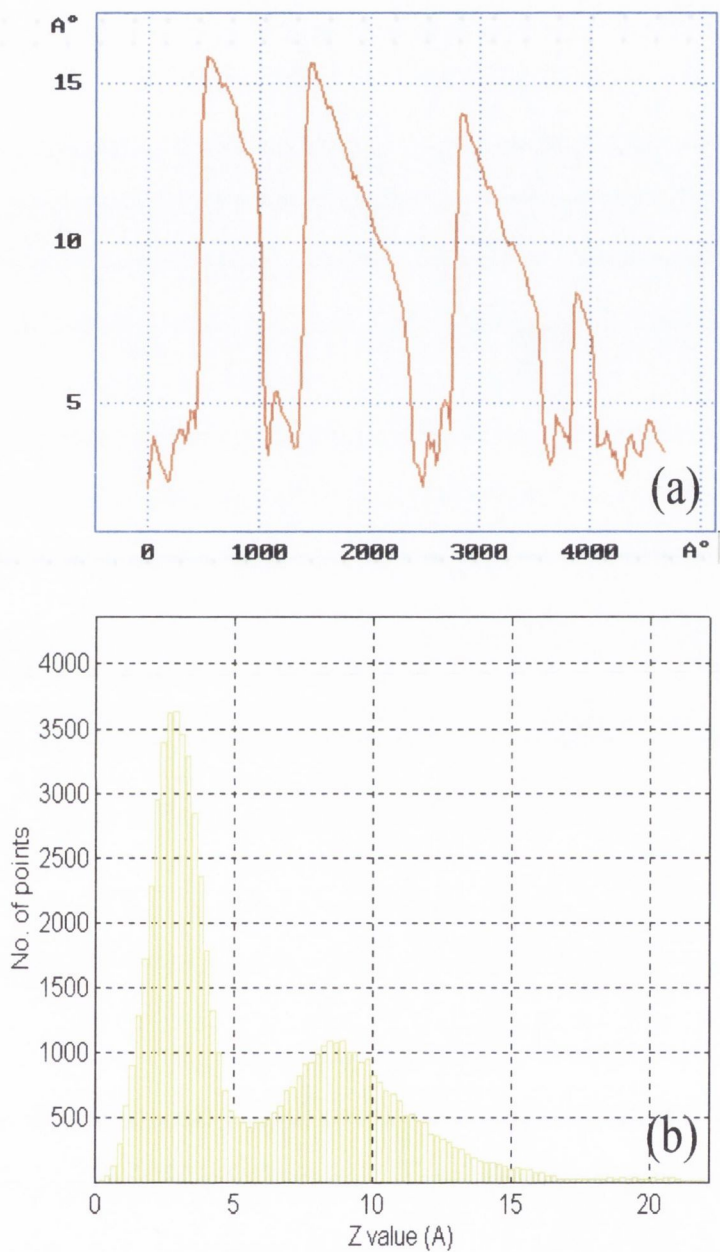


Figure 4.42: (a) Line-profile taken across a series of wedge-shaped Fe islands on film C1. The substrate terraces have appear as a saw-tooth corrugation underlying the islands. (b) A histogram of this surface - the first peak is due to the substrate, while the broader peak at higher z values is due to the Fe islands.

each direction were $36 \pm 1 \text{ \AA}$ and $51 \pm 1 \text{ \AA}$ respectively, which are in good agreement with the values obtained from the LEED data. Compared to the network observed for films grown near room temperature, the periodicity along the $[00\bar{1}]$ direction is identical, while the periodicity along the $[1\bar{1}0]$ direction is 14 % lower for films grown at 510 K. This implies that the strain relaxation by this mechanism is increased in films grown at elevated temperatures, but only along the $[1\bar{1}0]$ direction.

A similar dislocation network was also observed by Osing *et al.* [9] on a 6 $\text{\AA}$ thick film grown at 370 K, which exhibited wedge-shaped islands similar to those observed in the 500-750 K range. From an atomically resolved image of this network, the nearest-neighbour separation between regions of enhanced corrugation was determined to be $30 \pm 1 \text{ \AA}$, with a value of 2.46 $\text{\AA}$ for the Fe atomic separation along the same direction. This dislocation was therefore described as a (12×12) dislocation network. Since the separation between nearest-neighbour regions of enhanced corrugation (the bumps on the islands) was measured to be $30 \pm 2 \text{ \AA}$, it is likely that the network observed in the current study is identical to the one observed by Osing *et al.*

In their STM study of the Fe/Mo(110), Malzbender *et al.* [94] observed the onset of a dislocation network at a coverage 1.3 ML for films deposited at 600 K and $D = 0.2 \text{ ML.min}^{-1}$. The structure of this network was discussed in terms of the hexagonal arrangement highlighted in figure 4.43 (b). The dimensions of this hexagon were measured to be 33 $\text{\AA}$ along the $[00\bar{1}]$ direction and 38 $\text{\AA}$ along the $[1\bar{1}0]$ direction. By comparison, the measurements taken in this study yield values of 36 $\text{\AA}$ along the $[00\bar{1}]$ direction and 30-35 $\text{\AA}$ along the $[1\bar{1}0]$ direction. This may be due to different degrees of strain relaxation, due to the difference in deposition temperatures, or may relate to the x-y calibration errors in the respective STM instruments used in each study.

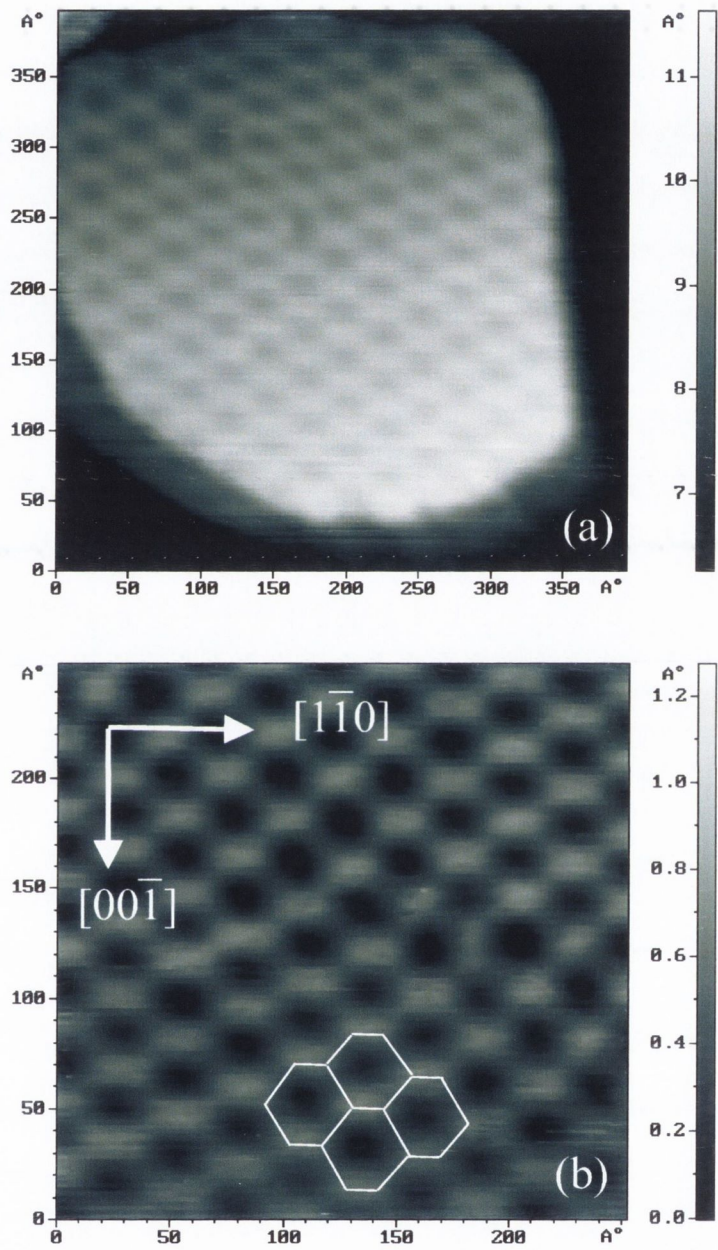


Figure 4.43: (a) $(400 \times 400 \text{ \AA}^2)$ STM image showing the 2D dislocation network on an Fe island covering two terraces. (b) Zoom-in showing an antiphase boundary along the $[1\bar{1}\bar{1}]$ direction between separate *domains* of the dislocation network. The quasi-hexagonal arrangement of the network (similar to the one illustrated in figure 4.35) is highlighted.

It is interesting to note that in figure 4.43 (b), there is evidence of an antiphase boundary between separate *domains*. This illustrates that the dislocation network can originate from more than one point on the Fe islands. The corrugation of the network was not observed to diminish significantly towards the thickening end of the islands, as has been observed by Osing *et al.* [9] and Bethge *et al.* [174]. Figure 4.44 shows how the dislocation network develops from an array of closely spaced dislocation lines in the second Fe layer. The typical separation between lines along the $[1\bar{1}0]$ direction in this layer is 29-32 Å corresponding to 7 Mo atomic spacings, while the full-width half-maximum of the lines appears to be between 10 and 15 Å. The dislocation lines deviate slightly from the $[00\bar{1}]$ propagation direction in a zig-zag fashion. It is clear that the 2D network is formed by the merging of these lines along the approximate $[1\bar{1}0]$ direction.

4.4 Conclusions

From LEED and STM analysis of the clean Mo(110) surface, it was determined that the surface was composed of terraces with an average width of 185 Å separated by monatomic steps of height 2.1 Å running along the $[1\bar{1}1]$ direction. Using these values, the miscut angle was estimated to be 0.65° off the (110) plane. Using a combination of LEED and AES analysis, an initial sticking coefficient of $s_0 = 0.55$ was determined for room temperature O_2 adsorption on the clean Mo(110) surface. This fits well with the results of a study by Bauer and Poppa [157], which indicate an increase in the sticking coefficient from 0.5-0.75 as the miscut angle increases from 0.05° to 11.40° - attributed to the increased step density. AES analysis of the outgassing effect of the AES set-up on the clean surface (described in section 3.3.3) suggest

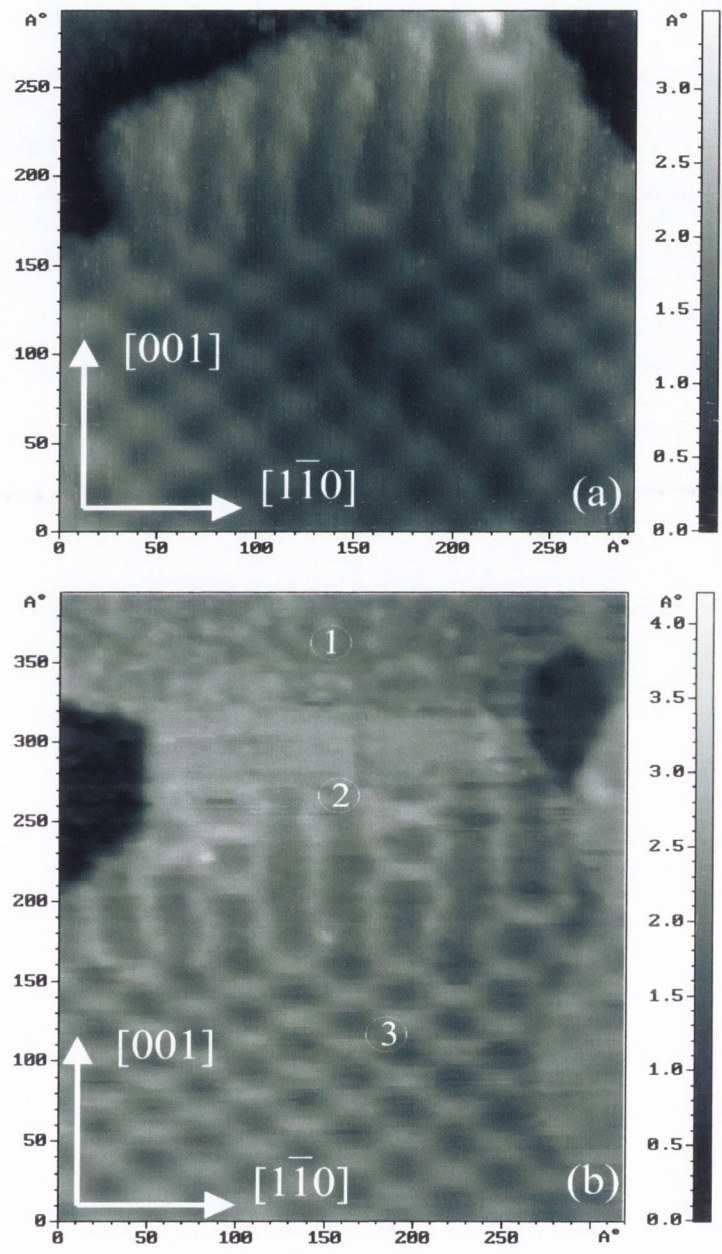


Figure 4.44: STM images taken on film D1, showing the onset of the 2D dislocation network from an array of 1D dislocation lines. The local Fe thickness is indicated in (b).

that for co-adsorption of carbon and oxygen, the latter is more site-specific leading to a saturation in the O/Mo Auger ratio at some critical coverage.

Near room temperature, the growth mechanism for low-coverage Fe films on Mo(110) depends sensitively on such factors as deposition rate and substrate temperature, which control adatom mobility. In contrast to studies by Malzbender *et al.* [94] and Osing *et al.* [10], it was found that the step-flow mechanism rather than island formation contributed largely to the growth of the first and second Fe layers. This was attributed to the slightly higher substrate temperature (330-340 K) used in this study. It was noted that a higher deposition rate increased the island density and reduced the step-flow contribution - associated with limiting the diffusion length of the Fe adatoms.

Both LEED and STM results indicate that the first Fe layer grows pseudomorphically despite the lattice misfit of -8.9 % between Fe and Mo(110). The second Fe layer relaxes some of this tensile strain by the formation a number of dislocation lines that propagate along the $[00\bar{1}]$ direction. Therefore, the strain is initially relaxed along the $[1\bar{1}0]$ direction, in agreement with the observation that the cost in energy to elastically strain the film along this direction is higher than along the $[00\bar{1}]$ axis [168]. An interesting feature of these dislocation line is that they are attractive to adatom nucleation and are responsible for the nucleation of the third Fe layer when the second is only 60-80 % closed.

At low coverages (1.6 ML), where the second Fe layer crosses a substrate step to produce a local thickness of 3 ML, the onset of a 2D dislocation network has been observed by STM. Upon deposition of subsequent layers, the growth mode switches from LBL or Frank-van der Merwe growth to Stranski-Krastanov growth. This can be attributed to an increase in misfit strain energy and a decrease in the interface free energy experienced by lay-

ers above the first and second layers. Anisotropic growth was observed, with elongation of islands along the $[00\bar{1}]$ direction becoming increasingly evident with increasing coverage. This has been explained in terms of anisotropic sticking probabilities [177] and the diffusion behaviour at island edges [176]. The strain energy is reduced in these Fe islands by two mechanisms: (a) inward relaxation of atomic positions at the island edges, (b) formation of a 2D dislocation network. The latter becomes evident in LEED analysis of films with a coverage above 2.4 *ML* and is described as a (12×12) pattern in LEED notation. In STM images this network appears as a quasi-hexagonal structure. Dislocation lines propagate along the general $[00\bar{1}]$ direction, but zig-zag along the approximate $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$ directions. With increasing local film thickness, adjacent lines merge to form regions of enhanced corrugation - elongated along the $[1\bar{1}0]$ direction. These regions appear as bumps on the surface that are arranged in a centred-rectangular fashion analogous to the Mo(110) conventional surface net. The dimensions of the hexagon encompassed by four of these bumps are: 36 Å along the $[00\bar{1}]$ and 45 Å along the $[1\bar{1}0]$, corresponding to 11.4 and 10 Mo atomic spacings respectively. A similar structure has been observed in the Fe/W(110) system [174].

Both LEED and STM analysis of films below 1.8 *ML* coverage display a $p(2 \times 2)$ adlayer structure on the first and second Fe layers. AES and LEED analysis of freshly deposited films indicates that this structure is most likely caused by carbon and/or oxygen introduced during deposition from bulk impurities in the Fe source rod. Atomically resolved STM images indicate that the adsorption characteristics of the first and second Fe layers differ, as the first layer structure is far more disordered than that observed on the second. This variation in adsorption properties may be due to interface effects such as d-band hybridisation and charge transfer or a strain related effect.

The $p(2 \times 2)$ structure does not appear in LEED patterns of thicker films that display satellite spots due to the 2D dislocation network. In STM images, this structure is not resolved on any part of the film covered by the dislocation network.

The first and second layers of films grown at elevated temperatures (495-525 K) were characterised by pure step-flow growth. Dislocation lines were formed in the second Fe layer above a critical Fe stripe width of 100 Å. A significant transformation in film morphology occurs at coverages above 2 *ML*. All Fe, excluding the first pseudomorphic layer (which remains partially intact) agglomerates into large, well-separated, wedge-shaped islands, with local thickness varying over several *ML* as they propagate across a number of terraces. These islands have a near-equilibrium shape, but there is still evidence of preferential growth along the $[00\bar{1}]$ direction. These results are similar to the observations of Malzbender *et al.* [94] and Osing *et al.* [9,187] for the Fe/Mo(110) system and Bethge *et al.* [174] for the Fe/W(110) system. The transition between an array of closely-spaced dislocation lines and a 2D network has been observed on a number of islands. This network is similar in character to that observed on films grown near room temperature. However, the dimension of the resulting hexagon is 14 % lower along the $[1\bar{1}0]$ direction, than for the network observed on films grown in the lower temperature range. The periodicity along the $[00\bar{1}]$ direction remains the same in both cases. This indicates an increased relaxation along the $[1\bar{1}0]$ direction in films grown at elevated temperatures. There was no evidence of complete relaxation of the film to bulk Fe (110) in either LEED or STM analysis for films grown in either temperature range.

Chapter 5

Fe/W(100) epitaxial system

5.1 The W(100) surface

5.1.1 Sample preparation

The W(100) sample was a $\phi 5 \text{ mm} \times 1 \text{ mm}$ crystal prepared from a 5N purity single crystal by RTI, Germany [188]. The crystal was orientated with a miscut angle within $\pm 0.3^\circ$ of the (100) plane and mechanically polished to a surface roughness of $0.01 \mu\text{m}$. This orientation was confirmed using X-ray diffraction by SPL, The Netherlands [155]. Taking an interlayer separation of $1.58 \text{ \AA}$, this miscut should yield an average terrace width of $300 \text{ \AA}$. The sample was fixed in a sample holder with a Ta cap and inserted into the UHV system. The cleaning procedure was similar to that used to clean the Mo(110) crystal - the main bulk impurities in the W crystal being carbon and sulphur. The sample was annealed at $1800\text{-}1900 \text{ K}$ in an oxygen atmosphere of partial pressure $P_{\text{O}_2} = 6.7 \times 10^{-7} - 1.3 \times 10^{-6} \text{ mbar}$ for periods of 30-45 minutes. The surface was subsequently flash-annealed in UHV to temperatures reaching 2500 K for short intervals of 10-20 seconds. Similar procedures have been

shown to produce a clean surface (with impurity concentrations <1 at.%) in a number of other studies [6, 77, 95, 189]. The early stages of cleaning were monitored by LEED and AES analysis using the retarding-field analyser.

5.1.2 LEED and AES

This procedure produced the set of LEED patterns shown in figure 5.1. The oxidation cycle was abandoned after images (a-b) were observed, the LEED pattern evolving as shown in images (c) through (f) with continued flash-annealing to 2500 K . Nominally, the pattern shows an arrangement of orthogonal $p(3 \times 1)$ domains oriented along the $[001]$ and $[010]$ directions. The parameters of the primitive surface net and superlattice were measured to be 2.9 ± 1 Å and 9 ± 1 Å respectively. Figure 5.2 shows an AES spectrum taken at the same period as images (e) and (f) in figure 5.1. The strong oxygen peak at 510 eV indicates that a considerable amount of oxygen is still present on the surface, while the broad peak (~ 29 eV wide) around 280 eV may be due to the presence of carbon. A number of studies have observed that high coverages of oxygen (1-1.4 ML) give rise to (3×1) and (3×3) on W(100) [190, 191], Mo(100) [192, 193] and Ta(100) [194]. LEED studies of the C/W(100) system, on the other hand, have observed the $c(2 \times 2)$, $c(3\sqrt{2} \times \sqrt{2})R45^\circ$ and $p(5 \times 1)$ structures [195, 196] - though this system is less studied than O/W(100).

The splitting of both the integral- and fractional-order spots in the better resolved patterns, indicates that the surface structure is more complex. The spot splitting is collinear with the $p(3 \times 1)$ superlattice and has an equal magnitude in both the $[001]$ and $[010]$ directions. Normally, splitting of both integral- and fractional-order spots is associated with the high step density of vicinal surfaces [12]. However, a step-induced origin for the spot-splitting

disagrees intuitively with the fact that the crystal has a comparatively low miscut angle (0.3°). The measured spot-splitting would correspond to an average terrace width of $32 \pm 5 \text{ \AA}$, requiring a miscut angle of 2.8° . It should be noted that the presence of anti-phase domains of a superlattice are also known to cause splitting. However, this causes only fractional-order spots to be split [12].

The sample was removed from UHV for a long period for the purposes of X-ray analysis. When it was re-inserted into UHV and cleaned, it was found that neither the $p(3 \times 1)$ pattern nor the spot-splitting re-appeared. Instead a (1×1) pattern was observed with varying degrees of sharpness. A less rigorous oxidation procedure was used on this occasion, with 60 minute cycles of annealing at $T \sim 1200 \text{ K}$ in an oxygen atmosphere of $P_{O_2} = 6.7 \times 10^{-10} \text{ mbar}$. It was found that an anneal temperature above 2600 K was required to completely remove the carbon and oxygen peaks from Auger spectra of the surface. The carbon- and oxygen-free surface gave a sharp (1×1) LEED pattern.

To investigate the effects of oxygen adsorption on this surface, the sample was continuously monitored by LEED while exposed to $P_{O_2} = 1.3 \times 10^{-9} \text{ mbar}$ at room temperature for 32 minutes and then at $P_{O_2} = 6.7 \times 10^{-9} \text{ mbar}$ for a further 72 minutes. No change in the LEED pattern, other than an increase in background intensity and (1×1) spot diffusivity was observed over the duration of the O_2 exposure. Exposing the sample to $P_{O_2} = 6.7 \times 10^{-9} \text{ mbar}$ for 30 minutes at 300 K and a subsequent anneal to 500 K also gave a (1×1) pattern. However, annealing the sample for 2 hours at 1565 K in $P_{O_2} = 6.7 \times 10^{-9} \text{ mbar}$ produced the LEED patterns shown in figure 5.3. Both patterns were observed at the same energy, but on different areas of the sample. This may have been due to a temperature

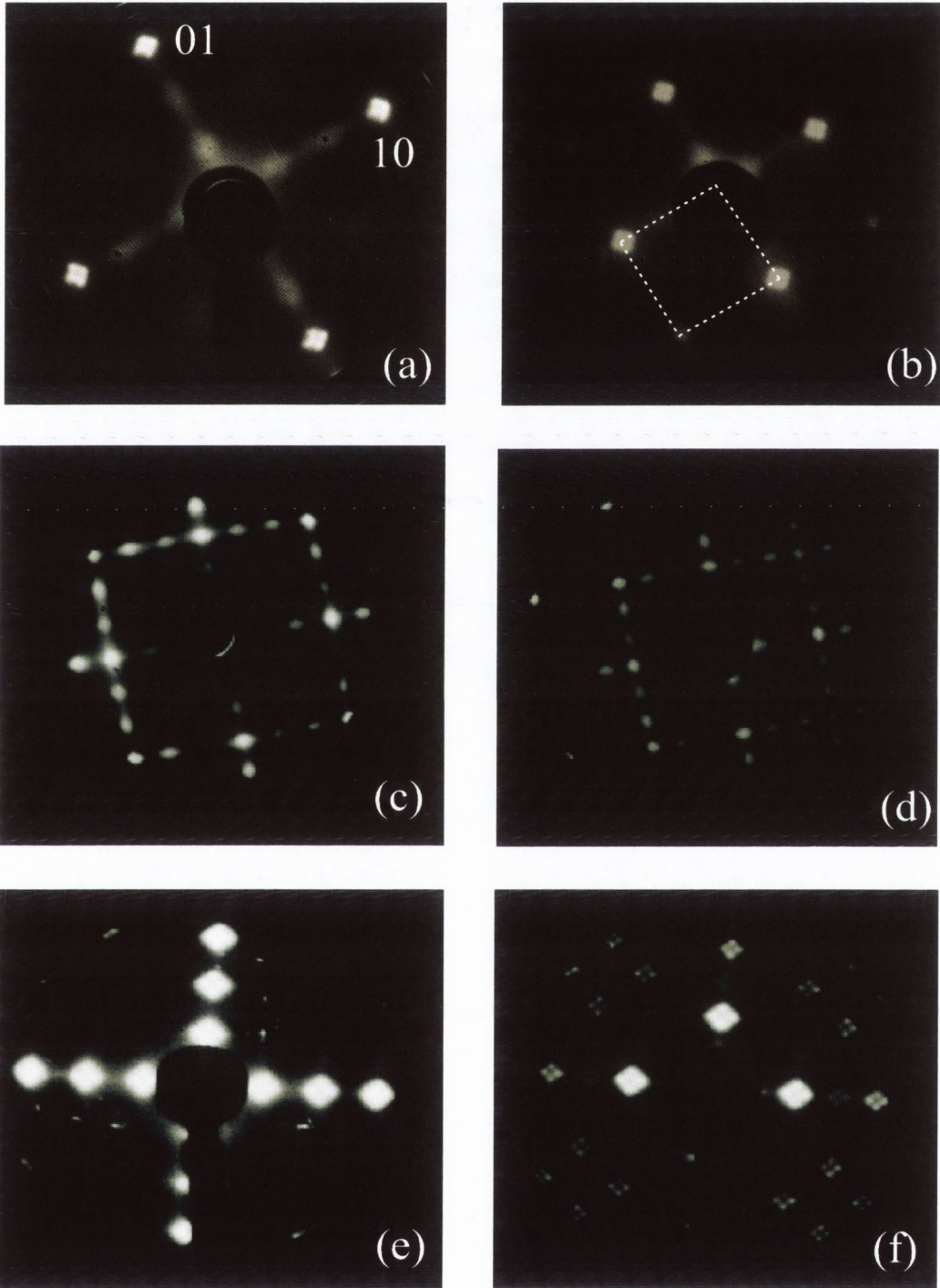


Figure 5.1: LEED images of the evolving pattern of orthogonal $p(3 \times 1)$ domains on W(100) - the unit cell is marked in (b). (a) $E_{beam} = 40 \text{ eV}$, (b) $E_{beam} = 96 \text{ eV}$, (c) $E_{beam} = 66 \text{ eV}$, (d) $E_{beam} = 122 \text{ eV}$, (e) $E_{beam} = 38 \text{ eV}$ and (f) $E_{beam} = 76 \text{ eV}$.

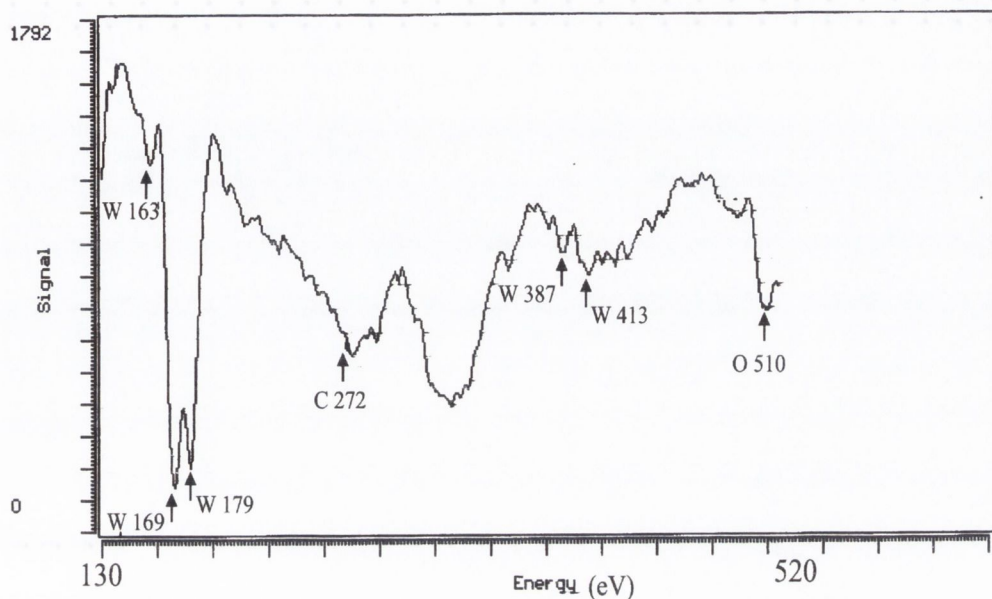


Figure 5.2: AES spectrum of the $p(3 \times 1)$ reconstructed W(100) surface. The standard positions of elemental peaks (taken from reference [113]) are marked. The data was collected in an energy range of 130-520 eV, using the retarding-field analyser set-up. $E_{beam} = 2\text{ keV}$. Lock-in sensitivity = 2 mV.

gradient across the sample surface during the anneal and exposure, since the e-beam heater used heats the sample from one side (*cf.* section 3.2.1). Bauer *et al.* have observed that annealing high coverages above 600-700 K results in reconstruction and faceting ($T \geq 1000\text{ K}$, $\theta \geq 1.4\text{ ML}$) of the surface W(100) surface [190]. With the exposure and substrate temperature used to obtain the patterns in figure 5.3, it is likely that a thin oxide layer was formed involving some surface reconstruction.

In view of the observations outlined above, it is suggested that the $p(3 \times 1)$ structure observed in figure 5.1 was due to a thin oxide layer created during the rigorous oxidation of the surface. This oxygen is clearly visible in Auger spectra taken on the surface during the period that the $p(3 \times 1)$ structure was

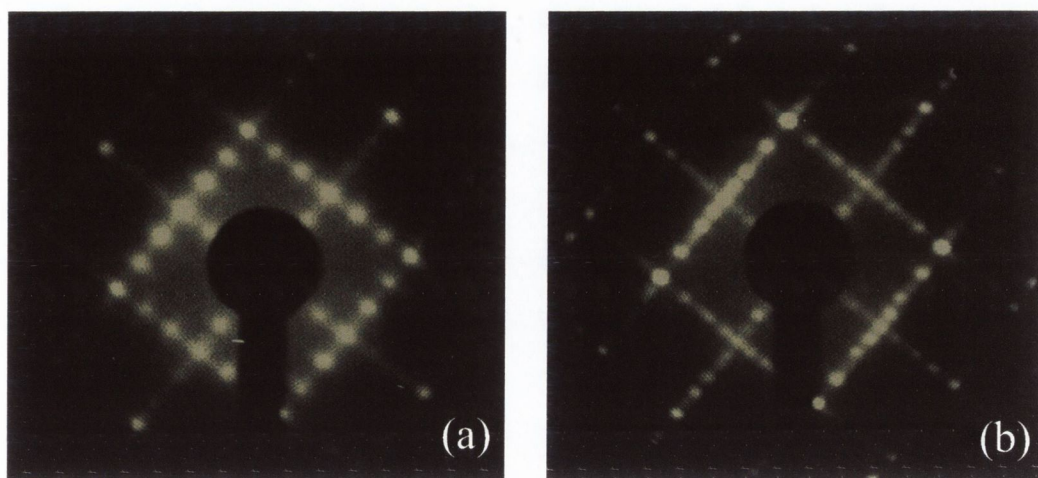


Figure 5.3: The complex LEED pattern observed after the clean W(100) surface has been oxidised for 2 hours at 1565 K in $P_{O_2} = 6.7 \times 10^{-9}$ mbar. (a) $p(3 \times 1)$ pattern and (b) streaked $p(6 \times 1)$ pattern - both patterns were observed at $E_{beam} = 162$ eV on different areas of the sample.

observed. It is noted that both carbon and oxygen persist on the surface after it has been repeatedly flashed to 2500 K and that a temperature in excess of 2600 K is required to remove all traces of oxygen (and carbon) from the surface. There is clearly a close relationship between this $p(3 \times 1)$ structure and the observed spot-splitting as both disappear under the same conditions. The surface does not appear to respond much to oxidation treatments below 500 K , but a $p(3 \times 1)$ pattern was observed when it was oxidised at 1565 K .

5.1.3 STM results

A variety of structures were observed by STM on this surface, which depended sensitively upon the anneal history of the sample. The surface structure shown in figure 5.4, was observed just after oxidation of the sample was

abandoned¹. Unlike the Mo(110) sample, where the surface appeared smooth over a large scan area, this surface is organised into a series of large mounds. The resulting distribution of terrace widths is much broader than one would expect for a smooth surface. Many of the terraces lie below the critical width of 100 Å, which corresponds to the *transfer width* of the LEED optics. This instrumental parameter determines the upper size limit at which the optics can act as an interference detector [197]. As a large number of terraces have widths below the transfer width, they can contribute to the interference pattern detected by the LEED optics. This could account for the spot-splitting observed by LEED analysis. Moreover, as steps appear on the surface along the general directions of both the [001] and [010] axes, this would account for the fact that spot-splitting is observed in both these directions. The absence of an ordered superlattice structure on the terraces reflects the fact that fractional-order spots were not well-resolved in LEED images taken at this period (*cf.* figure 5.1 (a-b)).

With continued cleaning by flash-annealing, the surface becomes well-ordered, which is clearly shown in figures 5.5. The wide distribution of terrace widths is evident in image (a), with terraces of various widths (10-300 Å) oriented along both [001] and [010] directions. Terraces are separated by mostly monatomic steps ~ 1.6 Å high, though double-steps are formed in some areas (*cf.* figure 5.6). The higher-resolution image (b) reveals the orthogonal domain structure of the $p(3 \times 1)$ superlattice. The horizontal domains are less well resolved as they lie parallel to the scan direction. A missing row structure is evident, where every third W $\langle 001 \rangle$ or $\langle 010 \rangle$ row is missing. This is similar to the high-temperature (>1300 K) W(100)- $p(2 \times 1)$ -O structure,

¹Note that the sample was cleaned by flash-annealing several times before the STM session.

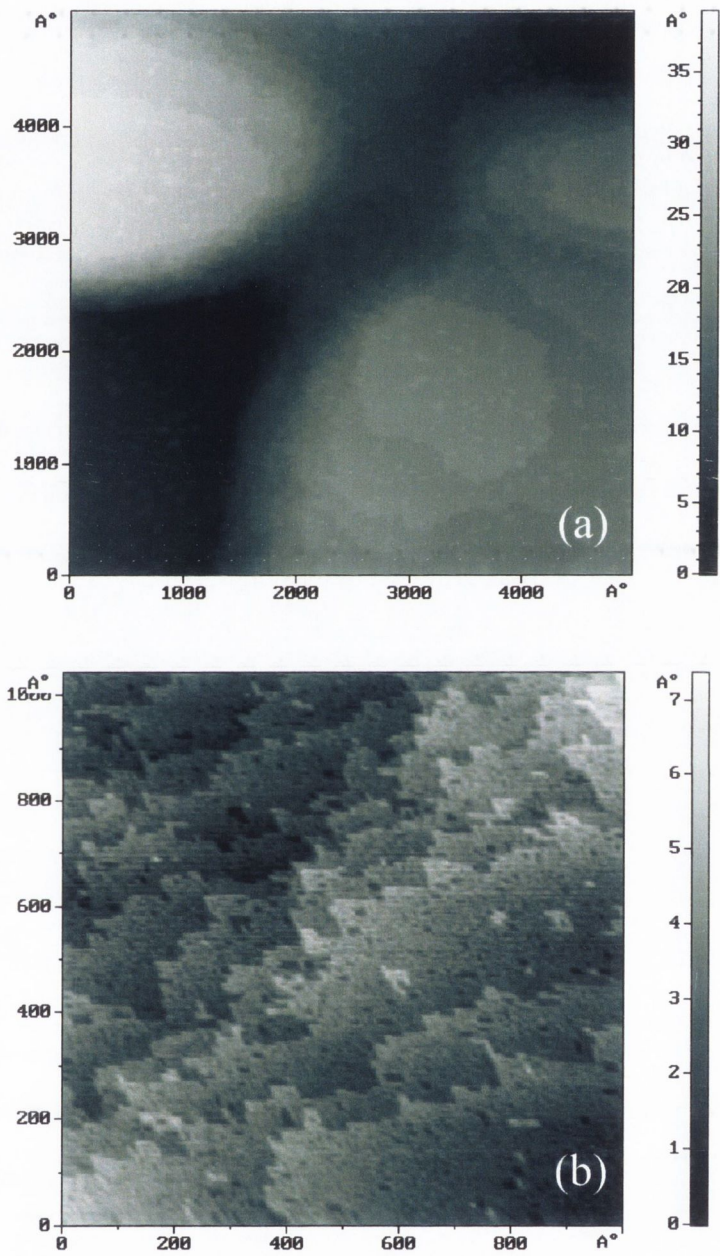


Figure 5.4: STM images of W(100) taken shortly after the oxidising cycle used in the cleaning procedure was abandoned. (a) ($5000 \times 5000 \text{ \AA}^2$) large-scale STM image showing surface roughness, (b) ($1000 \times 1000 \text{ \AA}^2$) image showing the nature of terrace order. PtIr tip. $V_{bias} = 100 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

which has been characterised by STM and LEED [198,199]. Domains appear on all exposed terraces, regardless of size, but are generally oriented along the major axis of the terrace *i.e.* parallel to the step-edge direction.

Figure 5.6 shows the domain structure on a relatively large terrace. In addition to the orthogonal domain structure, there is also evidence of an antiphase domain boundary between two horizontal domains (indicated by the arrows in image (b)) where the rows of atoms are shifted by a half-period. It was noted that this surface was quite stable, as the domain structure could be clearly resolved in STM up to 22 hours after cleaning. The adsorption of residual gas particles was manifested by a "speckling" of white dots on the surface.

Figure 5.7 shows zoom-ins of the central region of figure 5.5 (b), which atomically resolve the missing-row structure. In image (a) of this figure, two parallel domains are observed on different terraces that are separated by a monatomic step. On the lower terrace, the missing-row does not occur immediately at the step-up edge. Instead, a single $W\langle 001 \rangle$ runs along it, while the row adjacent to this is missing. This effect is clearly related to the higher stability of terrace atoms near step-up edges than on the open terrace. Another feature of this image is that upon crossing the terrace step, the positions of atoms in the non-missing rows are shifted along the $[001]$ direction by half an atomic spacing (dashed line). This is due to the stacking nature of the bcc crystal viewed from the (100) or equivalent surfaces.

The periodicity of the structure along the $[010]$ direction was measured to be $9.2 \pm 0.3 \text{ \AA}$, with a corrugation of $0.9 \pm 0.2 \text{ \AA}$. The typical width of the troughs representing the missing $W\langle 001 \rangle$ is $3.0 \pm 0.1 \text{ \AA}$. The periodicity of the depressions along the $[001]$ direction is $2.9 \pm 0.3 \text{ \AA}$, while their corrugation is $0.6 \pm 0.1 \text{ \AA}$. The contrast-reversed version of figure 5.7 (b) is compared

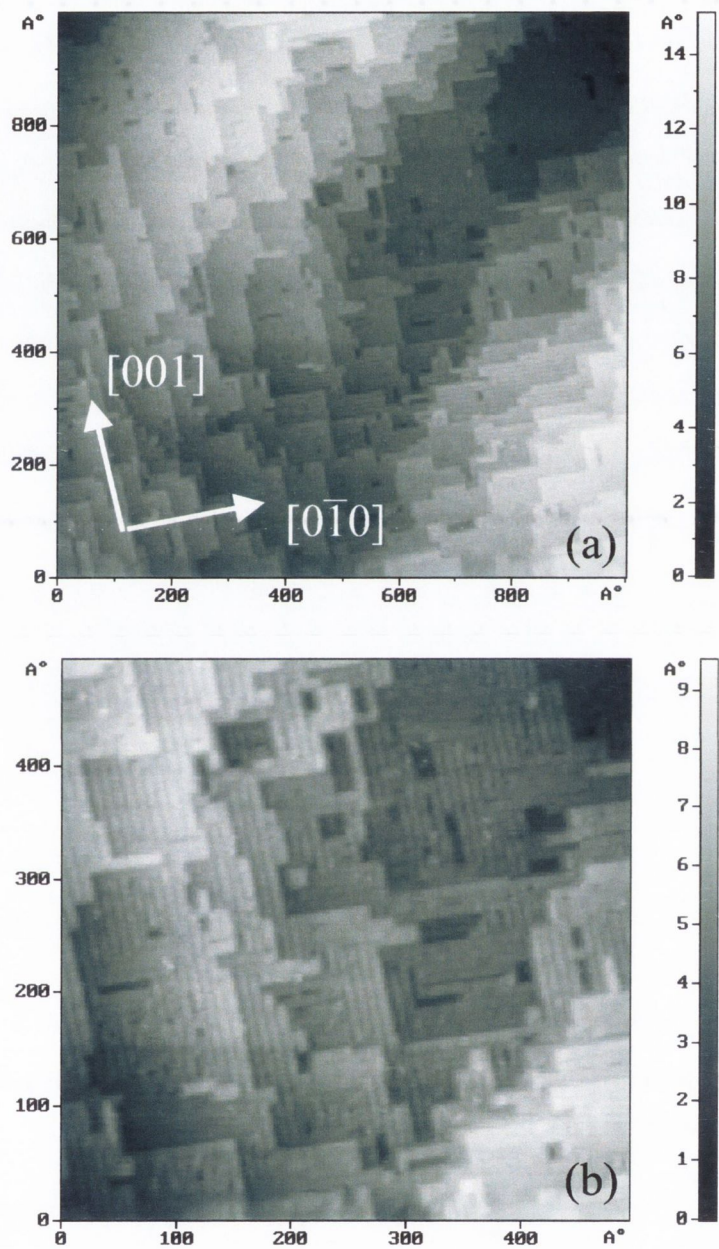


Figure 5.5: STM images of W(100) surface, taken after further flash-annealing to $T \geq 2500 \text{ K}$ in UHV. (a) ($1000 \times 1000 \text{ \AA}^2$) and (b) ($500 \times 500 \text{ \AA}^2$) STM images showing the $p(3 \times 1) - O$ domain structure on terraces oriented along the $[001]$ and $[0\bar{1}0]$ directions. MnNi tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

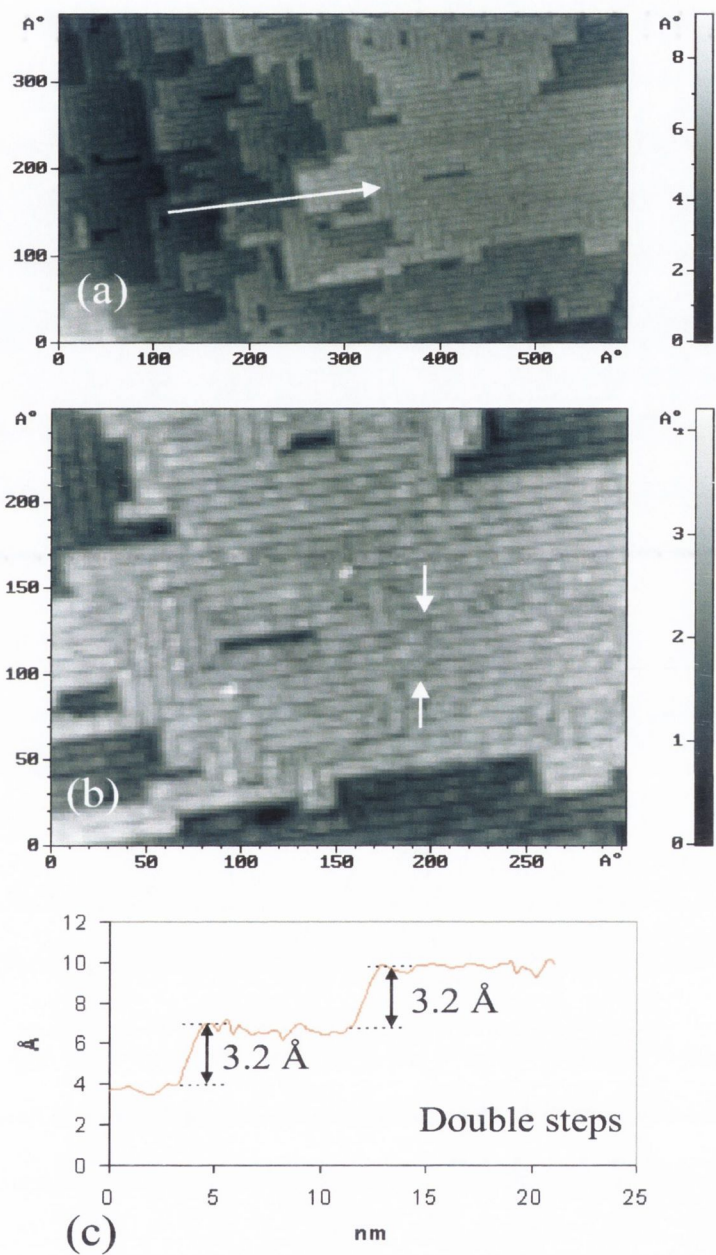


Figure 5.6: (a) $(600 \times 400 \text{ \AA}^2)$ image of domains on a large terrace, (b) zoom-in showing antiphase domain boundary (arrows) where horizontal rows are shifted by half a period and (c) a line-profile along the direction marked in (a) highlighting the presence of double atomic steps. $V_{bias} = 10 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

Image	$R_{[010]}$ (Å)	$a_{[010]}$ (Å)	$a_{[001]}$ (Å)
a	9.5 ± 0.3	2.8 ± 0.4	2.9 ± 0.2
b	8.9 ± 0.3	3.2 ± 0.3	3.1 ± 0.3

Table 5.1: A table comparing the important dimensions of the structures shown in images (a) and (b) of figure 5.8. $R_{[010]}$ is the missing row periodicity along the $[010]$ direction, $a_{[010]}$ the spacing along the same direction and $a_{[001]}$ the atomic spacing along the $[001]$ direction.

in figure 5.8 with another atomically resolved image, taken on the surface on another occasion. The dimensions of each structure compare favourably within the error margins, as highlighted in table 5.1. The atomic corrugation in figure 5.8 (b) was measured to be 0.3 ± 0.1 and 0.2 ± 0.1 along the $[010]$ and $[001]$ directions respectively.

The missing-row structure of the reconstructed surface increases the number of binding sites made available for oxygen atoms. From studies of the $p(2 \times 1)$ structure formed at $T > 1300$ K for an oxygen coverage around 0.5 ML [198, 199], it has been concluded that oxygen atoms bind randomly at three-fold sites and/or on top of second-layer tungsten atoms (see figure 5.9). It has also been suggested that at coverages ≤ 1.5 ML oxygen atoms may bind on top of tungsten atoms in the first layer *i.e.* on top of the non-missing row W atoms [200]. Additionally, Altman and Bauer [199], have proposed the occupation of four-fold hollow sites and bridge sites in the first tungsten layer to account for the oxygen coverages accommodated by the $p(4 \times 1)$ and $p(5 \times 1)$ structures.

In their comprehensive LEED study of the O/W(100) system, Bauer *et al.* [190] observed that a $p(3 \times 1)$ structure is formed at a coverage around 1.3 ML. This corresponds to a packing density of approximately four oxygen

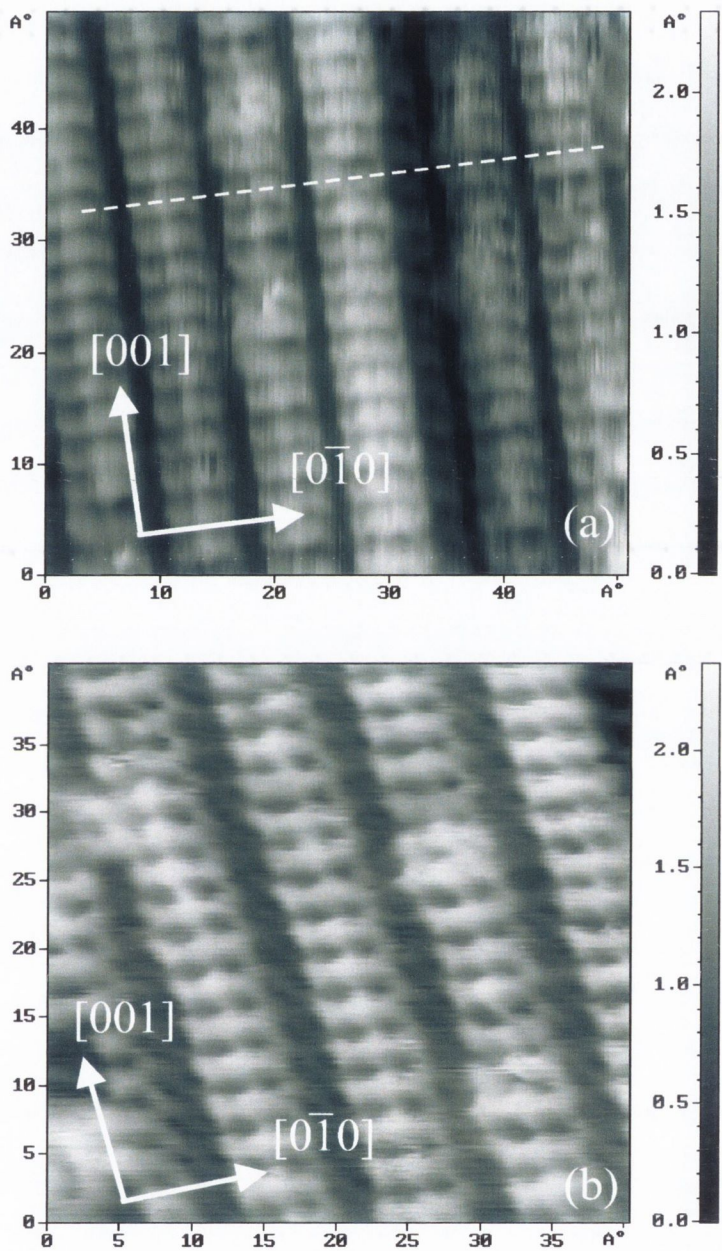


Figure 5.7: (a) $(50 \times 50 \text{ \AA}^2)$ y-scan of a terrace in the central region of figure 5.5, (b) $(40 \times 40 \text{ \AA}^2)$ atomically resolved x-scan image of the same region, showing the missing-row structure. The angular difference between the images is due to the different scan directions used. MnNi tip. $V_{bias} = 20 \text{ mV}$. $I_{tunnel} = 0.5 \text{ nA}$.

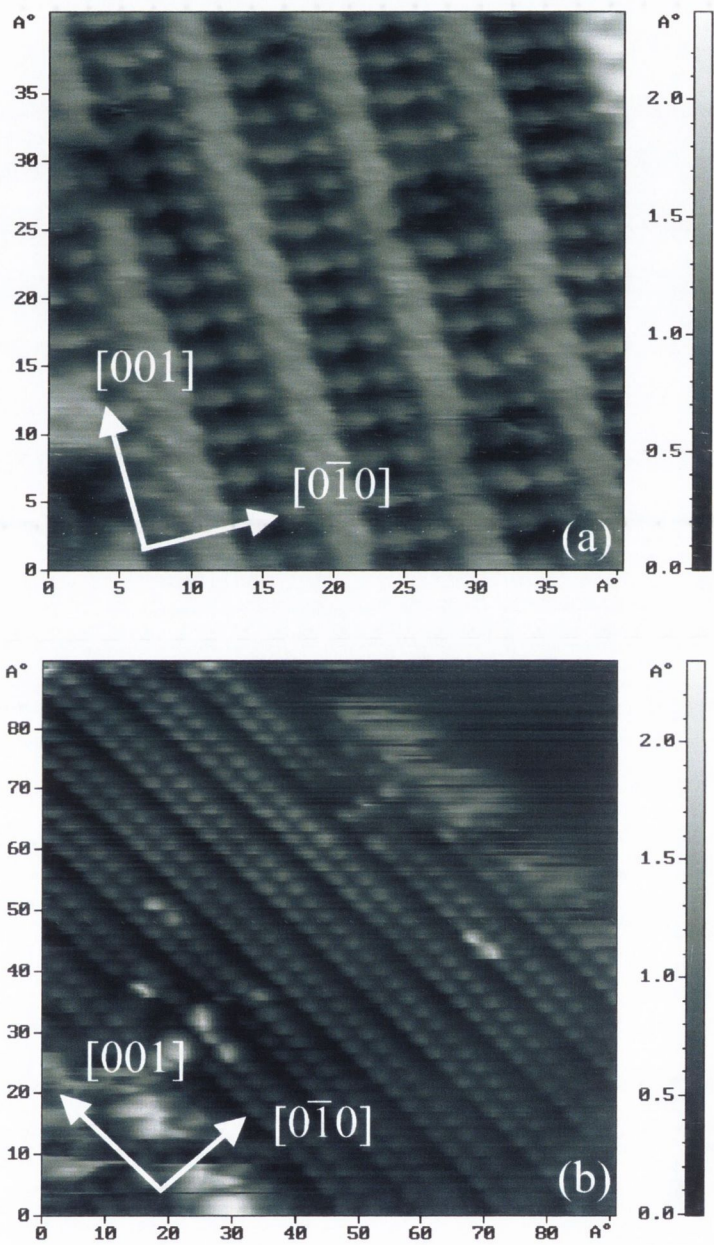


Figure 5.8: A comparison of (a) ($40 \times 40 \text{ \AA}^2$) contrast reversed version of figure 5.7 (b) with, (b) ($90 \times 90 \text{ \AA}^2$) atomically resolved missing-row structure taken at a later date on the surface shown in figure 5.13. MnNi tip. $V_{bias} = 10\text{-}20 \text{ mV}$. $I_{tunnel} = 0.3\text{-}0.5 \text{ nA}$.

atoms for every cell of the $p(3 \times 1)$ superlattice - three second-layer W atoms plus two non-missing row atoms. The model proposed by us for the resulting structure is illustrated in figure 5.10, where oxygen atoms adopt second-layer (or three-fold) sites and positions on top of the first-layer atoms. This model assumes no exchange of tungsten and oxygen atomic positions.

In their STM and STS study of the $p(2 \times 1)$ structure, Meyer *et al.* [198] observed that oxygen in excess of 0.5 *ML* caused the addition of extra W $\langle 001 \rangle$ and $\langle 010 \rangle$ rows that lie above the layer containing the missing rows - in effect multilayer growth of tungsten. A similar effect, shown in figure 5.11, is observed on certain domains of the surface imaged in figure 5.13. This structure has a row periodicity of $8.9 \pm 0.3 \text{ \AA}$ along the $[010]$ direction, with an atomic spacing of $3.1 \pm 0.3 \text{ \AA}$ along each row and atomic corrugations of $0.4 \pm 0.1 \text{ \AA}$ and $0.7 \pm 0.1 \text{ \AA}$ along the $[001]$ and $[010]$ directions respectively. The structure effectively comprises the initial missing-row structure shown in figure 5.8 (b), but with additional $\langle 001 \rangle$ row on top of the non-missing rows, shown schematically in figure 5.12. It is believed that the addition of these extra rows increases the number of three-fold sites made available.

Images (a) and (b) in figure 5.11 were taken on the same domain, but using different tunneling currents. In (a) the missing row appears to contain atoms in second-layer or three-fold positions, while in (b) there appears to be a zig-zag arrangement of atoms along the $[011]$ and $[0\bar{1}1]$ directions. The corrugation and height of these 'bumps' appears to be the same as that of the atoms in the non-missing rows below the extra W rows. The arrangement of atoms in the missing rows is somewhat ambiguous. It is tentatively proposed that these 'bumps' may be due to the presence of oxygen at displaced second-layer sites in the missing rows (see figure 5.12).

As already mentioned, Meyer *et al.* observed the formation of additional

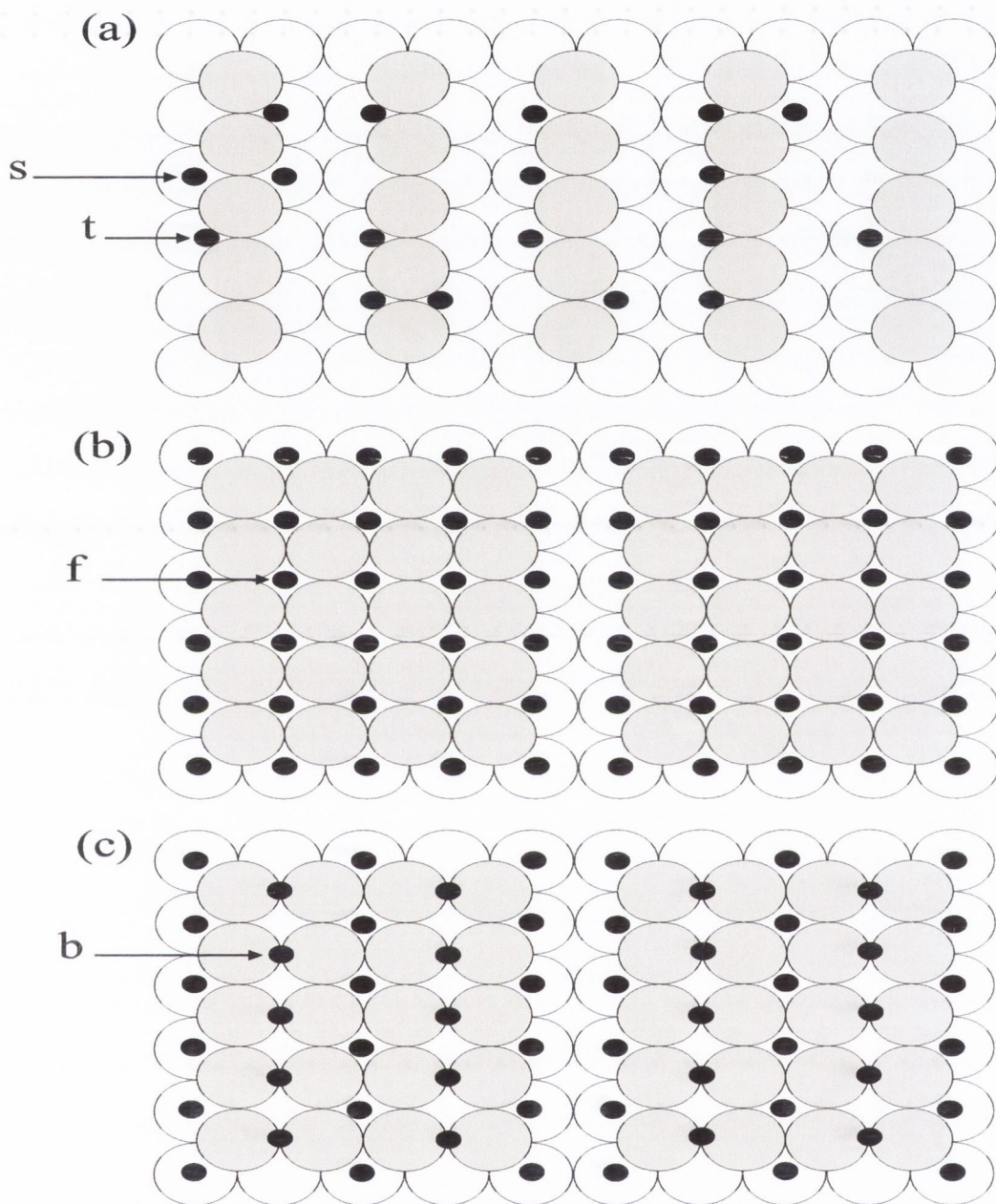


Figure 5.9: (a) Model of the W(100)-p(2 × 1)-O missing-row structure suggested in references [198,199]. Open circles are second-layer W atoms, shaded circles are first-layer W atoms, dark circles are O atoms, s - second-layer binding site and t - three-fold binding site. (b) and (c) Suggested models for the W(100)-p(5 × 1)-O structure in reference [199]. f - four-fold hollow site and b - bridge site.

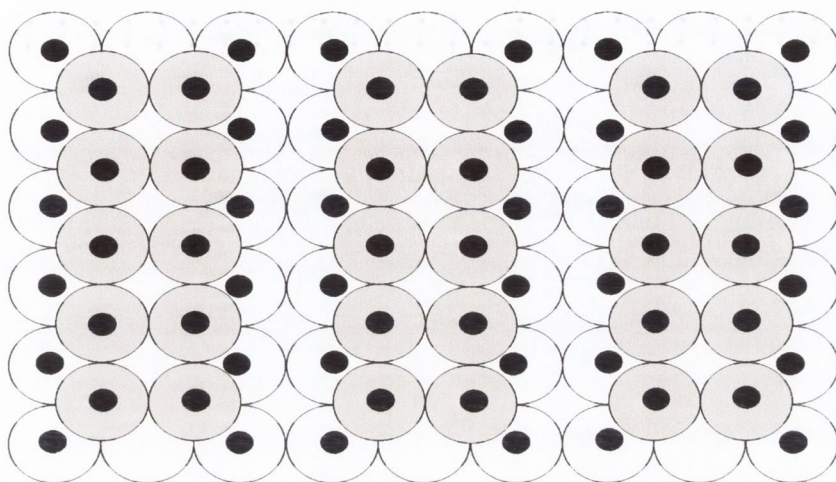


Figure 5.10: A suggested model for the $W(100)$ - $p(3 \times 1)$ -O missing-row structure. This model assumes a coverage of 1.3 *ML* and no exchange of tungsten and oxygen atomic positions. The oxygen atoms adopt second-layer (or three-fold) sites as well as binding on top of the first-layer W atoms.

W rows in the presence of excess oxygen [198]. It is interesting to note that another feature of the surface on which the above structure was recorded, is the apparent segregation of excess contaminants to the domain boundaries, which is clearly evident in figure 5.13. The width and height of these boundaries varies, but is typically 1.2 Å high and 9-12 Å wide. The boundaries may be due to segregation of carbon, sulphur or water, or excess oxygen diffused from the sub-surface region that forms a higher-order oxide (WO_3) between domains.

The carbon- and oxygen-free surface is shown in figure 5.14, which produced a sharp (1×1) LEED pattern with no spot-splitting and no visible carbon or oxygen peaks in Auger spectra taken with the cylindrical mirror analyser (apart from the contamination due to the outgassing of the analyser). There is no evidence of any missing-row structures on the surface. The

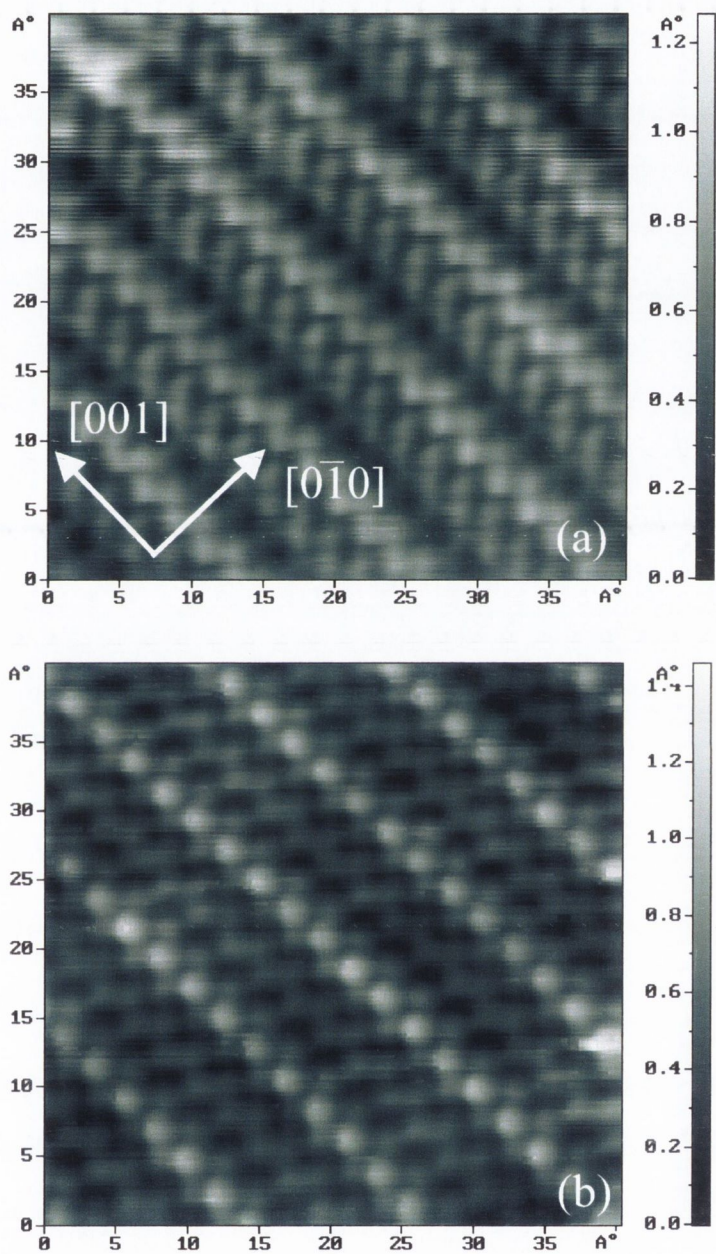


Figure 5.11: $(40 \times 40 \text{ \AA}^2)$ images of a missing-row structure with additional $\text{W}\langle 001 \rangle$ rows on top of the non-missing rows. Taken on a different domain of the same surface where figure 5.8 (b) was observed. MnNi tip. (a) $V_{bias} = 6 \text{ mV}$. $I_{tunnel} = 0.23 \text{ nA}$. (b) $V_{bias} = 6 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

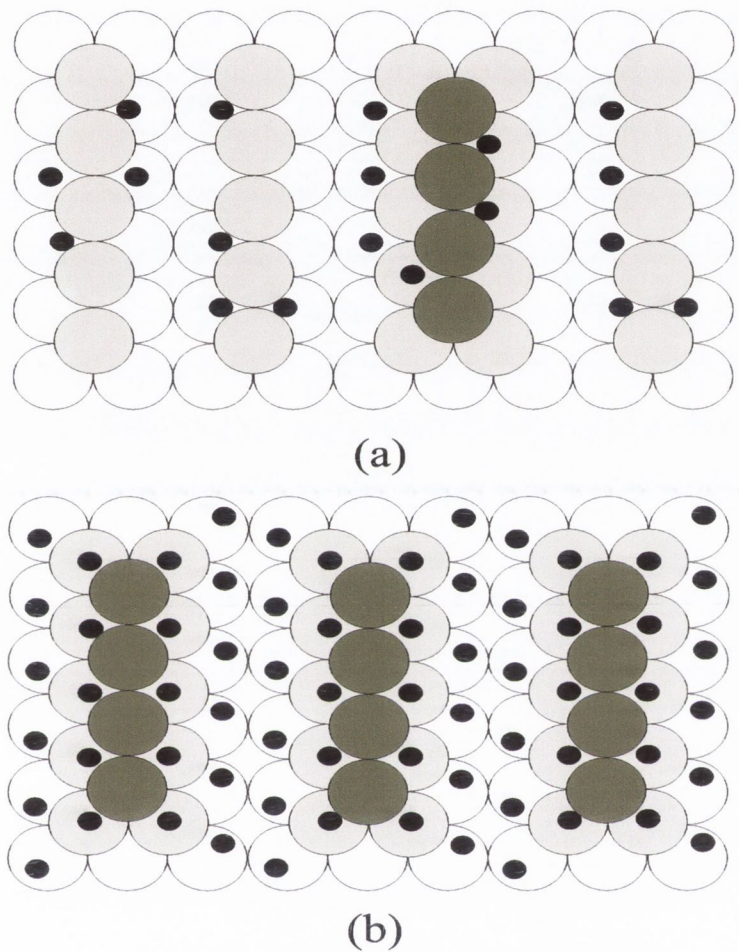


Figure 5.12: Open circles are second-layer W atoms, shaded circles are first-layer W atoms. The darker shade circles are W atoms in the additional rows on top of the missing-row layer. (a) The structure proposed by Meyer *et al.* for the formation of extra W atom rows, one layer higher than the $p(2 \times 1)$ missing-row structure. (b) Suggested model for the same effect on the $p(3 \times 1)$ structure. Oxygen atoms are shown in displaced second-layer positions in the missing W rows. Additional oxygen atoms may appear on top of the extra W rows to increase the coverage.

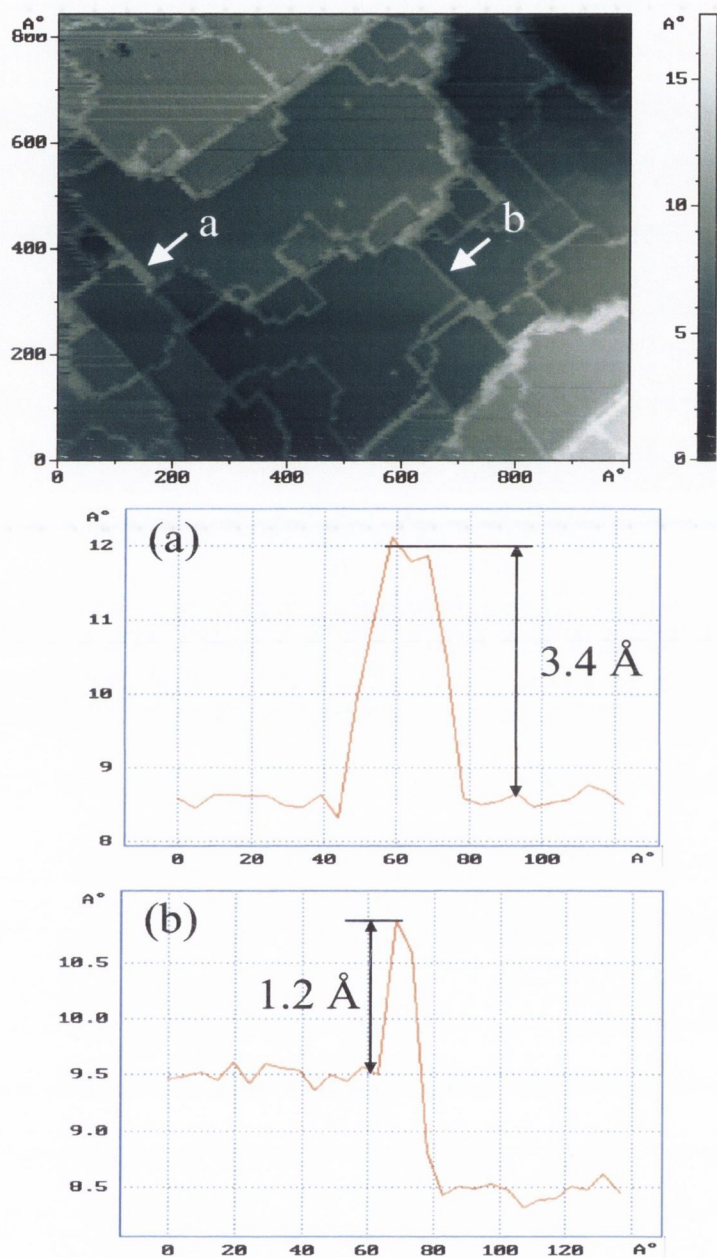


Figure 5.13: $(900 \times 800 \text{ \AA}^2)$ STM image of domain boundaries marked by the segregation of excess oxygen (or other contaminants). MnNi tip. (a) $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$. (a) and (b) line-profiles taken at points a and b, showing the variation in the boundary height and width.

distribution of terrace widths is still relatively broad, lying roughly in the range of 50-1000 Å. A similar feature was noted by Wengelnik *et al.* on a sample with a $\sim 2^\circ$ miscut, in their STM study of the clean and hydrogen-covered W(100) [201]. However, the surface has a much smoother appearance than was observed in the presence of the oxygen-induced structure, which may account for the absence of split spots in the LEED pattern.

It should be noted that the clean W(100) surface is particularly sensitive to hydrogen adsorption, which induces a $c(2 \times 2)$ structure on the surface at 300 K in the coverage range $0.1 \leq \theta_H \leq 0.35$ ML [202]. This structure is formed by dimerisation of surface W atoms along the [010] and [001] directions and is distinct from the $c(2 \times 2)$ structure of the clean surface, observed below 210 K [203]. The latter is formed by the displacement of surface W atoms along the [011] and equivalent directions, to form zig-zag chains [204]. Above 0.35 ML the surface develops the (1×1) structure of the hydrogen-saturated surface [202]. Meyer *et al.* have observed that after cleaning in UHV, there is sufficient exposure from residual gas in the interval before STM analysis (2-3 hours) to form the (1×1) H-induced surface [198].

5.2 Fe film growth

Despite a lattice misfit of -9.4 % ($a_{Fe} = 2.866$ Å, $a_W = 3.165$ Å), values determined for the surface free energies of iron and tungsten ($\gamma_{Fe} = 2.9$ J.m⁻², $\gamma_W = 3.4$ J.m⁻² [205]) indicate that Fe should wet the W(100) during initial film growth. This has been verified by a number of combined AES, LEED and TPD studies of the growth and properties of Fe films on W(100). These studies have shown that the first two monolayers grow pseudomorphically in a layer-by-layer fashion at $100 \leq T \leq 300$ K [6, 77, 95, 189]. Deposition of

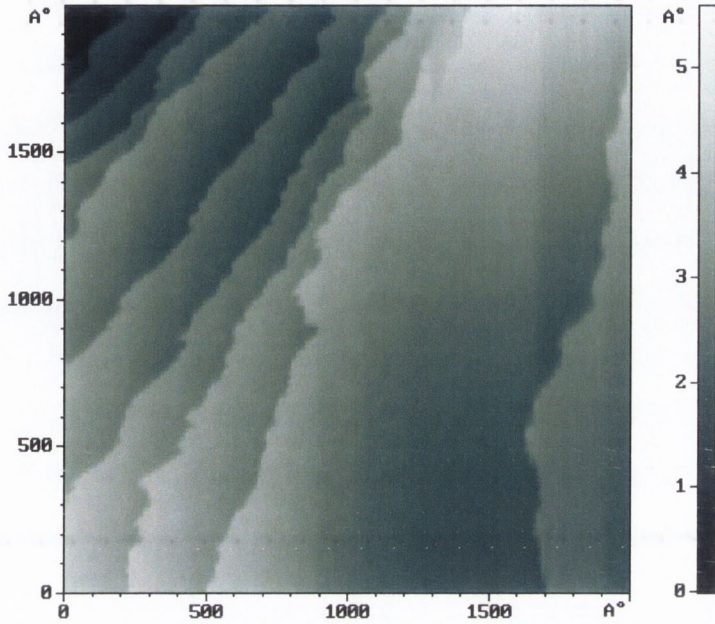


Figure 5.14: ($2000 \times 2000 \text{ \AA}^2$) STM image of the carbon- and oxygen-free W(100) surface. PtIr tip. $V_{bias} = 30 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

higher coverages at these temperatures results in disordered growth indicated by the absence of any LEED pattern at $\theta > 4 - 5 \text{ ML}$, where islands are only formed upon annealing (900 K) [6, 77]. Annealing of films to $> 700 \text{ K}$ has shown that the first pseudomorphic layer is stable against 3D islanding (and remains so to the Fe desorption temperature of 1200 K) [6, 77]. Other studies have indicated that the Fe bilayer may also be stable under certain deposition conditions to annealing above 700 K [95, 189].

In this case, Fe films were deposited using the same procedure as that used for preparing films on the Mo(110) surface. Films were deposited on both the clean surface and the $p(3 \times 1)$ reconstructed surface, the details are listed in table 5.2. The fractional coverage θ_{Fe} was calculated from the incident Fe flux (measured with the deposition monitor) after the manner described in section 4.2 for Fe deposition on Mo(110). The deposited thickness d_{Fe} , calculated by

the deposition monitor, is also recorded in table 5.2 for reference.

5.2.1 LEED and AES

LEED analysis performed on freshly deposited films on the $p(3 \times 1)$ reconstructed surface produced the spot-split $p(3 \times 1)$ pattern over the coverage range studied *i.e.* $0.43 \leq \theta_{dep.} \leq 6.82$ with varying degrees of resolution. An example is shown in figure 5.15, which displays the patterns obtained on film F, $\theta_{dep.} = 6.82$ ML deposited at 575 K. The features of the reconstructed substrate are clearly visible, which indicates that the film grows in clusters, leaving a suitable amount of the substrate surface bare or covered by only 1-2 ML.

LEED analysis of the films grown on the clean surface produced a (1×1) pattern with a diffuse background for both 2 ML coverage films, though the pattern was sharper for film H, which was deposited at 565 K. Film I, with a deposited coverage of 4.7 ML, also gave a (1×1) pattern, but with a very diffuse background. Earlier studies have shown that comparable coverages deposited at 200-300 K gave no discernible LEED spots [6,77]. In this case, the film was deposited at a slightly higher temperature (330 K), which may account for this difference.

Figure 5.16 compares the AES spectra for 2 ML and 4.7 ML films deposited at 565 K and 330 K respectively on the clean W(100) surface. Because the chamber pressure during deposition was comparatively high (low 10^{-9} mbar) sizeable carbon and oxygen peaks are detected. Comparing the two coverages, the substrate signal has almost completely disappeared at 4.7 ML Fe coverage. No Auger data were taken on films deposited on the $p(3 \times 1)$ reconstructed surface.

Film	d_{Fe}	$\theta_{dep.}$	t_{settle}	$T_{dep.}$	D	P	t_{STM}	surface
	Å	ML	min.	K	ML.min. ⁻¹	mbar	hrs.	
A	0.5	0.43	35	300 [†]	0.26	1.6×10^{-9}	1.8	$p(3 \times 1)$
B	1	0.85	35	300	0.51	4.0×10^{-9}	1.3	$p(3 \times 1)$
C	3	2.56	45	575	0.71	1.9×10^{-9}	2.5	$p(3 \times 1)$
D	3	2.56	16	725	0.57	4.7×10^{-10}	6.0	$p(3 \times 1)$
E	3	2.56	30	775	0.57	1.6×10^{-9}	4.4	$p(3 \times 1)$
F	8	6.82	45	575	0.90	1.3×10^{-9}	9.3	$p(3 \times 1)$
G	2.4	2.05	15	330	0.93	8.0×10^{-10}	2.1	clean
H	2.4	2.05	20	565	0.41	2.7×10^{-9}	1.7	clean
I	5.5	4.69	35	330	0.79	2.0×10^{-9}	1.4	clean

Table 5.2: Deposition details for each of the Fe films deposited on the W(100) surface. These are: (a) the deposited thickness d_{Fe} - read from the quartz crystal monitor, (b) the equivalent monolayer coverage $\theta_{dep.}$, (c) the period t_{settle} allowed before depositing the Fe film, (d) the sample temperature during deposition $T_{dep.}$ - read from the heating stage thermocouple, (e) the deposition rate D and (f) the chamber pressure P during deposition. The table also includes the period elapsed between film deposition and STM analysis. Also listed is the nature of the surface onto which the film was deposited. [†] Film A was also studied after a post-anneal to 575 K for 15 minutes.

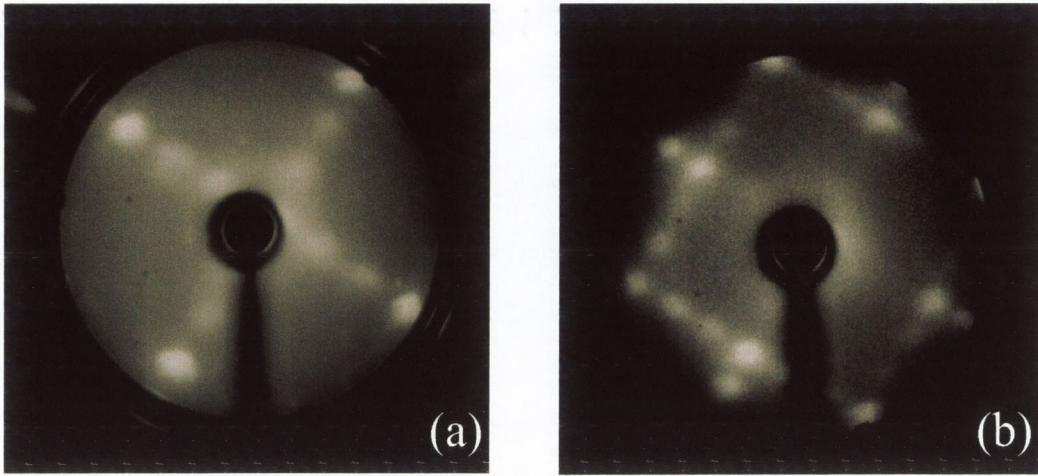


Figure 5.15: LEED images of film F, $\theta_{dep.} = 6.8 \text{ ML}$, deposited on the $p(3 \times 1)$ reconstructed W(100) surface at 575 K. (a) $E_{beam} = 40 \text{ eV}$ and (b) $E_{beam} = 52 \text{ eV}$.

5.2.2 STM results

STM analysis of Fe films grown on the $p(3 \times 1)$ reconstructed surface indicates that growth proceeds by the nucleation of a high density of clusters that grow three-dimensionally, resulting in a rough macroscopic film morphology. This high nucleation density is apparent in figure 5.17 (a) and (b), which shows an STM image of a 0.43 ML film deposited at room temperature. The missing-row structure of the substrate surface is covered by 1-2 ML high clusters. Images (c) and (d) shows the same surface after annealing to 575 K for 15 minutes. There is a noticeable decrease in the cluster density, while the missing-row structure is clearly visible. This suggests that upon annealing much of the deposited Fe becomes organised on top of the missing-row structure.

The morphology of a 0.85 ML film deposited at room temperature is displayed in figure 5.18. The $p(3 \times 1)$ structure of the substrate surface is

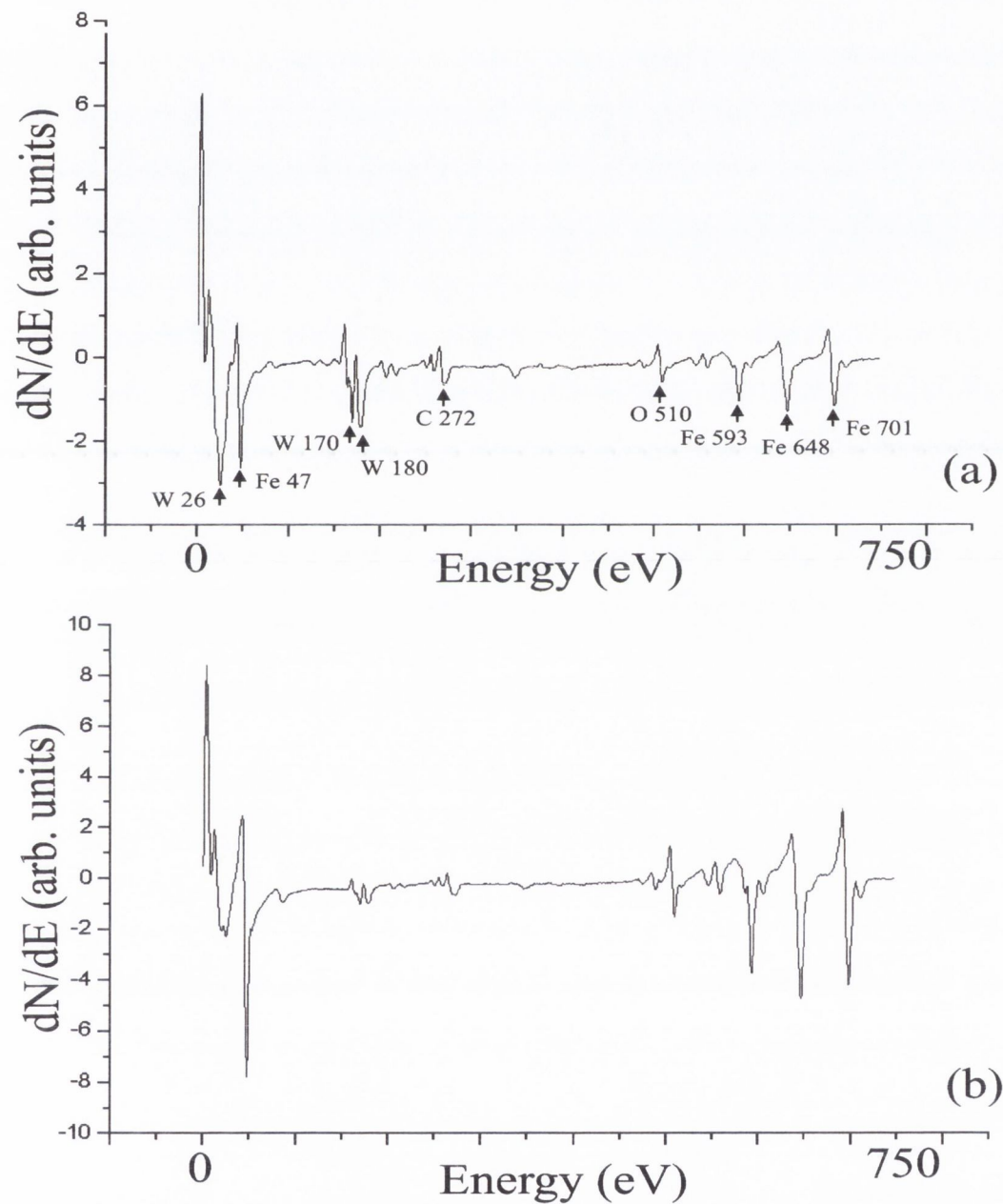


Figure 5.16: AES spectra taken of films (a) $H - \theta_{dep.} = 2 \text{ ML}$ Fe grown at 565 K and (b) $I - \theta_{dep.} = 4.7 \text{ ML}$ grown at 330 K .

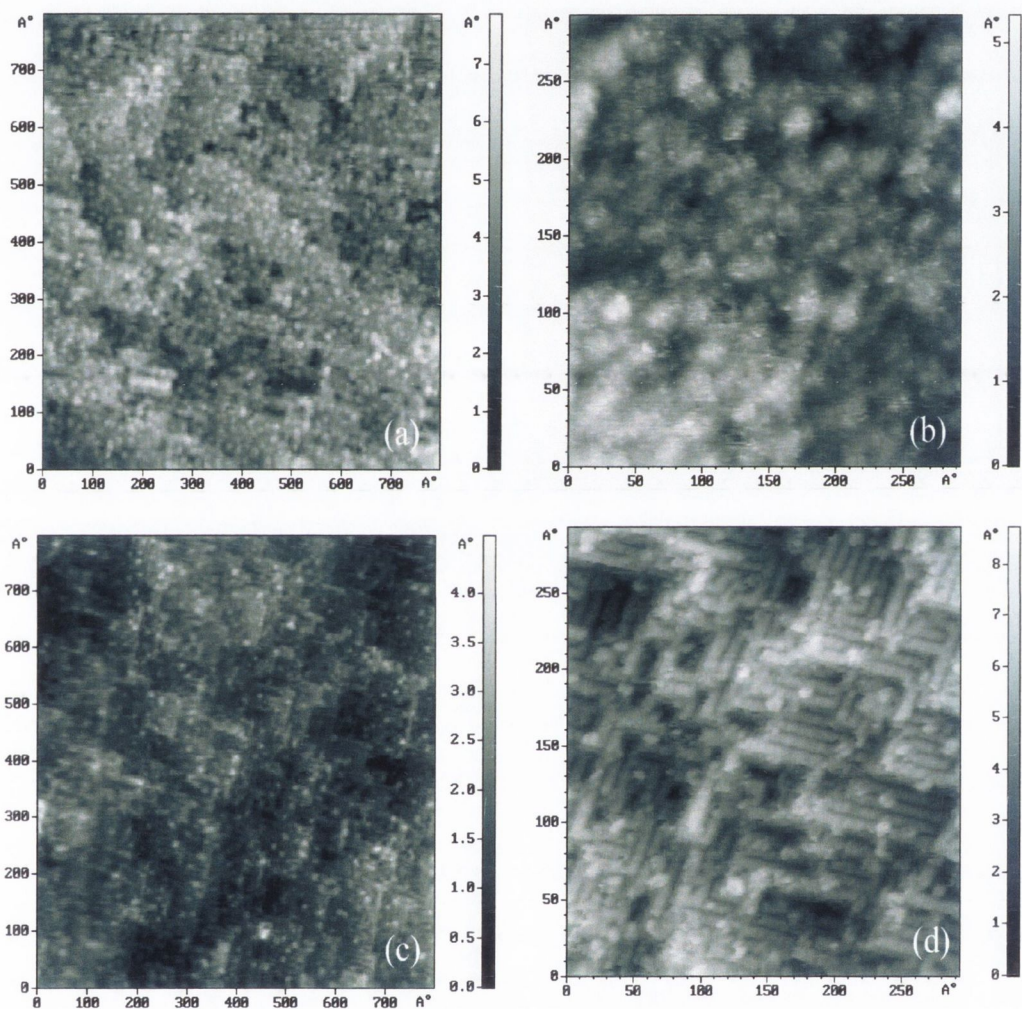


Figure 5.17: (a)(800 × 800 Å²) and (b) (300 × 300 Å²) STM images of film A, 0.43 *ML* Fe deposited at 300 *K*. (c) and (d) The same film post-annealed to 575 *K* for 15 minutes. W tip. $V_{bias} = 30\text{-}100$ mV. $I_{tunnel} = 0.1$ nA.

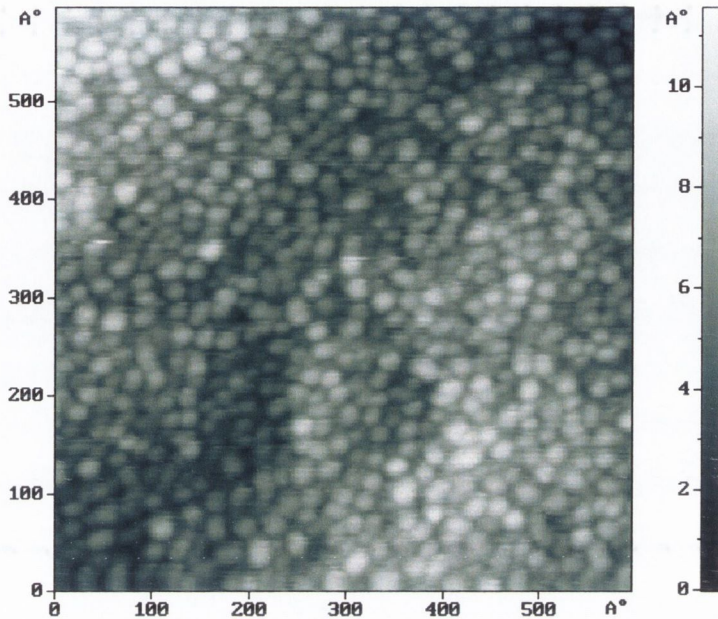


Figure 5.18: ($600 \times 600 \text{ \AA}^2$) STM image of film B, 0.85 *ML* deposited at 300 *K*. W tip. $V_{bias} = -30 \text{ mV}$. $I_{tunnel} = -0.1 \text{ nA}$.

obscured by a high density ($1.8 \times 10^{17} \text{ m}^{-2}$) of mostly 1 *ML* high Fe clusters, with a typical diameter of 15-30 $\text{\AA}$. These clusters may be monolayer islands growing pseudomorphically with the underlying substrate. It should be noted that the relatively high chamber pressures reached during each deposition means that contamination is likely to have some effect on film morphology. For example, the presence of contaminants on the surface could provide favourable nucleation centres for cluster formation. However, it is believed that in this case, it is the nature of the underlying substrate that predominantly influences the morphology of the film.

Figure 5.19 compares the morphologies of 2 *ML* films deposited on the clean W(100) surface at 330 *K* and 565 *K* respectively. The morphology of the film deposited at the lower temperature is typical of the cluster growth observed at lower coverages. However, for the film deposited at 565 *K*, the

Fe has coalesced into large islands with a rectangular shape characteristic of near-equilibrium growth. The local thickness of these islands can reach up to 8 *ML*. It is not clear whether a pseudomorphic first layer is present in either case, though the morphology of the latter film is suggestive of pure island growth. An interesting feature of the elevated temperature film, is the appearance of a 2D dislocation network on some of the larger islands (islands with dimensions of the order of ~ 100 Å), shown in figure 5.20. It is a square network of side ~ 37 Å, oriented along the [001] and [010] directions and appears at a local thickness of 3-4 *ML* (assuming Volmer-Weber growth). It corresponds to the insertion of an extra Fe atom for every twelve W atoms along the [001] and [010] directions. There was no evidence of any dislocation lines on the film. The formation of a dislocation network can be attributed to the relief of tensile strain in the Fe film due large misfit (-9.4 %) with the substrate. It does not appear on the smaller islands because the inward relaxation of atomic positions at the island edges is sufficient to relieve the strain in these islands.

Figure 5.21 compares similar size STM images of 2.6 *ML* films deposited at 575, 725 and 775 *K* on the $p(3 \times 1)$ reconstructed surface. The transition from 575 *K* to 725 *K* is accompanied by an apparent decrease in the cluster density, which can be attributed to greater coalescence of Fe at higher temperatures. The 25 % higher deposition rate used in the first case may also contribute to the higher cluster density. The films displayed in (b) and (c) were deposited at the same rate. At the higher deposition temperature, it appears that the Fe film largely follows the topography of the substrate, while the remaining Fe appears as very small clusters. It is possible that at some critical temperature between 725 and 775 *K*, an interaction between the Fe and the underlying oxygen-induced $p(3 \times 1)$ structure occurs, which

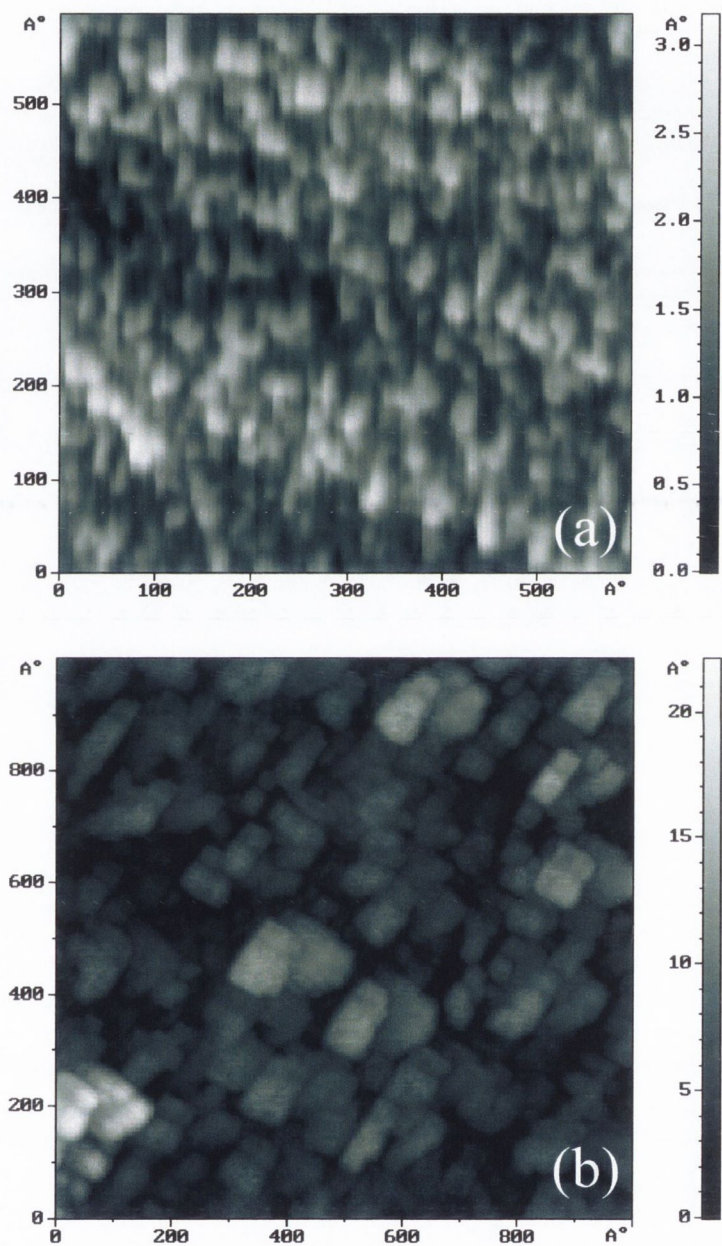


Figure 5.19: (a) $(600 \times 600 \text{ \AA}^2)$ image of $\sim 2 \text{ ML}$ deposited at 330 K and (b) the same coverage deposited at 565 K on the clean W(100) surface. W tip. $V_{bias} = 20\text{-}50 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

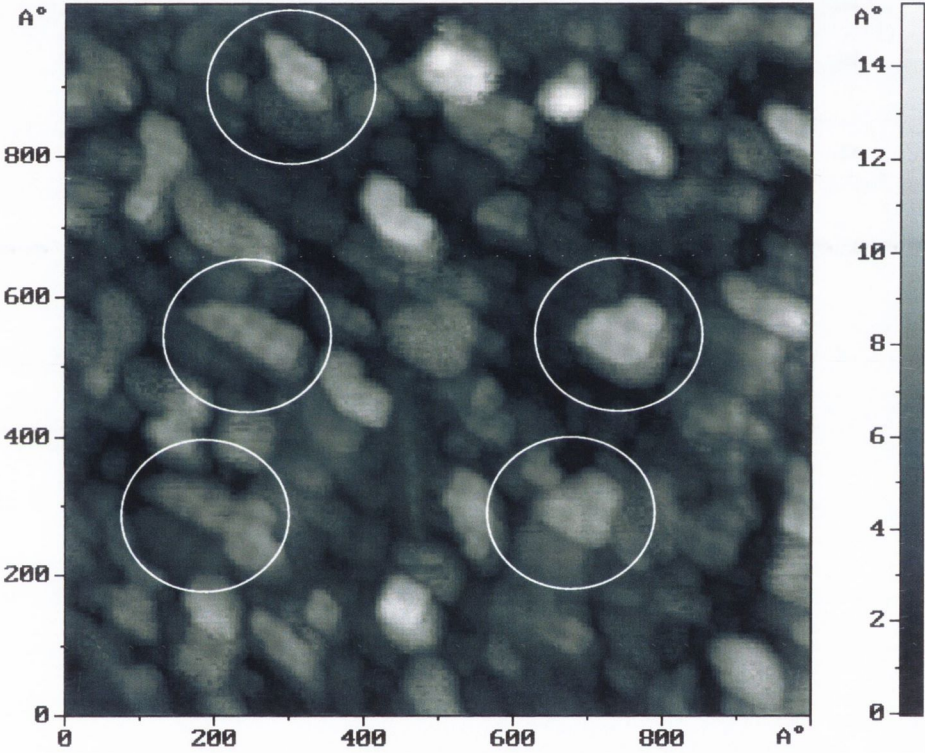


Figure 5.20: ($1000 \times 1000 \text{ \AA}^2$) STM image of film H, showing a 2D dislocation network on islands of local thickness $> 3 \text{ ML}$. $V_{bias} = 50 \text{ mV}$. $I_{tunnel} = 0.1 \text{ nA}$.

causes this morphological transition. This is unlikely to be an alloying effect, as previous studies have indicated that Fe films does not alloy with the W(100) surface up to the desorption temperature (1200 K) [77].

Finally, figure 5.22 shows the morphology of a 6.8 *ML* film deposited on the $p(3 \times 1)$ reconstructed surface at 575 K. The morphology is similar to the cluster growth observed for lower coverage films deposited on this surface. The local thickness of these clusters can take values in the range of 2-8 *ML*. Despite the high deposition temperature, the Fe clusters do not take on the rectangular shape observed for the 2 *ML* film deposited on the clean W(100) surface at a similar temperature. However, compared with figure 5.18, which shows an STM image of comparable area for a 0.85 *ML* film deposited at 300 K, it is clear that the average cluster size is considerably larger (30-60 Å).

5.3 Conclusions

The oxidation of the W(100) surface during the early stages of the sample cleaning procedure leads to the observation of a $p(3 \times 1)$ LEED pattern. A splitting of both the integral- and fractional-order spots is closely associated with the oxygen-induced reconstruction. STM analysis of this surface shows that the surface displays a broad distribution of terrace widths, with terraces oriented along both the [001] and [010] directions. A large proportion of these terraces have widths lying below the transfer width of the LEED optics. This may have been responsible for the observed spot-splitting. The surface is reconstructed in orthogonal domains with a missing-row structure oriented along the [001] and [010] directions, similar to the $p(2 \times 1)$ -O structure observed previously [198]. The missing rows are caused by diffusion of W atoms out of the surface, which increases the number of threefold binding

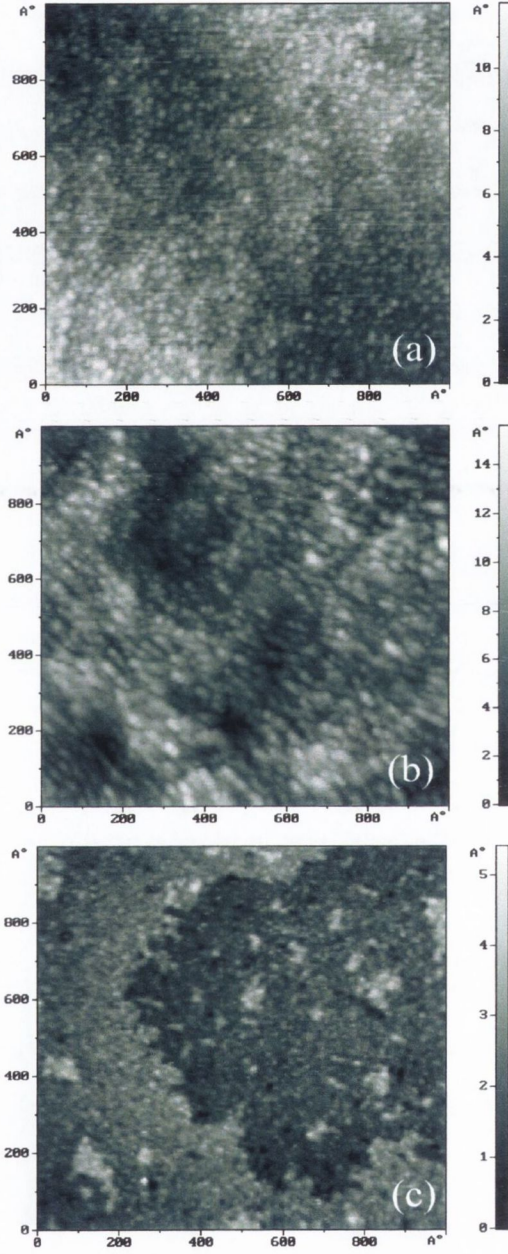


Figure 5.21: ($1000 \times 1000 \text{ \AA}^2$) STM images of $\sim 2.6 \text{ ML}$ deposited at (a) 575 K , (b) 725 K and (c) 775 K on the $\text{W}(100)\text{-}p(3 \times 1) - \text{O}$ surface. MnNi and W tips. $V_{\text{bias}} = 30\text{-}200 \text{ mV}$. $I_{\text{tunnel}} = 0.1 \text{ nA}$.

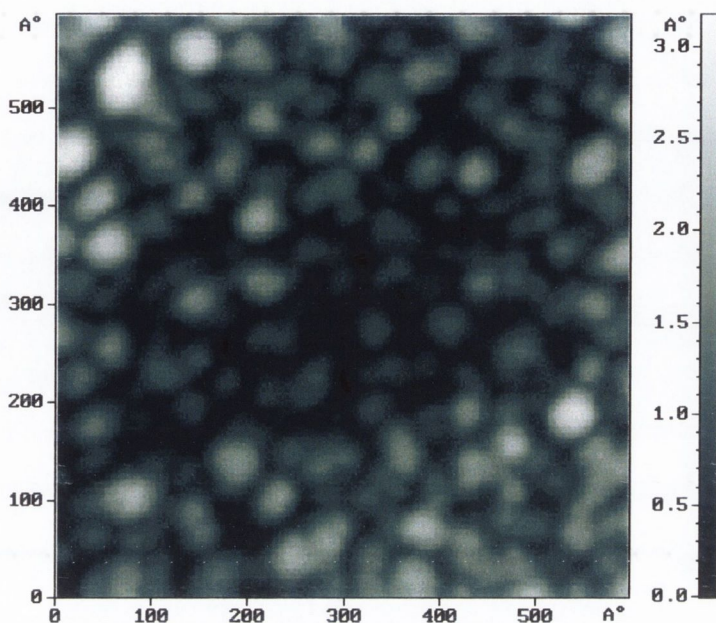


Figure 5.22: ($600 \times 600 \text{ Å}^2$) STM image of film F, $\sim 6.8 \text{ ML}$ Fe deposited at 575 K on the $\text{W}(100)\text{-}p(3 \times 1) - \text{O}$ surface. W tip. $V_{\text{bias}} = 30 \text{ mV}$. $I_{\text{tunnel}} = 0.1 \text{ nA}$.

sites for oxygen atoms. Increasing amounts of oxygen are accommodated by the formation of extra W $\langle 001 \rangle$ rows one layer above the non-missing W rows, which further increases the number of threefold binding sites. A LEED study of the O/W(100) adsorption system has indicated that the $p(3 \times 1)$ structure is formed at an oxygen coverage of $\sim 1.3 \text{ ML}$ [190]. On the basis of this result, a model is proposed for the structure of the $p(3 \times 1)$ reconstruction, including the positions of atomic oxygen in second-layer (or threefold) and on-top sites.

Deposition of Fe onto this surface at room- and elevated temperatures results in films with varying degrees of roughness. Growth is characterised by a high density of Fe clusters, whose average size increases with increasing deposition (or anneal) temperature. There is no evidence of pseudomorphic

layer-by-layer growth on the reconstructed surface, despite the fact that oxygen is known for its surfactant action in Fe/Fe(001) homoepitaxy [61]. There is also evidence that at elevated temperatures, there may be some interaction between the Fe film and the oxygen-covered surface, though it is assumed that no alloying of Fe and W occurs. Fe growth is more ordered on the carbon- and oxygen-free surface, the growth mode at room temperature may be Stranski-Krastanov, though this is not clear. At elevated temperatures, the growth mode appears to proceed by Volmer-Weber or pure island growth. The resulting islands have a rectangular shape and have a local thickness up to 8 *ML*. A 2D dislocation network observed on some of the larger islands, resulting from relief of the large tensile strain induced in the film by the substrate. This network reflects the symmetry of the bcc (100) surface and corresponds to the insertion of an extra Fe atom for every twelve W atoms.

Chapter 6

Summary

The epitaxial growth of Fe on the Mo(110) and W(100) surfaces has been studied using STM, LEED and AES. For the Fe/Mo(110) system, an initial sticking coefficient of 0.55 has been determined for oxygen adsorption on the Mo(110) surface, which has a miscut of $\pm 0.65^\circ$. Growth of the first two monolayers of Fe on the Mo(110) surface near room temperature is a mixture of the step-flow and 2D island growth mechanisms. The relative contributions of each mechanism depend on the deposition temperature and rate (which control adatom mobility), though the step-flow contribution is predominant. The first Fe layer grows pseudomorphically, while dislocation lines appear along the $[00\bar{1}]$ direction in the Fe bilayer. At higher coverages, growth proceeds in a layer-plus-island (Stranski-Krastanov) fashion. The tensile strain induced in the Fe film by its misfit with the Mo substrate induces the formation of a quasi-hexagonal strain-relieving dislocation network. This is formed by the $[1\bar{1}0]$ cross-over of parallel dislocation lines which zig-zag along the general $[00\bar{1}]$ direction. The dimensions of this network correspond to 11.4 and 10 Mo atomic spacings along the $[00\bar{1}]$ and $[1\bar{1}0]$ respectively. An ordered $p(2 \times 2)$ adlayer is atomically resolved on the Fe bilayer, which is attributed

to oxygen contamination during deposition. This structure is not resolved on the first layer which shows a disordered $p(2 \times 2)$ structure or on thicker layers where the dislocation network appears.

At elevated temperatures, the first two Fe layers are formed by pure step-flow growth. At higher coverages, the film morphology is characterised by the agglomeration of Fe into wedge-shaped islands, separated by areas covered with a pseudomorphic monolayer. The local thickness of these islands ranges from 2 to 10 *ML*, depending on the number of substrate steps crossed. Surface free energy minimisation is the driving force for the shape of the islands, which produces a flat Fe(110) surface, unbroken by steps. A transition between an array of closely-spaced dislocation lines and a 2D network, similar to that observed for room temperature growth, has been observed. The dimensions of the latter indicate a 14 % greater relaxation along the $[\bar{1}\bar{1}0]$ direction, than for the network observed on films grown in the lower temperature range.

Oxidation of the W(100) surface results in the formation of a $p(3 \times 1)$ missing-row structure. This structure appears in orthogonal domains oriented along the $[001]$ and $[010]$ directions. Atomically resolved STM images indicate that there are two forms of this structure. The first is formed by the reconstruction of the surface so that every third $W\langle 001 \rangle$ row is missing. The second is formed by the addition of an extra $W\langle 001 \rangle$ above each pair of non-missing rows in the first structure. In both cases, the arrangement produces threefold and second-layer binding sites at which oxygen atoms can be accommodated.

Deposition of Fe on this surface is typified by cluster growth, resulting in films which are macroscopically rough. The average area covered by these clusters increases with increasing deposition temperature due to increased

coalescence. There is no evidence that a smooth, pseudomorphic monolayer is formed on the surface, like that observed for deposition of Fe on the clean W(100) surface. STM analysis was performed on 2 *ML* Fe films deposited on the clean W(100) surface at 330 *K* and 565 *K*. The growth is more ordered than that observed for depositions on the $p(3 \times 1)$ -O reconstructed surface. Film growth at 330 *K* appears to grow in a Stranski-Krastanov fashion. The film grown at 565 *K* appears to have grown in the Volmer-Weber mode. The resulting islands have local thicknesses reaching 8 *ML* and a rectangular shape. On some of the larger islands a strain-relieving dislocation network was observed. This network appears to have the symmetry of the substrate and corresponds to the insertion of an extra Fe atom for every twelve W atoms along the [001] and [010] directions.

6.1 Further work

The replacement of the retarding-field analyser with a cylindrical mirror analyser for AES analysis has improved the analytical capabilities of the system. This opens up the possibility of studying the adsorption properties of the Fe/Mo(110) and Fe/W(100) epitaxial systems for different gas species. As indicated in both this study and the study of Fe growth on the vicinal Mo(110) surface by Osing [10], these bimetallic systems can display novel chemical properties due to film strain and interface effects. The effects on film growth of controlled oxygen (and hydrogen) pre-adsorption on the substrate surface would also be interesting to study. The growth of Fe on the clean W(100) surface should be studied in more detail with STM, particularly the dislocation network observed on the 2 *ML* film grown at 565 *K*.

A surface magneto-optical Kerr effect set-up, designed by L. Seravalli

[206], is to be added to the UHV system. This will allow the magnetic characterisation of the Fe films deposited on the Mo and W surfaces. The effects of gas adsorption on the magnetic properties of Fe films grown on these surfaces can then be investigated using this set-up. For example, an adsorption-driven spin reorientation transition has been observed in the Fe/W(110) system upon exposure to residual gases in a UHV chamber [207]. Another application of this technique would be the investigation of the magnetic anisotropies of Fe films grown on Mo(110) surfaces with different step densities. It has been shown for the Fe/W(100) and Fe/W(110) systems that a step-induced anisotropy is induced on surfaces with a high step density [208, 209].

Much of the motivation for this study was the investigation of suitable candidates for spin-polarised STM (SPSTM) experiments to obtain magnetic contrast on the atomic scale [98, 141]. Though no magnetic experiments were performed, the morphology of the wedge-shaped Fe islands formed during film deposition at elevated temperatures on the Mo(110) surface make them attractive candidates for such experiments. The magnetic order in a wedge-shaped island is expected to change over its thickness range, starting from the non-magnetic pseudomorphic first layer (observed for the Fe/W(110) system [210]). SPSTM experiments would involve imaging films with this morphology using antiferromagnetic tips, in the presence of a reversible magnetic field.

It has been shown that novel STM tips may be fabricated from polycrystalline MnNi, which is known to be a bulk antiferromagnet at room temperature. These tips have an imaging capability rivalling that of their non-magnetic (W and PtIr) counterparts, with atomic resolution routinely obtained on a number of sophisticated surface topographies (Fe_3O_4 , Fe/Mo(110) and W(100)- $p(3 \times 1)$ -O). If such tips are to be used in spin-polarised STM

experiments, there must be some characterisation of the magnetic properties near the tip apex. For example, if the tip preparation procedure results in the formation of a ferro- or ferrimagnetic order at the tip apex, this may be detectable using Lorentz microscopy. Here, a transmission electron microscope is used to map the stray magnetic field from a sample by the field-interaction with the transmitted electrons.

Appendix A

LTSTM chamber

PORT	FLANGE	TUBE	FOCAL POINT	LENGTH ±0.5	φ° ±0.5°	θ° ±0.5°	USE
1	CFR114-70	69.8 O.D. × 1.6mm	A	106	0	180	CRYOSHROUD
2	CF114-70	69.8 O.D. × 1.6mm	A	165	158	90	WOBBLESTICK
3	CF114-70	69.8 O.D. × 1.6mm	A	165	202	90	WOBBLESTICK
4	CF70-41	41.2 O.D. × 1.6mm	A	180	236	90	MAG. DRIVE
5	CF70-41	41.2 O.D. × 1.6mm	-	83.8	0	0	NUDE GAUGE
6	CFB200	108.0 O.D. × 3.0mm	A	303	270	90	ION PUMP
7	CFR114-70	69.8 O.D. × 1.6mm	A	139	330	90	SPARE
8	CF114-70	69.8 O.D. × 1.6mm	A	144.5	56	90	BELLOWS
9	CFR114-70T	69.8 O.D. × 1.6mm	A	125	111	90	ROTARY DRV.
10	CF114-70	69.8 O.D. × 1.6mm	A	218	180	50	VIEWPORT
11	CF70-41	41.2 O.D. × 1.6mm	A	182	236	55	VIEWPORT
12	CF114-70	69.8 O.D. × 1.6mm	B	218	330	50	VIEWPORT
13	CF114-70	69.8 O.D. × 1.6mm	A	270	0	0	LINEAR DRV.

Table A.1: LTSTM chamber port table.

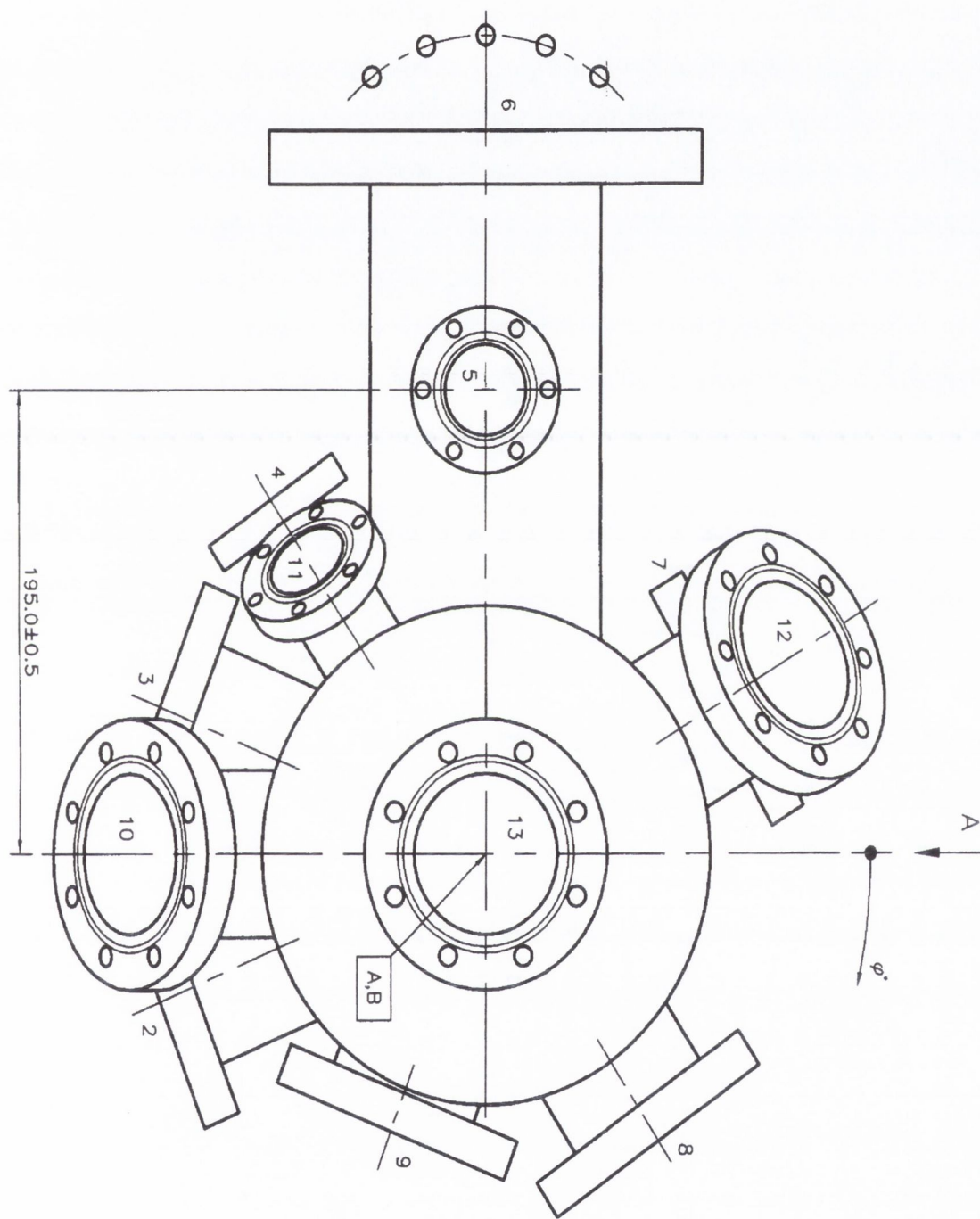


Figure A.1: Top view.

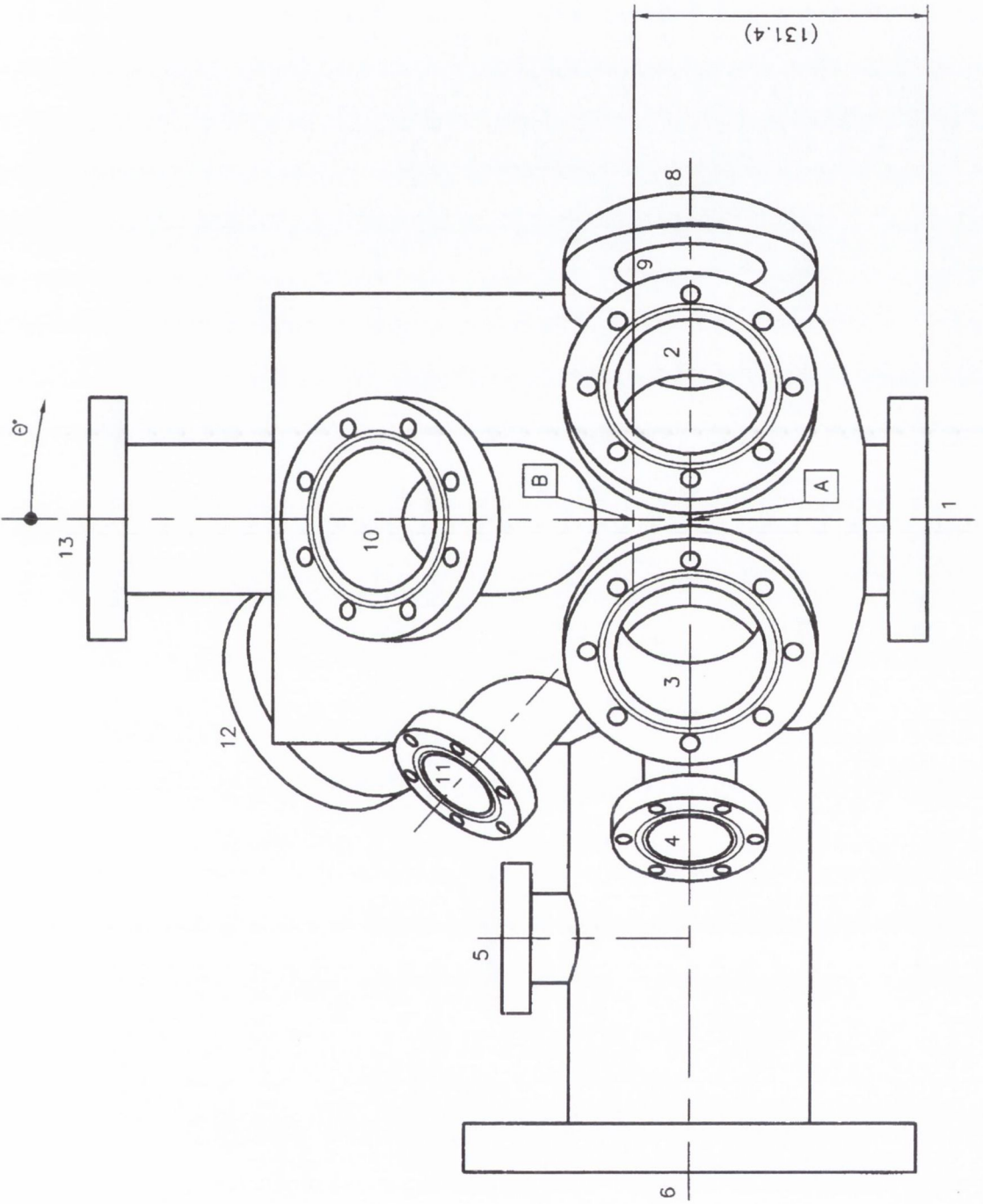
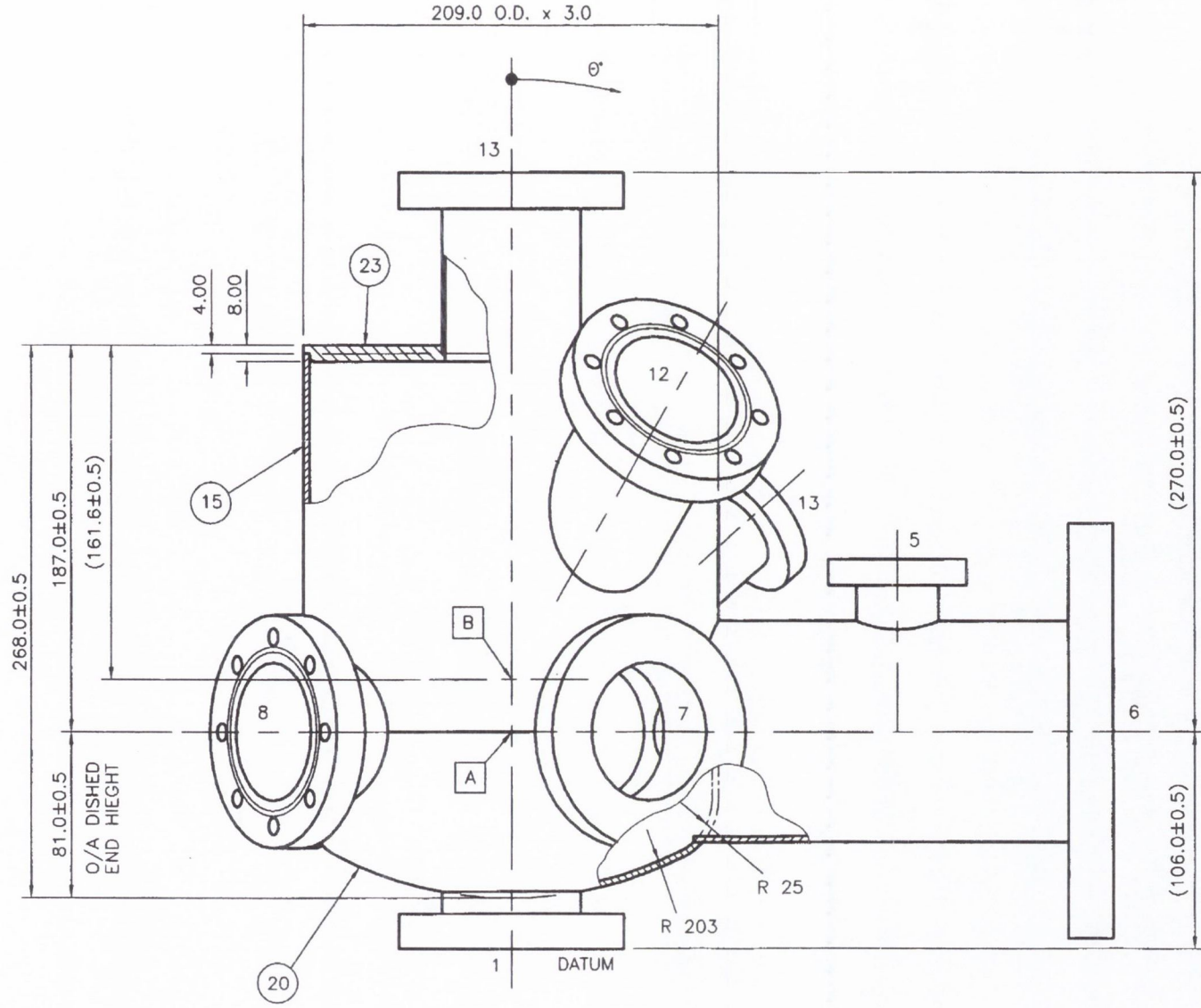


Figure A.2: Front view.



Appendix B

Preparation chamber

PORT	FLANGE	TUBE	FOCAL POINT	LENGTH ±0.5	φ° ±0.5°	θ° ±0.5°	USE
1	CFR114-63	63.5 O.D. × 1.6mm	A	168.5	0	0	GATE VALVE
2	CF70-70	69.8 O.D. × 1.6mm	A	150	270	48	WOBBLESTICK
3	CF114-63	63.5 O.D. × 1.6mm	A	200	270	90	HEATER STAGE
4	CF114-63	63.5 O.D. × 1.6mm	A	230	308	90	VIEWPORT
5	CF200-156	156.0 O.D. × 3.0mm	A	167	0	90	CLUSTER
6	CF70-41	41.2 O.D. × 1.6mm	A	160	47.7	63.5	VIEWPORT
7	CFR70-41	41.2 O.D. × 1.6mm	A	150	90	56	SPARE
8	CFR70-41	41.2 O.D. × 1.6mm	A	157	90	90	GATE VALVE
9	CFR114-63	63.5 O.D. × 1.6mm	A	210	90	124	GATE VALVE
10	CFR200-156	156.0 O.D. × 3.0mm	A	167	180	90	EVAP. STAGE
11	CFR70-41	41.2 O.D. × 1.6mm	B	140	270	90	SPARE
12	CF70-41	41.2 O.D. × 1.6mm	B	140	315	90	SPARE
13	CF114-63	63.5 O.D. × 1.6mm	C	140	180	90	XYZ DRV.

Table B.1: Preparation chamber port table.

PORT	FLANGE	TUBE	FOCAL POINT	LENGTH ±0.5	φ° ±0.5°	θ° ±0.5°	USE
14	CFR114-63	63.5 O.D. × 1.6mm	C	200	270	90	SPARE
15	CF70-70	69.8 O.D. × 1.6mm	D	166	270	124	WOBBLESTICK
16	CF114-63	63.5 O.D. × 1.6mm	C	214	308	90	VIEWPORT
17	CF114-63	63.5 O.D. × 1.6mm	C	235	330.2	125.4	VIEWPORT
18	CF150-108	108.0 O.D. × 3.0mm	C	167	0	90	CMA
19	CF114-63	63.5 O.D. × 1.6mm	C	235	29.8	125.4	VIEWPORT
20	CF70-41	41.2 O.D. × 1.6mm	C	140	53	90	SPARE
21	CFR200-156	156.0 O.D. × 3.0mm	G	167	180	90	ION PUMP
22	CF150-108	108.0 O.D. × 3.0mm	E	270	270	130	GATE VALVE
23	CF150-108	108.0 O.D. × 3.0mm	F	167	0	90	SPARE
24	CF70-41	41.2 O.D. × 1.6mm	C	430	0	169	VIEWPORT
25	CF70-41	41.2 O.D. × 1.6mm	C	430	90	169	SPARE
26	CF70-41	41.2 O.D. × 1.6mm	C	430	180	169	SPARE
27	CF70-41T	41.2 O.D. × 1.6mm	A	651.5	0	180	MAG. DRIVE

Table B.2: Preparation chamber port table (*continued*).

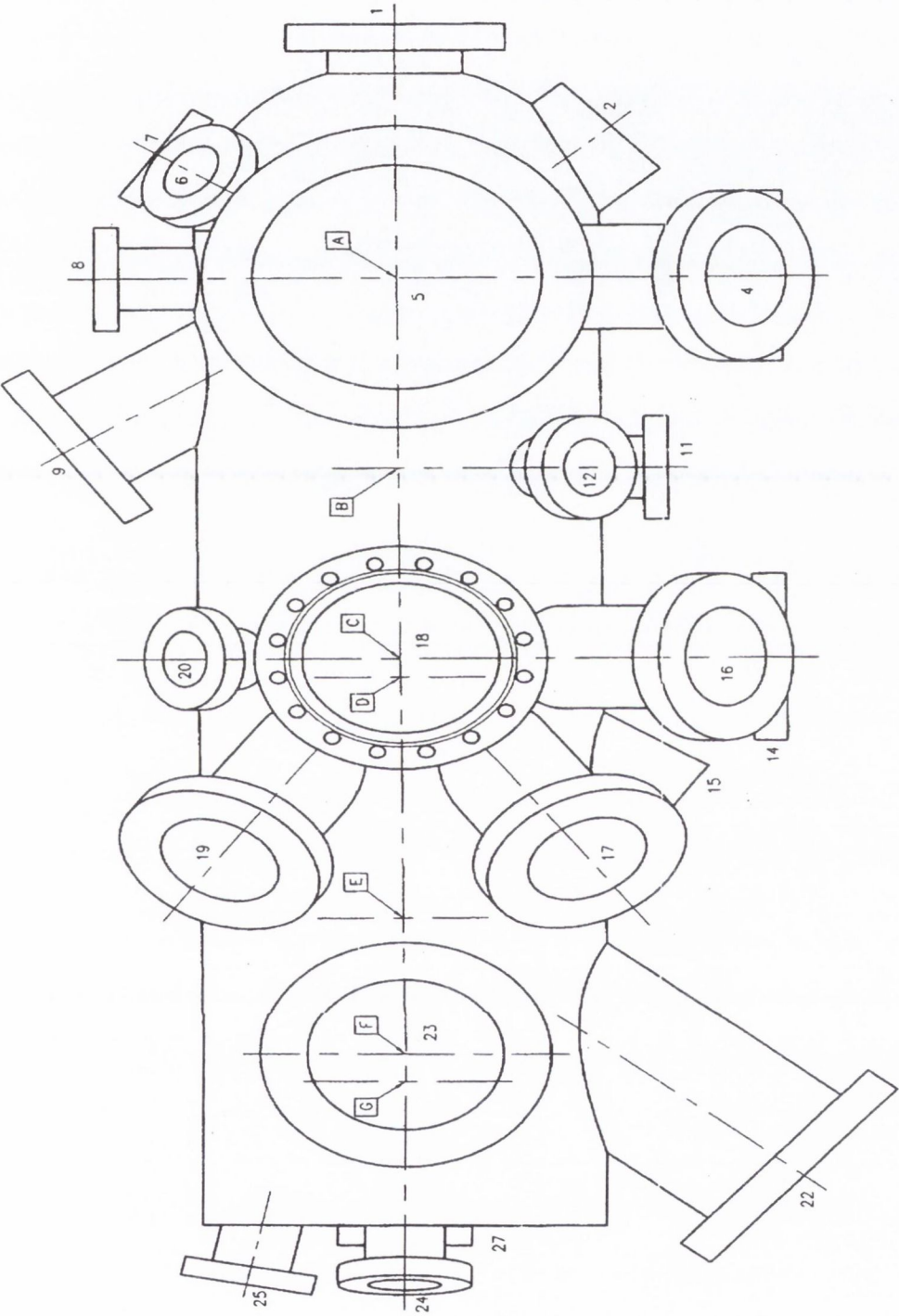


Figure B.1: Top view.

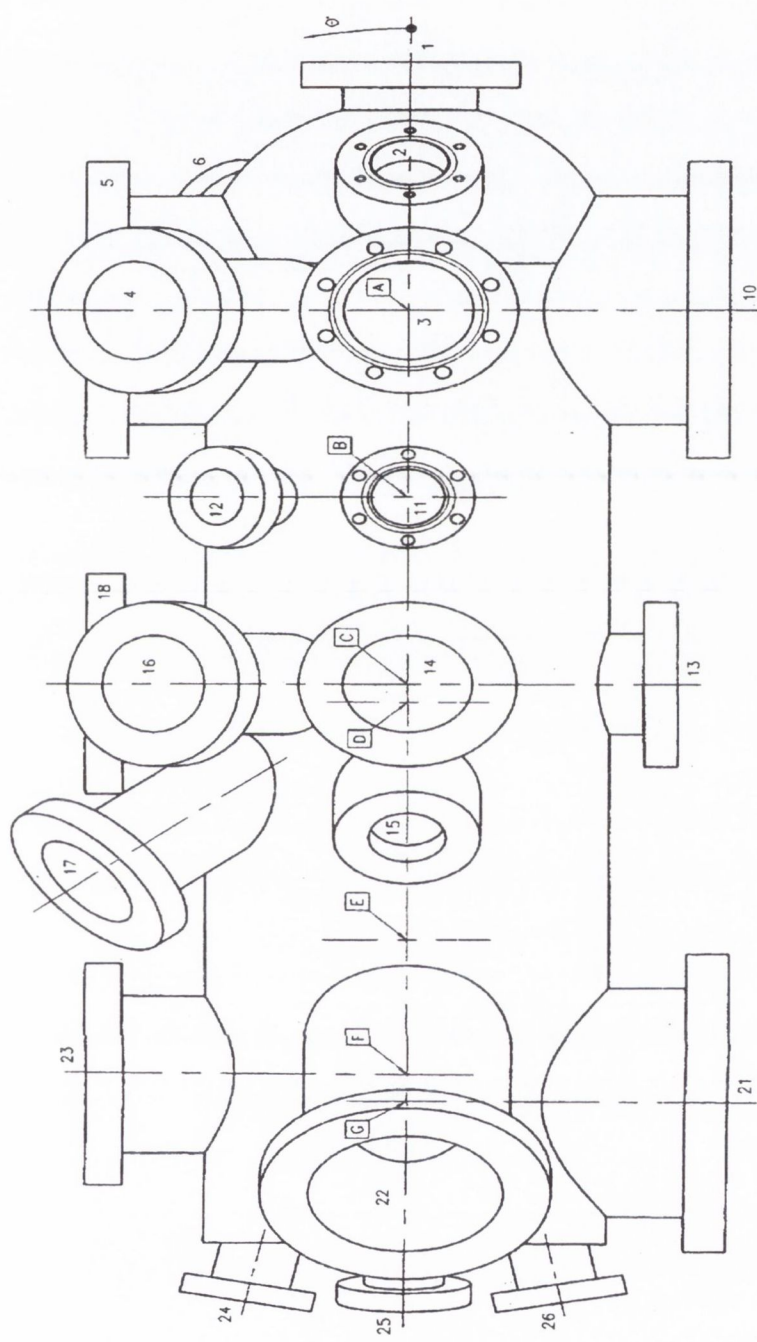


Figure B.2: Left side view.

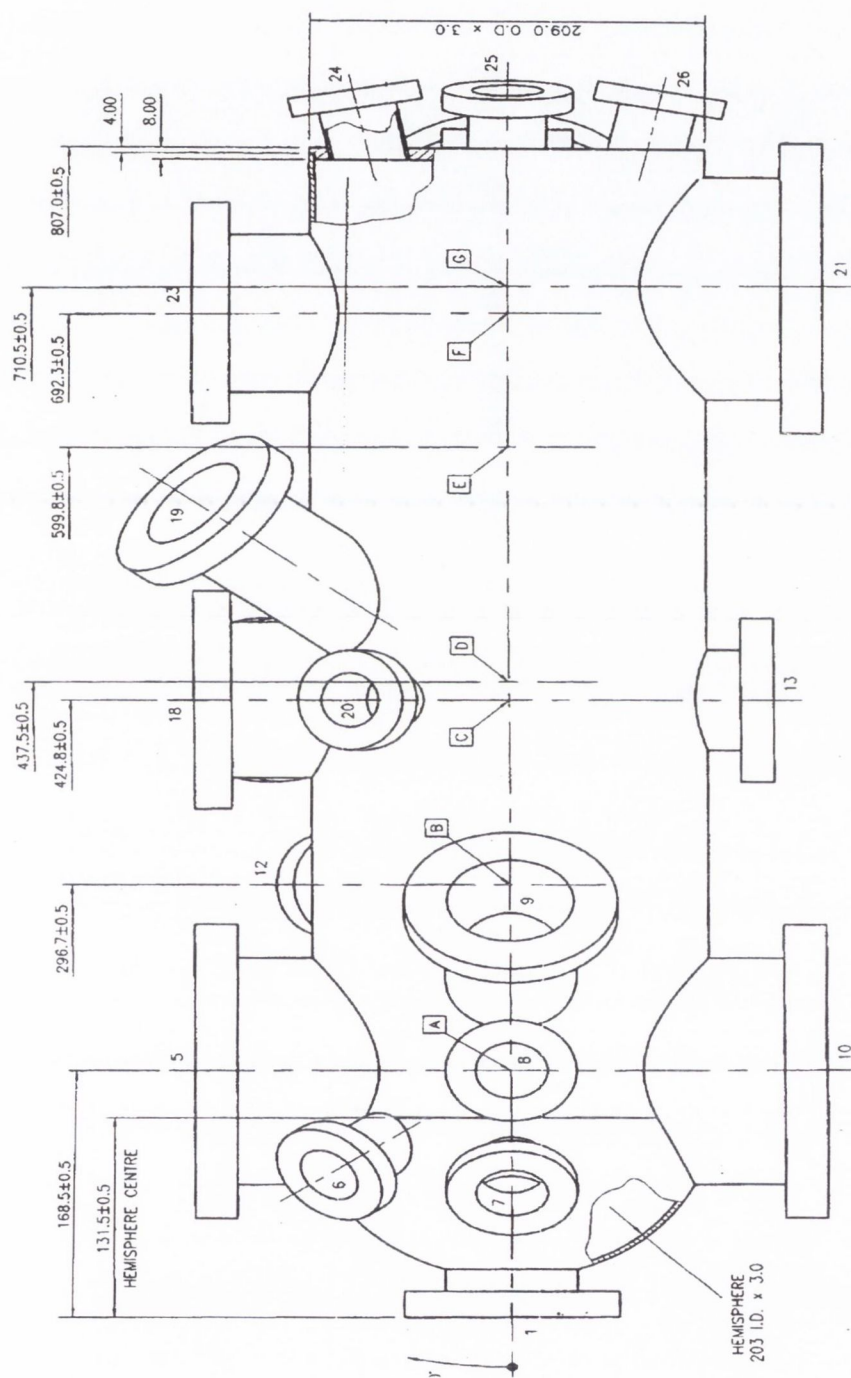


Figure B.3: Right side view.

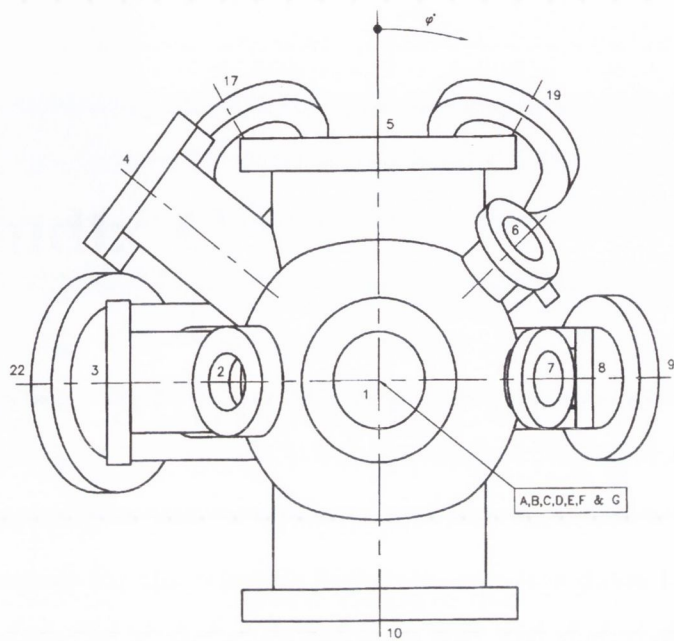


Figure B.4: Front view.

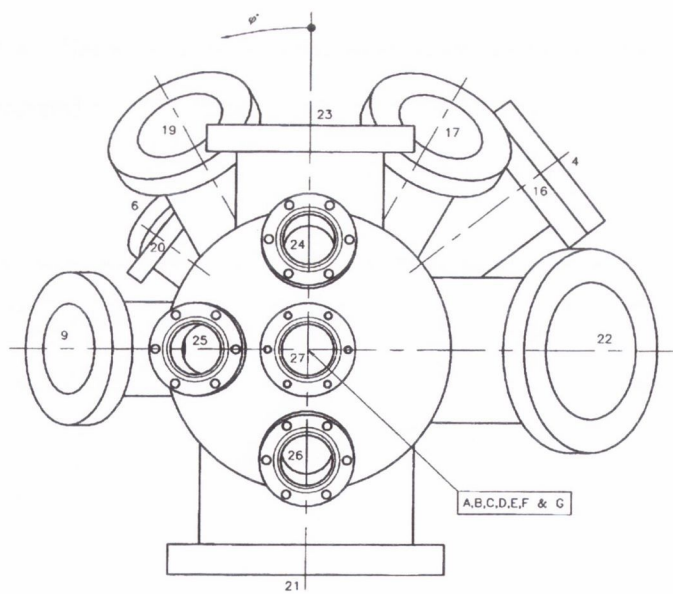


Figure B.5: Rear view.

Appendix C

Heater calibration curves

Calibration curves for the resistive heater on separate dates for different filaments. (a) gives the temperature readings with the thermocouple attached in various positions, while (b) gives the reading for the thermocouple spot-welded to the face of an upside-down sample-holder. The calibration in the first case was carried out by J. Naumann. The latter calibration was performed by Dr. C. Seoighe and G. Mariotto, after the original filament in the heater was changed.

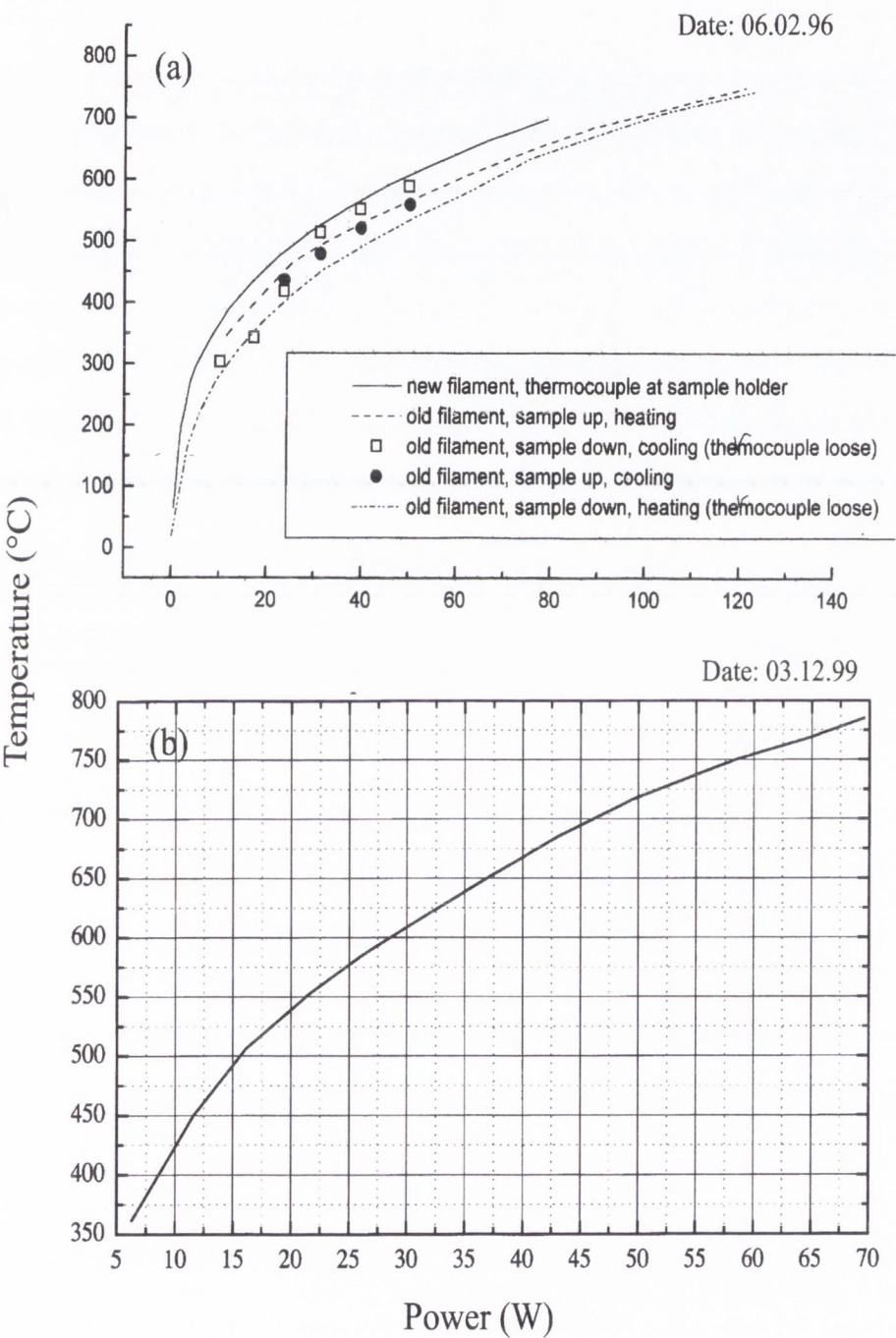


Figure C.1: Resistive heater calibration curves.

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