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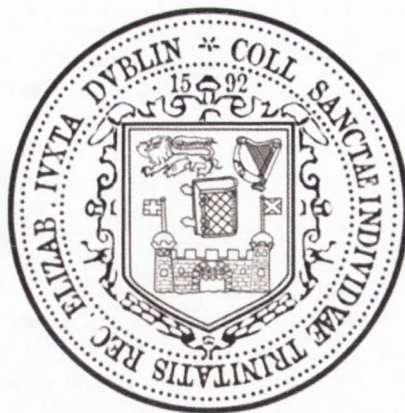
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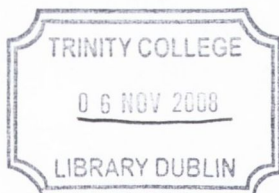
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A novel scanning probe microscopy study of the (110)
surface of rutile titanium dioxide

Simon Joseph O'Brien



Thesis submitted for the degree of

Doctor of Philosophy

March 2008

Supervised by Prof. J.B. Pethica

THESIS
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Declaration

The work in this thesis is based on research carried out in the Nanomechanics research group of Professor John B. Pethica at Trinity College Dublin. This work has not been submitted as an exercise for a degree at this or any other University. This thesis is entirely my own work unless referenced to the contrary in the text . I agree that the Library may lend or copy the thesis upon request.

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Abstract

This work describes the application of a novel multi-parameter scanning probe technique to the study of a model semiconductor and a metal oxide surface. Our novel scanning probe technique enables the simultaneous measurement of tunneling current, force gradient, barrier height and dissipation through the use of sub-Angstrom oscillation amplitudes.

Investigation of the Si(111) (7×7) revealed that the force gradients are generally more attractive over the corner holes than over the surface adatoms. The influence of possible crosstalk with the STM topography was eliminated by performing flat-trajectory imaging with only a moderate reduction in the force gradient corrugation. Evidence of some dependance on the tip material was discovered by using silicon as well as tungsten tips. Silicon tips sometimes showed an inverted contrast (corner holes less attractive) which was likely due to a tip change. Such contrast was never observed using tungsten tips.

Simultaneous measurement of the variation in tunneling current and force gradient with distance has been made on the $\text{TiO}_2(110)$ (1×1) surface. Both silicon and tungsten tunneling tips at setpoint currents of between 0.1-0.4 nA experience a force interaction which is likely to be close to or beyond the minimum of the force gradient curve and may in certain cases become repulsive. This would indicate that the assumption of a non-interacting tip as assumed in Tersoff and Hamann models is not valid for the imaging of the $\text{TiO}_2(110)$ (1×1) surface.

In our images of the $\text{TiO}_2(110)$ (1×1) a variety of different contrast regimes are observed showing defects as both bright and dark objects in simultaneous STM topography and force gradient imaging. In fact, the majority of our STM images show defects as dark objects between dark rows, indicating that in most of the images the STM topography reflects the actual topography of the surface and is not dominated by the electronic structure. This is contrary to the orthodox understanding of STM contrast on this surface (i.e. that electronic structure dominates) which is supported by local density of states calculations. The simultaneously acquired force gradient images however, show that defects generally appear as bright objects on bright rows i.e. less attractive, regardless of the contrast in STM. Furthermore, simultaneously acquired barrier-height data also show defects as dark objects i.e. lowered barrier-height, which is consistent with theoretical calculations made on the electronic structure of the surface.

Our results show that with STM imaging, identification of surface defects is risky since STM contrast may be greatly affected by the tip electronic structure. By recording multiple parameters simultaneously during scanning however, there is the possibility of more rigorous labeling of atomic features where ambiguity regarding tip and registry are removed. Comparison of different sets of images of defects show features which are consistent in STM, force gradient and barrier height .

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Acknowledgments

Firstly, I would like to thank my supervisor Prof. John Pethica for his support, guidance and encouragement throughout my time in the nanomechanics research group. I would also like to thank the other members of the team; Dr. H. Özgür Özer for his expertise and leadership in modifying the AFM/STM, Dr. Graham Cross for his assistance with the nano-indenter and FIB, and my fellow graduate students Andrew Norris and Barry O'Connell for their support and camaraderie. I would also like to thank Prof. Ahmet Oral and the staff of Nanomagnetics Instruments for their technical support with the software and assistance in the optimisation of the interferometer.

I would like to thank the members of the support staff within the SFI-Trinity Nanoscience Laboratory (later the Centre for Research in Adaptive Nanostructures and Nanodevices) and the School of Physics; Jacqueline Ballentine-Armstrong, Tracy Byrne, Mick O'Reilly, Mike Finneran, Ciaran Clinton, Susan Dunne, Ger Hanley, Collette Keleher, Aoife Ní Dhubhlaoich, Camilla Kelly, Catherine Smith, John Kelly, Joe McCauley, Ken Concannon and Chris Smith.

I would like to acknowledge the financial support of Science Foundation Ireland and Intel Ireland Ltd. At Intel I would particularly like to thank Paul Ahern and Pdraig O'Murchu.

I would like to thank Dr. Georg Herborg Enevoldsen, Dr. Gregory Cabailh, Dr. Chi Lun Pang, Dr. Markus Heyde, Dr. Clemens Barth, Prof. John Sader, Prof. Russ Egdel and Prof. Uzi Landman for support and useful discussions.

I would like to thank all the people I have had the pleasure and privilege to work alongside over the last few years including ... Sandhya Chandola, Lee Carroll, Justin Wells, Prof. Iggy McGovern, Alan Farrell, Emma Kerr, Ken Jordan, Eoin Clifford, Guiseppe Manai, William Signac, Michael Higgins, Takeshi Fukuma, Takeyuki Uchihashi, Jason Kilpatrick, Anika Mostaert, Gillian Kaggwa, James McGarry, Geraldine Kelly, Paula Maguire, Davy Corish, Niamh Murray, Géraldine Guex, Christian Riener, James Doyle, Rob Gunning, Richard Langford, Cathy Boothman, Franklyn Burke, Kaan Oguz, Ciarán Fowley, Gen Feng, Zhu Diao, David Blonde, John Sheridan, Niall Kinahan, Peter Ryan, Shane Murphy, Martin Polcik and many more.

Finally, I would like to thank my parents and family for their encouragement and I would like to give special thanks to my wife Suzi for her support and advice, and to our son Liam for always knowing what is most important (Liam!).

List of Abbreviations

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
DFT	Density Functional Theory
FIB	Focussed Ion Beam
FM-AFM	Frequency Modulation Atomic Force Microscopy
LEED	Low Energy Electron Diffraction
MEIS	Medium-Energy Ion Scattering
NC-AFM	Non-Contact Atomic Force Microscopy
PES	Photoemission Spectroscopy
PhD	(Scanned-energy mode) Photoelectron Diffraction
PZT	Piezoelectric tube
SEM	Scanning Electron Microscope
SPM	Scanning Probe Microscopy
STM	Scanning Tunnelling Microscopy
SXRD	Surface X-Ray Diffraction
UHV	Ultra-High Vacuum
UPS	Ultra-violet Photoelectron Spectroscopy
XPD	X-ray Photoelectron Diffraction
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

1.1 Motivation

The study of solid surfaces and the interaction of other molecules with them is of fundamental importance in many aspects of modern technology. How molecules are adsorbed at a surface, their bonding, diffusion and aggregation there, all affect their catalytic behaviour and their use as substrates for the growth of other materials.

The semiconductor microelectronics industry in particular, relies on the preparation and growth of high quality surfaces. The growth of thin films ranging in thickness from a few microns down to a few nanometres is an integral part of device fabrication. Surface science is therefore key to advances in semiconductor device manufacturing. For decades the semiconductor industry has depended on the near ideal interface between Si and the insulating SiO_2 oxide layer for the construction of logic and memory devices. In 1965 Gordon Moore published an article which proposed that the density of devices would double every 18 months, a prediction which was to become known as Moore's Law [1]. So far the prediction has proven an accurate description of the progress made in

Si-based technology. However with current device dimensions pushing the limit of what can be achieved using SiO_2 (i.e. gate oxides only a few atomic layers thick (see Fig.1.1 adapted from [2]) it has become clear that a change in material is due. Such narrow gate widths lead to increasing problems with current leakage across the dielectric. To solve this problem device manufacturers have already begun introducing dielectrics of higher permittivity (high- κ) [3]. This has enabled the use of a thicker layer of this high- κ dielectric [4].

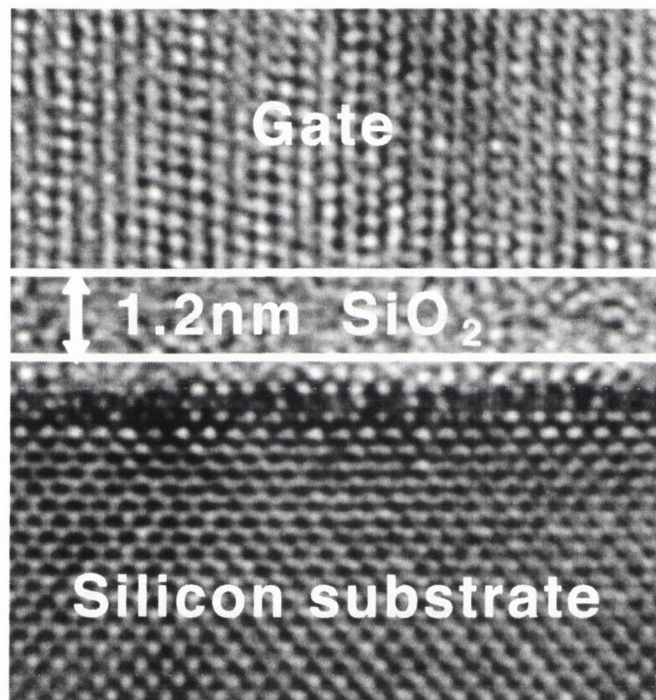


Figure 1.1: TEM cross-section of a silicon oxide gate. This was implemented in the Intel 90 nm (gate length) technology node. Advancements due in part to the development on novel high- κ gate dielectrics means that the current technology node is 45 nm (adapted from Chau *et al* 2004).

The difficulties involved in carrying out such a fundamental change in the construction of such devices cannot be understated. The excellent properties and simple preparation

ration of the Si/SiO₂ interface has allowed the rapid development of semiconductor technology since its inception and finding a worthwhile replacement is a major challenge [5]. Understanding the physics and chemistry of oxide surfaces at the nanoscale is crucial if a lasting solution to the gate dielectric problem is to be found [6].

Another area where surfaces are of fundamental importance is that of catalysis. Catalysis is the use of surfaces to selectively promote or control chemical reactions without the surfaces themselves being consumed in the process. This makes catalysis a very important resource for many major industries and hence worth billions to the economies of the world. They also have an important role to play in the development of alternative future energy sources such as hydrogen fuel cells [7]. This area of renewable energy is of particular relevance due to the growing concern surrounding the reliance of the global economies on finite supplies of fossil fuels and the environmental impact this has. Most of the development of catalysts has been done based on trial-and-error, however a more fundamental knowledge of physics and chemistry of these materials is required in order for the design of future catalysts to develop from an art into a science. The field of surface science developed largely in order to further our understanding of how the structure and energetics of surfaces affect their catalytic behaviour [8]. To this end a vast array of surface science techniques have been developed [9]. The contribution of surface science to catalysis was recently acknowledged with the awarding of the 2007 Nobel prize for chemistry to Gerhard Ertl.

Much of the literature on surface science of catalysts deals with characterising the adsorption of molecules on model surfaces (usually simple metals). These studies are of great importance since the bonding of a molecule to a surface (and how strongly it is bound to the surface) will determine how that surface will function as a catalyst.

While these studies have revealed much, the model surfaces are a very long way from the type of surfaces actually used in industrial applications [10]. Catalysts are often based on more complex materials such as metal oxides, nitrides, carbides etc. Despite their great technological importance, knowledge of the physics and chemistry of metal oxide surfaces is very limited compared to metal or semiconductor surfaces [11]. This is at least in part due to the significant technical challenges encountered when applying many surface science techniques such as photoemission and electron diffraction to these, often robustly insulating, materials. In recent years however, greater attention has been focussed on the surface science of metal oxides [12].

The application of techniques which are able to provide nanoscale information on catalytically important surfaces may provide key information on particular aspects of their behaviour. Firstly, while the study of adsorption of molecules on clean metal single crystals provides valuable information, real catalysts often consist of small metal particles on a metal oxide support [13]. The chemical behaviour of these surfaces is known to be highly dependent on the size of these particles. In the case of gold particles it has been found that clusters of radius of less than ~ 3.5 nm are highly active for a range catalytic reactions yet if the particle size is reduced below 3 nm the activity begins to drop [14]. Secondly, the clean stoichiometric basal surfaces of these materials (often studied in surface science experiments) are largely unreactive. Their reactivity increases however when defects are introduced and this presents a great challenge to surface science. Many surface science techniques use a probe such as a beam of photons (PES, XPS, UPS) or electrons (AES) which is incident upon the surface. The area of the surface which is exposed and on which data is collected is typically of the order of microns. The signal from surface defects is therefore much less than that from the

stoichiometric surface. Diffraction techniques such as x-ray photoelectron diffraction (XPD), surface x-ray diffraction (SXRD) and low-energy electron diffraction (LEED) are suited to surfaces over which there is reasonable long-range order and the ability of these techniques to provide information on surface defects is limited. The power of scanning probe techniques in real-space imaging of surfaces and adsorbates with atomic resolution has been demonstrated however, the quantitative and unambiguous interpretation of scanning probe data is still a major challenge to their application [15, 16].

In this thesis I have applied a novel scanning probe technique capable of imaging surfaces at atomic resolution to the study of a model oxide surface. It is shown that this novel multi-parameter approach to scanning probe microscopy may lead to a more realistic picture of how these techniques image this surface. It is also shown that by obtaining more information simultaneously and with the same tip more information can be obtained on important atomic scale defects.

1.2 Scanning tunneling microscopy

Invented in 1982 by Gerd Binnig and Heinrich Rohrer [17], the scanning tunneling microscope was an evolution of an earlier instrument developed by Russell Young and co-workers called the topograpfiner [18]. The basic components of the scanning tunneling microscope are a sharp conducting tip mounted on a scanner which can precisely position the tip close to a sample surface (Fig. 1.2). A bias voltage is applied between the tip and the sample so that once the tip-sample distance is small enough a tunneling current passes between the tip and the sample. The tunneling current signal is used in a feedback loop to control the z -position of the tip. The tip is then raster scanned across an area of the surface in either topographic or constant height mode. In topographic mode the z -position of the tip is adjusted so as to keep the tunneling current constant and the variations in z are recorded. In constant height mode the z -position remains fixed while the tip is scanned across the surface and modulations in the tunneling current are recorded. The constant current mode is most commonly used since operating in constant height mode can result in the tip crashing into the surface due to drift or a misalignment of the tip and sample.

The principle behind the operation of the STM can be described by considering the tip in close proximity to the sample as a 1-dimensional tunneling junction (Fig. 1.3). Quantum mechanically, a particle such as an electron can penetrate a potential barrier where the height of the potential barrier (ϕ) is greater than the energy of the particle (E). Within the forbidden region of the potential barrier the wave function of the particle (ψ) decays exponentially as a function of distance i.e.

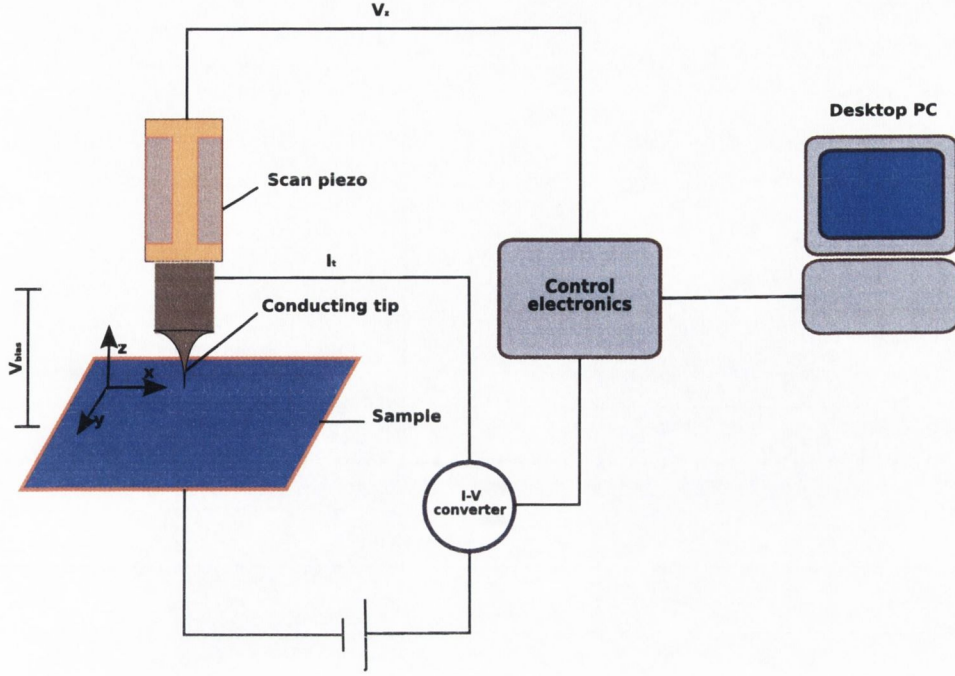


Figure 1.2: Schematic of scanning tunneling microscope. A bias voltage is applied between the sharp conducting tip and the sample. The tunneling current is converted to a voltage which provides the signal to a feedback circuit regulating a scan piezo which controls the z -height of the tip.

$$\psi(z) = \psi(0) \exp - 2 \frac{\sqrt{2m(\phi - E)}z}{\hbar} \quad (1.1)$$

where m is the mass of the particle and $\hbar$ is 1.05×10^{-34} Js. Applying this to the case of the STM, where the potential barrier is the gap between the conducting tip and the sample and z is the gap width, an expression for the tunneling current (I_t) can be obtained by modifying Eq. 1.1 to include the density of states at the sample Fermi edge ($\rho_s(E_f)$) and the tip-sample bias voltage (V).

$$I_t \propto V \rho_s(E_f) \exp \left[-2 \frac{\sqrt{2m(\Phi - E)}z}{\hbar} \right] \propto V \rho_s(E_f) e^{-1.025 \sqrt{\Phi} z} \quad (1.2)$$

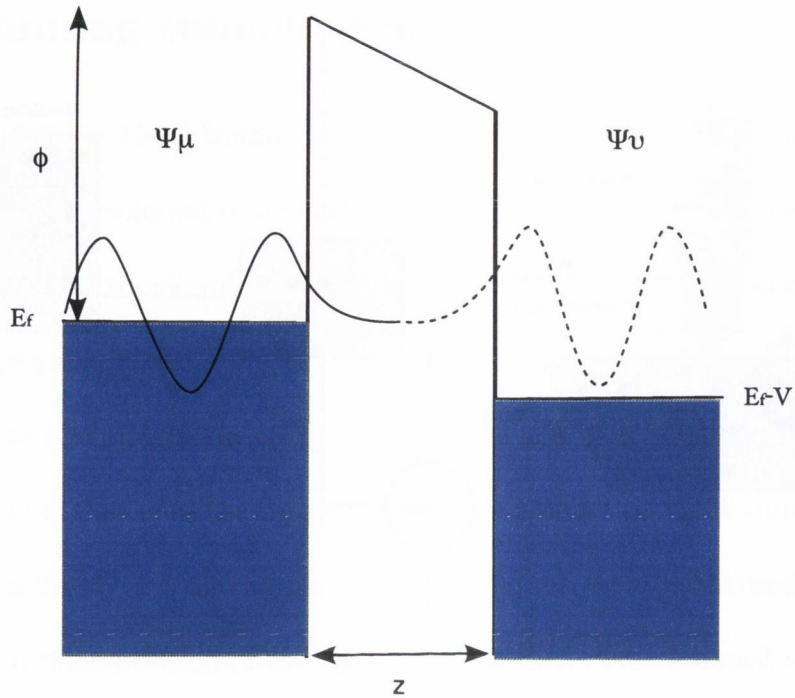


Figure 1.3: Energy-level diagram for a 1-dimensional tunneling junction

This gives an exponential dependence of the tunneling current (I_t) on the z -position of the tip relative to the sample. For example, taking as a barrier height the value of the work function of gold (5 eV), an increase of $1\text{\AA}$ in the vacuum gap results in an order of magnitude drop in the tunneling current. The exponential dependence of the tunneling current on the tip-sample separation is what makes atomic resolution possible in STM experiments. The possibility of resolving the atomic structure of flat surfaces in real-space made the STM an attractive tool for surface science [19]. In 1983 work by Binnig et al helped uncover the complex structure of the 7×7 reconstruction of the Si(111) surface using an STM in ultrahigh-vacuum (UHV) [20]. To date STM has been used to investigate a wide variety of surfaces, from semiconductors and metals to superconductors and oxides [21]. In 1990 Eigler et al published work on how the tip of an STM could be used to move individual atoms on a surface in a controlled

manner [22], this opened up another facet to this new technique; the ability to precisely and controllably manipulate single atoms on a solid surface [23, 24] and thereby create atomic scale devices [25, 26].

The simple 1-dimensional picture of the tunneling junction in STM presented above was extended to 3-dimensions by Tersoff and Hamann [27, 28]. Their model utilises the theory developed by Bardeen to describe tunneling between two superconductors through a oxide barrier [29]. According to Bardeen the tunneling current is given to the first order by

$$I_t = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} (f(E_\mu)[1 - f(E_\nu + eV)] \times |M_{\mu,\nu}|^2 \delta(E_\mu - E_\nu) \quad (1.3)$$

where V is the voltage applied between the probe and sample, $M_{\mu,\nu}$ is the tunneling matrix between the tip state ψ_μ and the surface state ψ_ν and $f(E)$ is the Fermi function

$$f(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}} \quad (1.4)$$

In the limits of room temperature or below and small applied voltage (as is the case in tunneling between metals), the tunneling current can be expressed as,

$$I_t = \frac{2\pi}{\hbar} e^2 V \sum_{\mu,\nu} |M_{\mu,\nu}|^2 \delta(E_\nu - E_F) \delta(E_\mu - E_F) \quad (1.5)$$

From Bardeen the tunneling matrix can be written as

$$M_{\mu,\nu} = -\left(\frac{\hbar^2}{2m}\right) \int dS \cdot (\psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^*) \quad (1.6)$$

where the integral is over any surface which lies entirely within the barrier (in this case the vacuum gap).

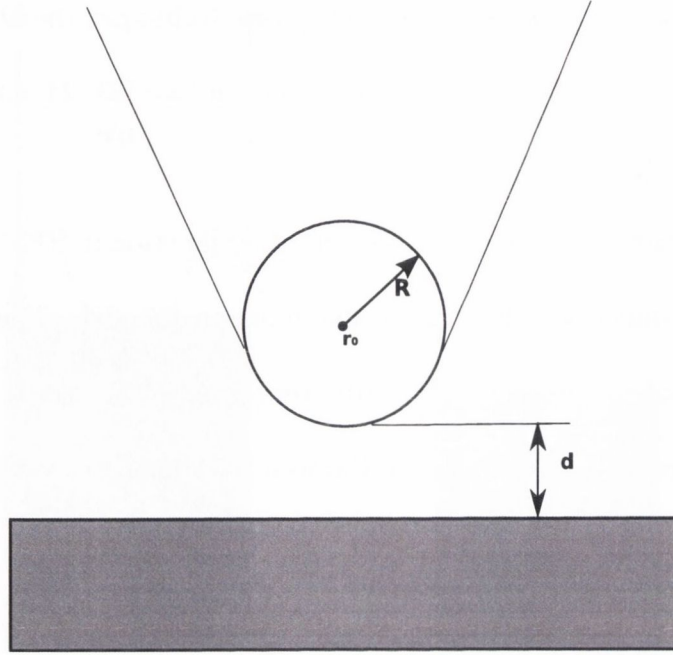


Figure 1.4: Schematic of the tunneling geometry used in the Tersoff-Hamman model. The tip is assumed to be locally spherical with the centre of curvature at r_0 and a radius R . The distance of closest approach is d

Assuming the tunneling geometry shown in Fig 1.4 where the tip apex is a sphere with radius R , the distance of closest approach to a flat surface d and the position r_0 is located at the centre of curvature of the tip, Tersoff and Hamann found an expression for the tunneling current

$$I_t \propto V_t \sum_{\nu} | \psi_{\nu}(\vec{r}_0) |^2 \delta(E_{\nu} - E_F) \quad (1.7)$$

where the sum is the local density of states at the centre of tip. What this expression means is that for the idealised Tersoff and Hamann model the STM topography in constant current mode is determined by the local density of states at the tip.

The Tersoff-Hamann theory provided an simple model for quantitative comparison with STM data and endures as the standard model for interpretation of STM experi-

ments. Unfortunately it makes several approximations which limit its application. The model assumes an idealised probe tip which has a spherical s-wave electronic structure, which for real tips may not be the case. At close separations the theory does not take into account the influence of the tip-sample interactions on the observed tunneling current. Furthermore the assumption that the applied voltage between the tunneling tip and the sample is small, while valid for tunneling into metals, is not valid for tunneling into other materials such as semiconductors and semiconducting oxides.

Even in the case of simple metals the Tersoff-Hamann approach cannot explain some of the observed atomic corrugations [30, 31]. Chen attributed the unexpectedly large corrugations to the presence of tip-states other than an s-wave [32]. Ciraci *et al.* introduced the concept of tip-induced localised states to explain the results [33]. A study by Doyen *et al.* showed that at small separations, where the assumptions of no interaction in Tersoff-Hamann theory are no longer valid, inversions in the apparent topography may occur [34]. The observation of forces acting during tunneling on metals [35, 36, 37, 38] has indicated that tip-sample forces and relaxations may have a significant role in STM [39, 40, 41, 42]. From this it can be seen that while the Tersoff and Hamann model is very useful plenty of evidence exists which would suggest that the model does not reflect what is actually happening in many experiments and that may be due to the role of the tip electronic structure and tip-sample forces.

1.2.1 Scanning barrier-height microscopy

By taking the log of the variation in tunneling current (δI) over a distance (δz) a measure of the local barrier height can be obtained. For a 1-dimensional barrier of height ϕ the barrier height may be expressed as

$$\phi(eV) = \frac{\hbar^2}{2m} \left(\frac{\delta \ln I}{\delta z} \right)^2 = 0.952 \left(\frac{\delta \ln I}{\delta z} \right)^2 \quad (1.8)$$

The barrier height is qualitatively equivalent to the work-function of the surface (Φ). When measured in scanning tunneling microscopy however there is often a considerable variation in the measured barrier-height. A number of possible factors were considered in the interpretation of measured barrier-heights from STM experiments. The effect of a classical image potential between an external charge and a planar metal surface has been studied by many authors [43, 44, 45, 46]. This was considered in a study by Binnig *et al* where the authors investigated the variation in barrier-height with applied bias and found that for a range of values $< 10 \text{ \AA}$ the apparent barrier-height showed little variation with separation [47]. This they explained by considering the induced image potentials canceling each other out. In a later study by Gimzewski and Möller [48] the authors found that for very low separations a significant reduction in the measured barrier-height was observed. This they explained by extending the calculations of Binnig *et al* to distances $< 3 \text{ \AA}$ where the onset of metallic conduction occurs. In a theoretical analysis both Lang [49] and Garcia [50] reported that the barrier effectively collapses at small separations. Another explanation for the observation of low barrier-heights in STM was provided by Coombs and Pethica [51] where the variation in tunneling current with separation is affected by the presence of contaminant particles between the tip and sample leading to an erroneous measurement of the tip excursion. This was supported

in a study by Mamin *et al* [52].

By modulating the tip height (z) at a frequency beyond the cutoff of the feedback electronics the variation of δI with respect to δz can be recorded during STM imaging [53]. Since the value of Φ depends on the local site potential it was hoped that the measurement of the local barrier-height variation across the surface would provide more information on the surface composition than STM alone.

This scanning barrier-height technique has been used to build up images of the variation of the local average barrier height across a surface [54]. In a study of the adsorption of sulphur atoms on the Mo(001) surface by Marchon *et al* both topographic and barrier-height mode STM was used [55]. The authors used the barrier-height images to support their identification of the sulphur adsorption site. They acknowledge however that the quantitative interpretation of the barrier-height images is difficult due to the contributions of the surface topography and local density of states. In an effort to account for the variation in the topography Gomez-Rodriguez computed the contribution of the cosine of the microscopic topography gradient to the measured normal variation in barrier-height [56]. On the atomic scale however it is not as clear how to separate out the contribution of the topography as highlighted by Pethica *et al* [57].

Later experimental investigations presented conflicting evidence as to whether or not the barrier height varies significantly at small separations [58, 59]. Differences in tip condition and relaxations due to the tip-sample interaction are thought to be at least partly responsible for the discrepancy.

1.3 Atomic force microscopy

The invention of the scanning tunneling microscope (STM) in the 1980's had opened up a new means with which scientists could study surfaces with atomic-scale resolution. Soon after the invention of the STM it was discovered that forces acting between the tip and the sample could explain some puzzling features of the measurements such as unusually low barrier heights [51, 60] and very large atomic corrugations [61]. The invention of the atomic force microscope [62] was motivated by the possibility of using the short range forces that act on an atomically sharp tip when it is brought into close proximity to a flat sample to themselves generate images.

Also from the point of view of studying insulating surfaces, STM still had the drawback of being limited to conducting or semiconducting samples since it relied on measuring the tunneling current. With the advent of the AFM came the possibility of making significant advances in the study of insulating surfaces akin to what had already been achieved with STM on semiconductors [20]. While closely related to the STM, AFM relies on the measurement of the forces acting on a cantilever with a sharp tip as it is scanned across a surface.

As shown in Fig. 1.5, a standard AFM setup consists of a flexible cantilever (typically silicon) which has a sharp tip on one end. The sample is mounted on a piezoelectric tube (PZT) which can accurately position the sample in x y and z directions. As the sample approaches the sharp tip the tip-sample interaction results in a deflection of the cantilever. If we treat the cantilever as a linear spring this deflection can be related to the force by Hooke's Law,

$$F = -kx \tag{1.9}$$

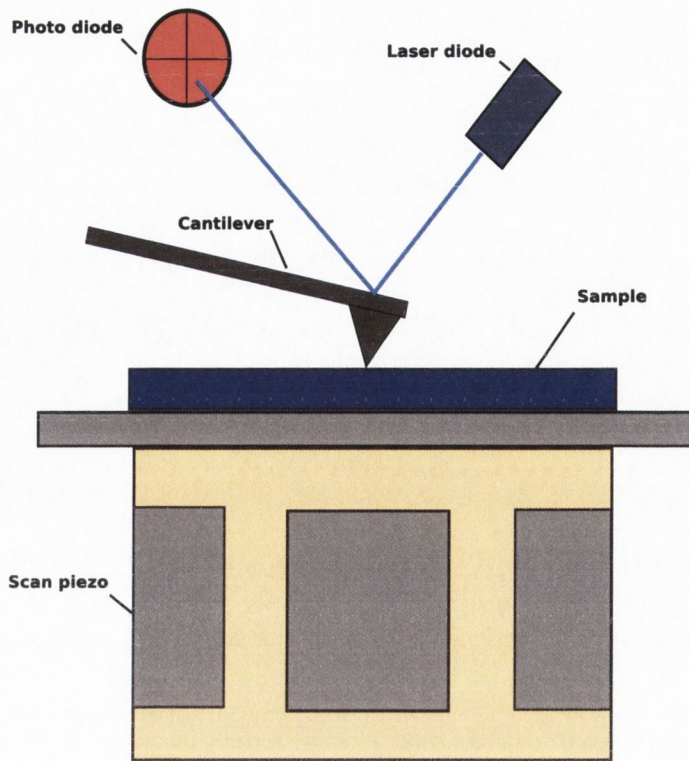


Figure 1.5: Schematic of a conventional atomic force microscope with a beam deflection detection system. A sharp tip mounted on a flexible cantilever is brought into close proximity or even in contact with the sample. The forces acting on the tip result in a deflection of the cantilever. This deflection is detected by the motion of a laser spot on a quadrant photo-diode.

where k is the stiffness of the spring (or cantilever) and x is the extension of the spring (displacement of the cantilever). From this it can be seen that for meaningful force data to be extracted from such a setup accurate values for the lever deflection and the lever stiffness are required.

In most standard commercial AFM instruments the deflection of the cantilever is detected using a setup like the one shown in Fig. 1.5. This consists of a laser-beam which is reflected off the back of the cantilever and onto a quadrant photodiode. The

cantilever deflection results in a change in path of the beam and hence the point on the photodiode at which beam arrives. This optical beam deflection detection system, while almost certainly the most widely used, is only one of many different setups which have been tried. The first AFM used a tunneling tip mounted behind the cantilever to detect the displacement of the cantilever [62]. While very sensitive, this method suffers from some drawbacks. As with an STM the displacement signal (tunneling current) is sensitive to contamination of the tip of cantilever. Also the measured tunneling current will be affected by the topography of the cantilever surface, this will affect the measured deflection of the cantilever as the tip position on the cantilever changes over time due to drift. Another widely used detection method is optical fiber interferometry [63, 64]. This detection method (discussed in more detail in section 3.1) is highly sensitive, providing a direct measurement of the cantilever deflection calculated from the wavelength of the light. Other detection systems involve the use of piezoresistive cantilevers where the deflection of the cantilever is detected as a change in the resistance of the lever. Using a quartz tuning fork the Q-plus sensor detects the tip-sample interaction as a change in the resonance frequency of the tuning fork [65]. These type of detection systems are particularly suited to low-temperature applications where external detection systems suffer from drift due to temperature gradients across the apparatus.

Regardless of which detection system is used, in order to obtain quantitative force information, accurate values for the deflection and the stiffness of the cantilever are required. Quantitative deflection measurement necessitates the calibration of the deflection detection system. One method of calibrating the deflection detection is to decrease the tip-sample distance until the tip and sample are in contact. The tip is then pushed a known distance past the point of contact. If the scanner PZT z-height is correctly

calibrated and significant deformation of the tip into the sample is discounted then it can be taken that the known displacement of the cantilever corresponds to the resultant change in detected signal. This has the disadvantage of effectively destroying the tip.

There are various methods for calibrating the stiffness of the cantilever. One indirect method is to calculate the stiffness of the cantilever beam using the geometry and the known bulk stiffness of the material. Another uses the measured thermally induced vibrations of the cantilever at resonance which can be related to the mechanical energy. The most reliable method for determining the stiffness is to push the cantilever against a known spring and measure the resultant displacement. These methods for obtaining a stiffness value are further discussed in section 3.2.

There are various different modes of AFM operation but they can be broadly grouped under either static or dynamic modes as described in the following sections.

1.3.1 Static atomic force microscopy

Static AFM techniques involve measuring the tip-sample interaction forces by monitoring the static deflection of a cantilever as the tip is scanned across a flat surface. Unlike STM, the imaging signal in AFM (i.e. the tip-sample force) does not necessarily vary monotonically with separation. This is because the measured forces may be a convolution of both attractive and repulsive forces.

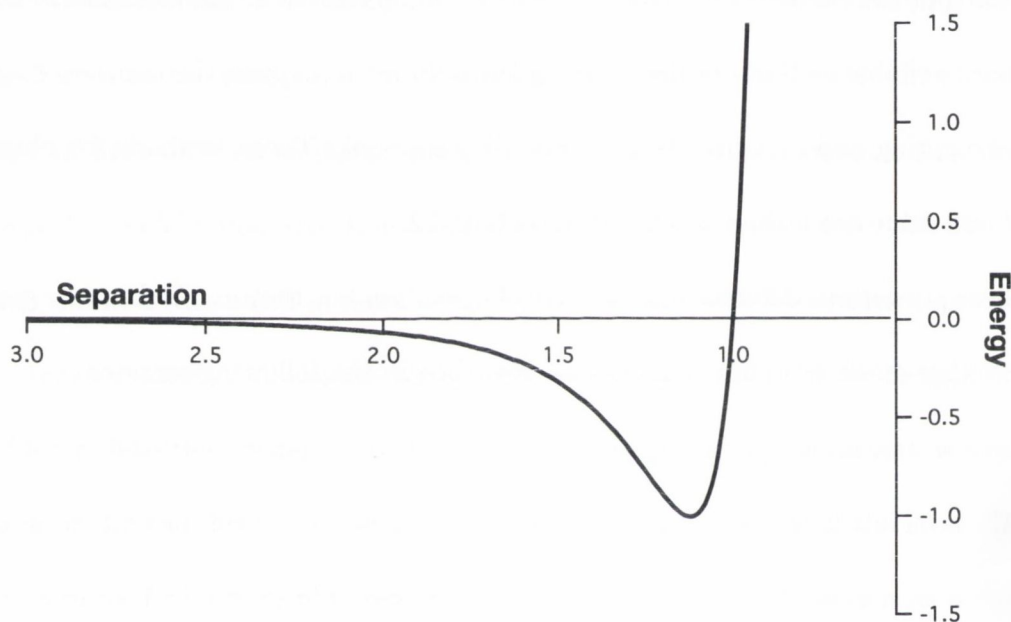


Figure 1.6: Graph of a Lennard-Jones potential.

This is illustrated by the Lennard-Jones potential which describes the forces between two neutral noble gas atoms (Fig.1.6). At large separations there is an attractive interaction potential which varies with separation R^{-6} due to a van der Waals interaction which has its origin in the varying dipoles of the atoms. At small separations there is a repulsive interaction which varies as R^{-12} with separation. This short-range repulsive interaction is due to the overlap of the electron orbitals of the atoms and arises from

the Paul exclusion principle [66].

One of the first questions to be asked of AFM was whether or not it could image single atomic features in real-space as had already been achieved with STM under UHV conditions. In early static AFM experiments levers of very low stiffnesses ($\ll 1$ N/m) were used in order to increase the sensitivity of the force measurement. As a result of this, early UHV AFM experiments suffered from an instability at very small separations which resulted in a jump-to-contact [67]. This instability occurred when the interaction stiffness (or force gradient) exceeded the stiffness value of the cantilever, causing the tip to snap into the surface. This leads to the formation of an adhesive contact of finite area between the tip and sample even at very small applied loads [68]. This finite area has been calculated to be greater than one atomic site. This implies that the images from some experiments, while they show atomic periodicity, are tip-averaged. In order to prevent the jump-to-contact the most obvious solution is to use much stiffer levers, resulting in a loss of sensitivity. In 1993 Ohnesorge and Binnig described an experiment where they immersed their sample in water in order to screen the long-range attractive forces [69]. This enabled them to achieve resolution of atomic scale defects on calcite. While successful, this solution to the jump-to-contact problem was limited in the kinds of samples and environment to which it could be applied.

The problem of how to access the short-range atomic forces which would provide the imaging signal for true atomic resolution in UHV was a major obstacle. To overcome this obstacle required the application of dynamic AFM techniques.

1.3.2 Dynamic atomic force microscopy

To avoid problems arising from operating with the AFM tip in contact, non-contact dynamic AFM techniques were developed. In early dynamic AFM experiments the tip was oscillated at a fixed frequency close to the first resonance. The tip-sample force gradient results in a shift in the resonance frequency which is detected as a change in oscillation amplitude (see Fig. 1.8). This technique was known as slope-detection since what was measured was related to the change in the gradient of the force interaction.

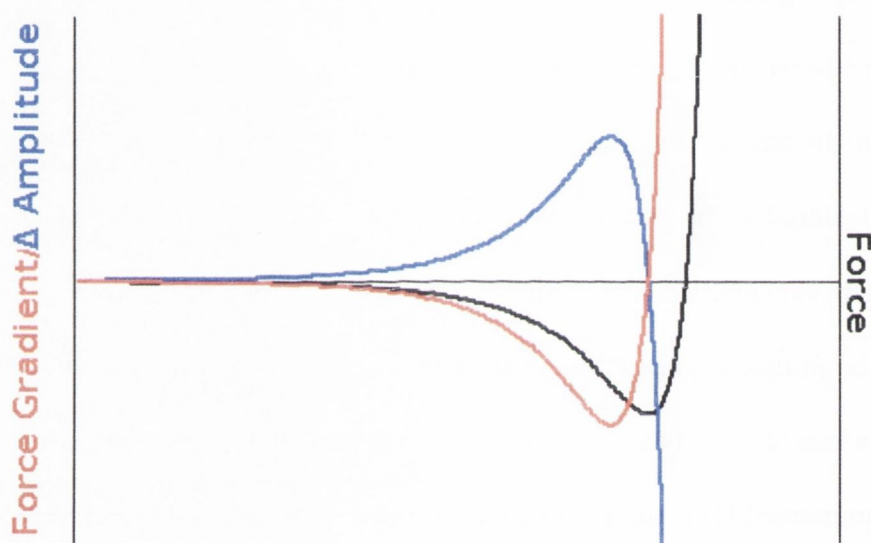


Figure 1.7: Plot showing the variation of force, force gradient and amplitude with separation. The zero of the x-axis (separation) is on the right. The curves were all calculated using a Lennard-Jones potential.

In order to maximise the signal-to-noise ratio it was desirable to use levers with a high quality factor (Q-factor). Increasing the Q-factor of the lever however results in an increase in the time constant (i.e. the response time) of the system. In 1991 Albrecht and co-workers developed a method for enhancing the sensitivity of high-Q AFM cantilevers

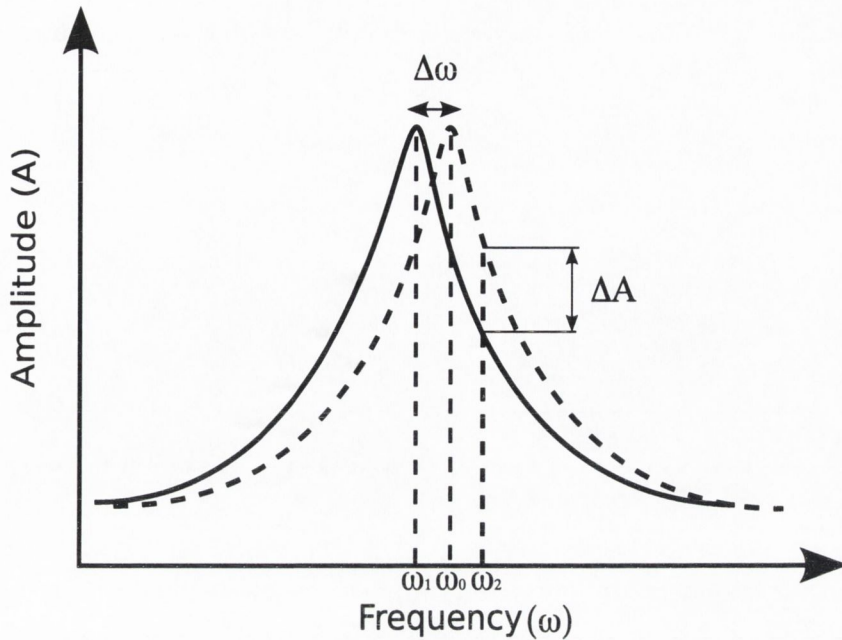


Figure 1.8: The cantilever is driven at a frequency ω_2 close to resonance frequency ω_0 . Due to the tip sample interaction the resonance frequency shifts by a certain amount ($\Delta\omega$) and as a result the amplitude at the driving frequency changes (ΔA).

without losing bandwidth by using them as the oscillators in a frequency shift feedback circuit [70]. This frequency-modulation (FM) technique recorded the change in resonant frequency of an oscillating cantilever due to the tip-sample interaction. This technique provided the means to improve the stability and sensitivity of AFM operation.

By applying this new technique in UHV Giessibl [71] and Kitamura and Iwatsuki [72] obtained true atomic resolution AFM images of the Si(111) 7×7 reconstruction. This was considered a milestone in the development of AFM as a technique capable of producing the same resolution on reactive surfaces as had already been achieved with STM [73, 74]. Subsequently FM-AFM became the technique of choice in UHV and has been used to image insulating oxide surfaces such as alumina [75] and MgO [76] .

As the tip approaches the surface the force gradient acting on the tip results in a

change in the effective stiffness of the lever. This new stiffness is the sum of the lever stiffness and the interaction stiffness:

$$k_{eff} = k_{lever} + k_{int} \quad (1.10)$$

where

$$k_{int} = -\frac{\partial F}{\partial z} \quad (1.11)$$

If we treat the oscillating cantilever as a simple harmonic oscillator then the frequency can be related to the spring constant by

$$\omega = \sqrt{\frac{k_{eff}}{m}} \quad (1.12)$$

then the frequency shift due to the an attractive force gradient will be

$$\omega = \left(\frac{k_{lever} - k_{int}}{m}\right)^{\frac{1}{2}} = \left(\frac{k_{lever}}{m}\right)^{\frac{1}{2}} \left(1 - \frac{k_{int}}{k_{lever}}\right)^{\frac{1}{2}} = \omega_0 \left(1 - \frac{k_{int}}{k_{lever}}\right)^{\frac{1}{2}} \quad (1.13)$$

where m is the effective mass and ω_0 is the resonance frequency of the cantilever. If k_{int} is small compared to k_{lever} then it can be said that

$$\omega \approx \omega_0 \left(1 - \frac{k_{int}}{2k_{lever}}\right) \quad (1.14)$$

and therefore

$$\frac{\Delta\omega}{\omega_0} = -\frac{1}{2k_{lever}} \frac{\partial F}{\partial z} \quad (1.15)$$

This approximate equation of frequency-shift and force gradient is however, only valid for oscillation amplitudes which are small compared to the length scale of the

interaction being measured i.e. where the force gradient is constant over the entire oscillation cycle. Such small amplitudes are difficult to achieve when working at resonance where an applied dither to the cantilever results in a much larger oscillation at the tip. For larger amplitudes more complex mathematical deconvolution is necessary.

Several methods of obtaining quantitative force data from measured frequency shifts for large oscillation amplitudes have been proposed. Giessibl developed a method based on first-order perturbation theory using a Hamilton-Jacobi approach where

$$\Delta f(z) = -\frac{f_0^2}{kA} \int_0^{\frac{1}{f_0}} F_{ts}(z_b + A \cos(2\pi f_0 t)) \cos(2\pi f_0 t) dt \quad (1.16)$$

where z_b is the vertical rest position of the tip [77]. Gotsmann *et al* presented a method based on a numerical algorithm to fit the results of a computer simulation to the frequency shift versus distance curves. Dürig [78] and Hölscher [79] proposed semi-analytical methods which work best in cases where the oscillation amplitude is much larger than the length-scale of the interaction. Dürig proposed another method which would work also for smaller amplitudes but requires detailed knowledge of the higher harmonics of the cantilever [80]. Later Giessibl published another algorithm which could be applied to arbitrary amplitudes yet was inconsistent in that the derivation of the algorithm relied on approximations based on the small amplitude case [81]. More recently Sader and Jarvis presented a set of formulae based on fractional calculus which are valid for arbitrary amplitudes [82].

From this discussion it can be seen that obtaining quantitative force data from large amplitude frequency shift data is seldom straightforward. Whatever deconvolution tools are employed however the fact remains that what is happening at larger amplitudes is that the force is integrated over the oscillation cycle and that the short range chemical

forces which should result in atomic resolution only act on the tip for a very small portion of the total oscillation cycle.

In an effort to impose some order on the required parameters for effective atomic resolution imaging Giessibl *et al* presented a set of first principles calculations of detailing the effect of varying oscillation amplitude on the signal-to-noise ratio for a variety of force interactions [83]. In this study it was shown that the optimal signal-to-noise was obtained where the oscillation amplitude and the length-scale of the interaction are equal. For typical short-range chemical forces responsible for atomic resolution in AFM this means an oscillation amplitude of $\sim 1 \text{ \AA}$. In order to probe the internal structure of the short-range interaction however, requires the use of even smaller oscillation amplitudes.

A recent study by Sugimoto *et al.* described their use of large-amplitude dynamic force spectroscopy and extensive modeling of a variety of tips in order to discriminate between different chemical species present on a surface [84].

1.4 Rutile titanium dioxide

Of all the metal oxide surfaces, titanium dioxide is probably the most widely studied. Its broad range of applications in areas such as gas sensing, pigments, catalysis, medical implants and microelectronics motivates the study of its physical and chemical properties. For surface scientists the material is appealing as a model oxide for a number of reasons, chief among them being that unlike many metal oxides it is not a robust insulator and therefore accessible via a wider range of surface science techniques. Recent interest in this surface has been increased due to its possible application in the electrochemical photolysis of water [7].

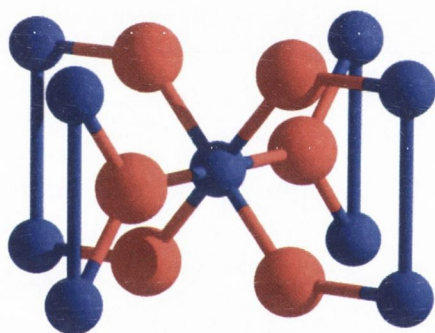


Figure 1.9: Titanium dioxide unit cell. Titanium atoms are shown in blue and oxygen atoms in red.

Ultra-thin coatings of TiO_2 have been deposited on glass in order to create a hydrophilic surface which also helps in the photocatalytic breakdown of organic materials on the glass, thereby creating 'self-cleaning' glass [85]. Crystalline titanium dioxide occurs in three different forms; rutile, anatase and brookite, rutile being the most stable. The rutile crystal structure is tetragonal with the space group $P4_2/mnm$. The bulk unit

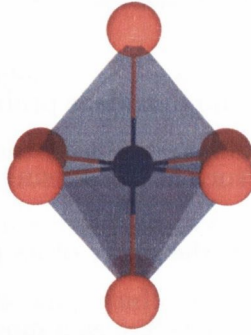


Figure 1.10: Titanium atom (blue) surrounded by six oxygen atoms (red) in a distorted octahedron

cell has the dimensions $a = b = 4.587 \text{ \AA}$, $c = 2.953 \text{ \AA}$ [86].

Single crystals of rutile TiO_2 are available from a number of sources supplying research substrates and optical materials. These crystals are translucent pale yellow in colour and can be reduced by annealing in vacuum which also results in the crystal colour changing to pale and then dark blue. The rutile crystal structure is made up of octahedra consisting of titanium atom surrounded by six oxygen atoms. These octahedral units are longer along one axis and neighbouring units share a corner along the $[110]$ directions with the long axis of each alternating unit rotated 90° .

1.4.1 The (110) surface of rutile titanium dioxide

In this section the rutile $\text{TiO}_2(110)$ surface is described and the status of the literature on the surface is reviewed, with more emphasis on the contribution of scanning probe techniques in Section 1.4.2.

Of the low-index surfaces, the (110) surface has the lowest surface energy and is therefore the most stable. Cleaving (or fracturing) the ideal bulk crystal along the (110) plane results in a surface consisting of rows of five-fold coordinated Ti atoms and 2-fold coordinated bridging O atoms running along the [001] direction. The rows of oxygen atoms are 6.5 Å apart in the [110] direction (see Fig 1.11). The bridging oxygens form the top layer, the next layer is a mixture of five-fold and six-fold coordinated Ti atoms and three-fold coordinated O atoms. The 5-fold coordinated Ti atoms have one dangling bond perpendicular to the surface plane. The bridging O atoms are undersaturated and are the focus of much of the discussion in the literature, as their removal by annealing is thought to be a dominant source of point defects on the surface. This bulk-like surface termination has a (1×1) structure which can be confirmed using LEED and other diffraction techniques.

The relaxation of the surface structure is another still developing topic in the literature. Early experimental [87] and theoretical [88, 89, 90] studies concluded that there were significant relaxations at the surface compared to the bulk. In 1997 Charlton *et al* published results of a SXRD study of the surface relaxations [91]. These results showed a significant relaxation of the surface atoms, and in particular the bridging oxygen atom which was measured to relax towards the surface by 0.27 ± 0.08 Å. That the bridging O-atoms should relax in this way had been predicted by surface energy calculations, quantitatively however the magnitude was almost twice what had been expected.

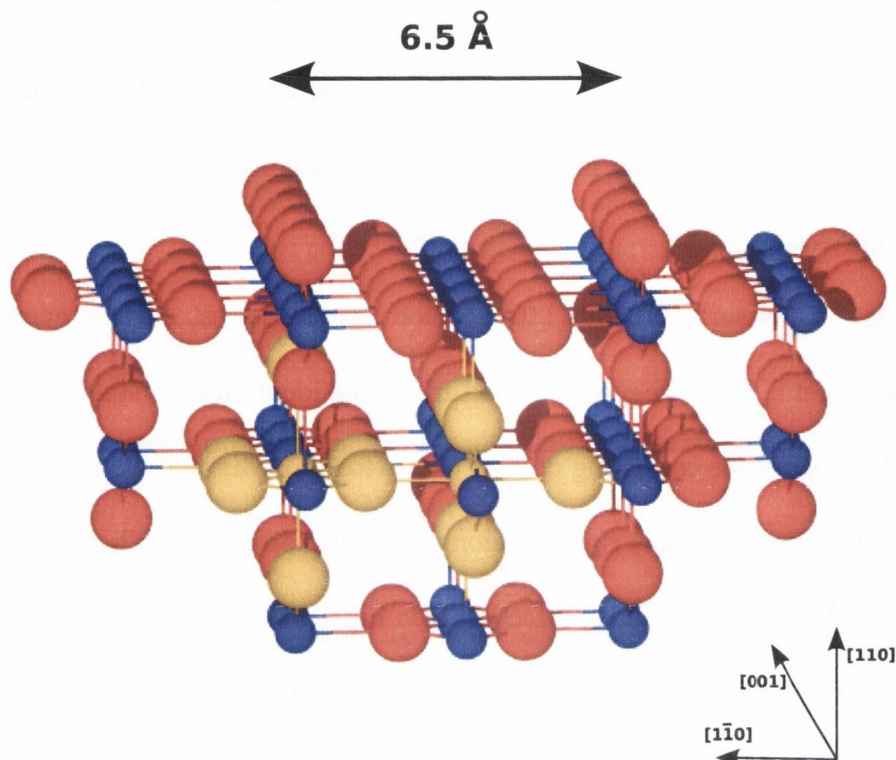


Figure 1.11: A ball-and-stick visualisation of the crystal structure of rutile TiO_2 (110) surface with two octahedral structural units highlighted in yellow

Further theoretical modeling studies did little to narrow the gap between theory and experiment and this was thought to be due to the existence of soft vibrational modes at the surface at room temperature [92], something which is not taken into account in simulations which usually assume zero temperature.

In a comparative study of computational modeling of the surface by Swamy *et al* [93] force field results based on a variable-charge potential and Matsui-Akoagi model were compared with quantum mechanical local density approximation (LDA) and Hartree-Fock (HF) simulations. The result of the variable-charge models were mutually inconsistent whereas the LDA and HF results were in agreement with each other but still quantitatively a long way from the relaxations measured by the SXRD study of Charlton

et al.

New experimental data was then introduced in a quantitative LEED (or LEED-IV) study from Lindsay *et al* [94] who showed that by modeling their diffraction data using adjustable parameter self-consistent phase shifts, good agreement could be achieved with the LDA and HF relaxation values obtained by Swamy *et al* except in the case of the bridging O-atoms. The results of the LEED-IV study obtained a positive (i.e. away from the surface) relaxation value of $0.10 \pm 0.05 \text{ \AA}$ whereas DFT-LDA and HF obtained little or no relaxation. Lindsay *et al* performed DFT simulations to check the possible effect of the soft vibrational mode on the surface and it was found to have a negligible effect on the results and could not account for the difference.

These new results were followed by generalized gradient approximation DFT calculations for slabs of varying thickness by Thompson and Lewis [95]. Quantitatively their results were still not in agreement with experiment, however their results were in better agreement with the LEED-IV results regarding the sign of the relaxation of the bridging O-atoms, showing an outward relaxation of as much as $0.23 \text{ \AA}$. These results were followed by medium-energy ion scattering (MEIS) [96], scanned-energy mode photoelectron diffraction (PhD) [97] and a new thorough SXRD study [98] all of which show an outward relaxation of the bridging O atoms of between $0.10 - 0.17 \text{ \AA}$.

These results demonstrate that despite the fact that this is the most studied of all metal oxide surfaces there are still unknowns regarding important features of its surface geometry.

1.4.2 Scanning probe microscopy of the $\text{TiO}_2(110)$ surface

A number of scanning probe investigations of the $\text{TiO}_2(110)$ surface have been reported in the literature [99, 100]. In the STM results, while there are variations in the operating parameters used, the vast majority of the studies reported (and all those shown here) apply a positive bias to the sample with respect to the tip and thereby tunnel into empty states. Constant current STM topographs of the (1×1) surface show alternating bright and dark rows running along the $[001]$ direction. These rows are separated by $\sim 6.5 \text{ \AA}$ which corresponds to the bulk unit cell dimension along the $[110]$ direction. The assignment of these rows to either 2-fold coordinated bridging oxygen atoms or 5-fold coordinated in plane Ti atoms is not straightforward. According to the standard Tersoff-Hamann type picture, STM images are dependent on the surface geometry and current density (see Section 1.2 for more detail). If one of these were to clearly dominate then assigning surface species would be straightforward. Unfortunately, for the (110) surface of TiO_2 , and many other surfaces, this is not the case.

From the structural model (see Fig.1.11 or Fig.1.12) it can be seen that the bridging oxygen atoms protrude significantly from the surface. Intuitively this would lead one to expect that, if topography were to dominate, the bridging oxygen rows would be imaged as bright and the titanium atoms as dark. From electronic band-structure calculations however, it can be seen that the conduction band is dominated by the Ti 3d states [101]. STM reports by Sander and Engel [102] and Onishi and Iwasawa [103] observed strands of 1×2 reconstructed TiO_x surface as well as bulk-like 1×1 surface. From these results they were able to assign the bright rows as most likely 5-fold coordinated Ti atoms based on band structure calculations [104] and they proposed models for the 1×2 reconstruction. The structure of the 1×2 reconstruction is a topic which is continually

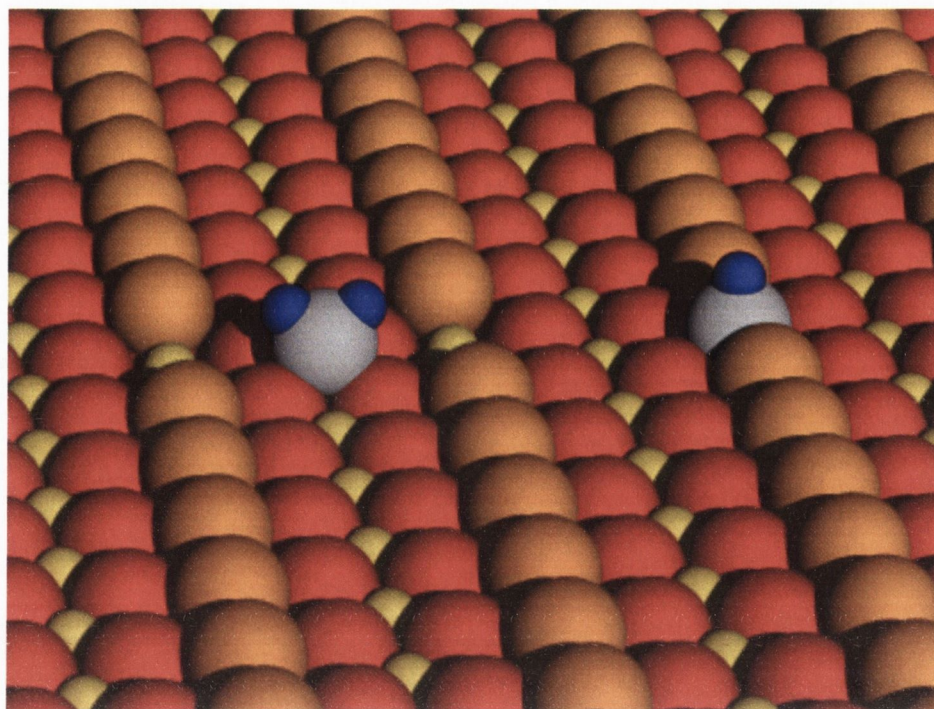


Figure 1.12: 3-dimensional model of the $\text{TiO}_2(110)$ surface showing bridging oxygen row defects including a vacancy and an adsorbed hydroxyl group. Also shown are an adsorbed water molecule atop the five-fold coordinated Ti 5+ site. In this model the Ti atoms are coloured yellow and the in-plane O atoms red. Bridging O-atoms are shaded orange for clarity.

revisited in SPM studies of this surface [105, 106, 107]

Another study by Novak *et al* [108] showed similar results but they concluded that a more rigorous theoretical analysis was required as plausible arguments could be made for the dominance of electronic structure or topography which made assigning either Ti or O to the observed bright rows difficult. Fischer *et al* [109] reported a high resolution study of the $\text{TiO}_2(110)-(1 \times 1)$ surface which showed a variety of surface features including atomic scale defects appearing as dark objects on top of bright rows (see Fig.1.13). These defects were thought to be vacancies created by the desorption of bridging O-

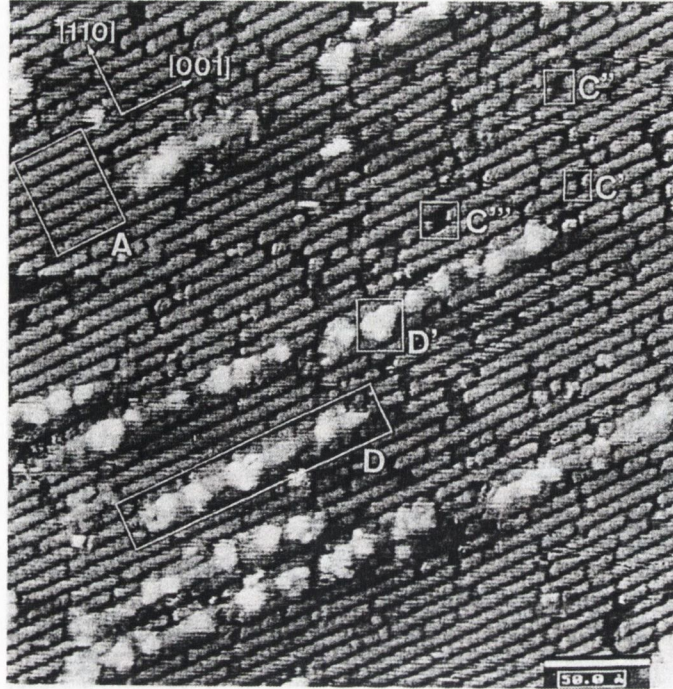


Figure 1.13: Image of defects on the (110) (1x1) surface from (Fischer *et al* 1995).

atoms. Hence the authors favour the assignment of bridging O-atoms to the bright rows although they acknowledge that this is not conclusive.

Diebold and co-workers presented a combined experimental and theoretical study of the $\text{TiO}_2(110)-(1 \times 1)$ surface in an effort to resolve the issue of whether geometry or electronic structure dominates in STM [110]. Starting with a surface which appeared nearly perfectly stoichiometric in STM topographs, they then annealed it in UHV and observed that after annealing a uniform random distribution of bright atomic scale defects appeared between bright rows on the surface. They identified these defects as bridging-O row defects based on the predictions of first-principles plane-wave pseudopotential calculations using a local-density approximation. This theoretical analysis showed that for a relaxed surface geometry the constant current density contours showed a higher current density over the Ti-atoms compared to the bridging O-atoms and that

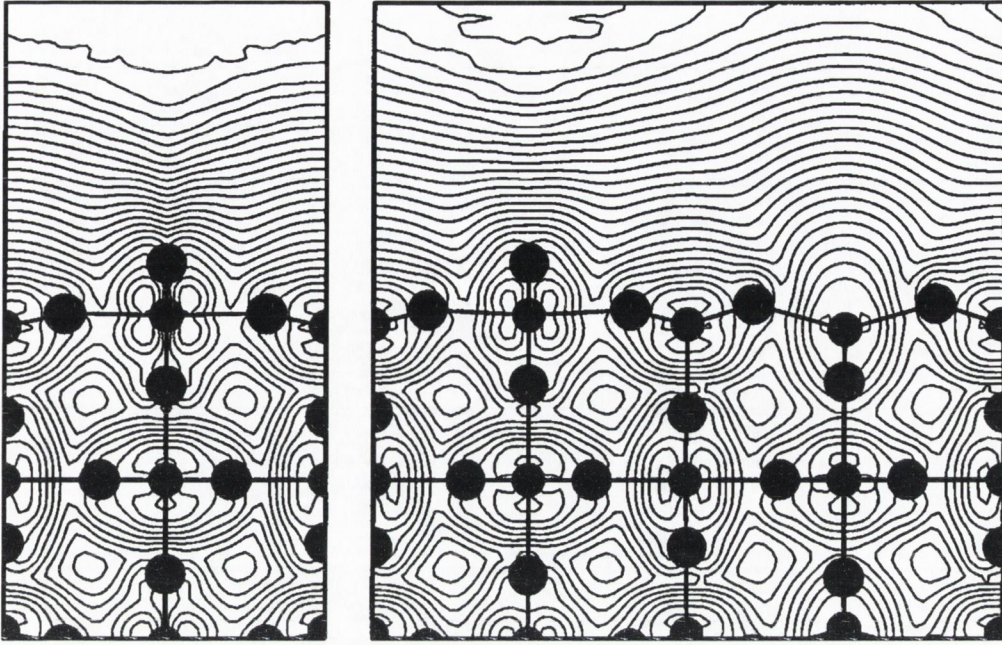


Figure 1.14: Contour plots of $[001]$ averaged charge densities associated with electron states within 2 eV of the conduction band minimum for (left) a relaxed stoichiometric (1×1) surface and (right) a relaxed oxygen deficient surface. Note the variation in the spacing of the charge contours which indicates the change in barrier-height across the surface (from Diebold *et al* 1996).

the creation of a defect by the removal of a bridging O-atom resulted in an increase in the local charge density at the site (see Fig.1.14, adapted from [110]). Interestingly, it can be seen from the results of their calculations that there is a difference in the barrier-height above the bridging O-atoms compared with the in-plane Ti atoms and that there is a significant drop in barrier-height where a oxygen vacancy has been created.

A collaborative STM investigation of the intrinsic surface defects on the surface was presented by the groups of Diebold and Varga [111]. The authors reported the variety of defects appearing on the surface after annealing in vacuum (see Fig 1.15). They also report in this paper the significant role of the tip in determining the appearance of the

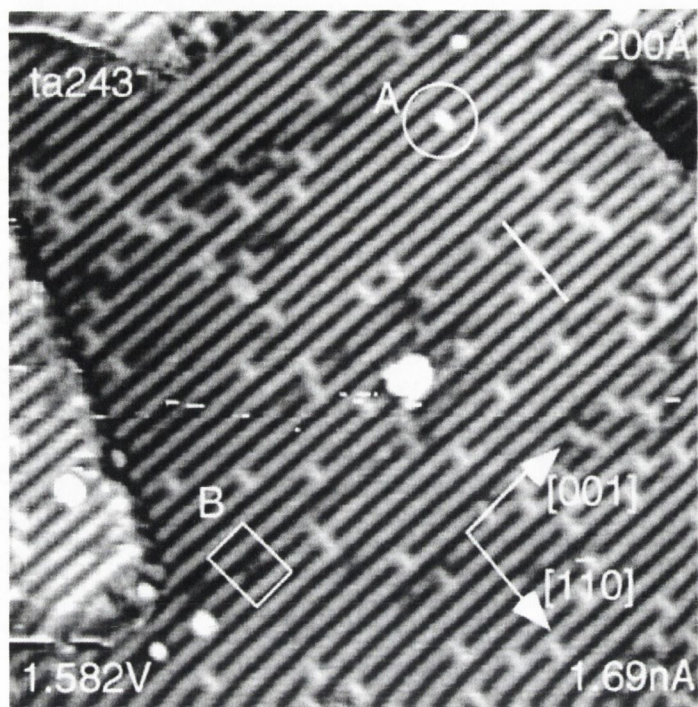


Figure 1.15: Constant-current STM topograph showing a number of surface defects, most of which appear as bright objects between bright rows (from Diebold *et al* 1998).

defects and how the tip can modify the surface defects by high voltage scanning, an effect which was further explored by Suzuki and co-workers [112]. They also present an image showing a tip change where prior to the tip change all the defects appear as bright objects between bright rows and after the tip change the defects all appear as dark objects between dark rows (see Fig. 1.16, adapted from ref. [111]). While the authors acknowledged that they had seen evidence of other imaging modes such as this during their experiments they stated that they would not be discussing them since they would be more difficult to interpret and therefore labelled the contrast dominated by electronic structure as 'normal'.

With the STM contrast of the surface and its intrinsic defects seemingly resolved researchers moved on to more catalytically interesting systems such as the adsorption of

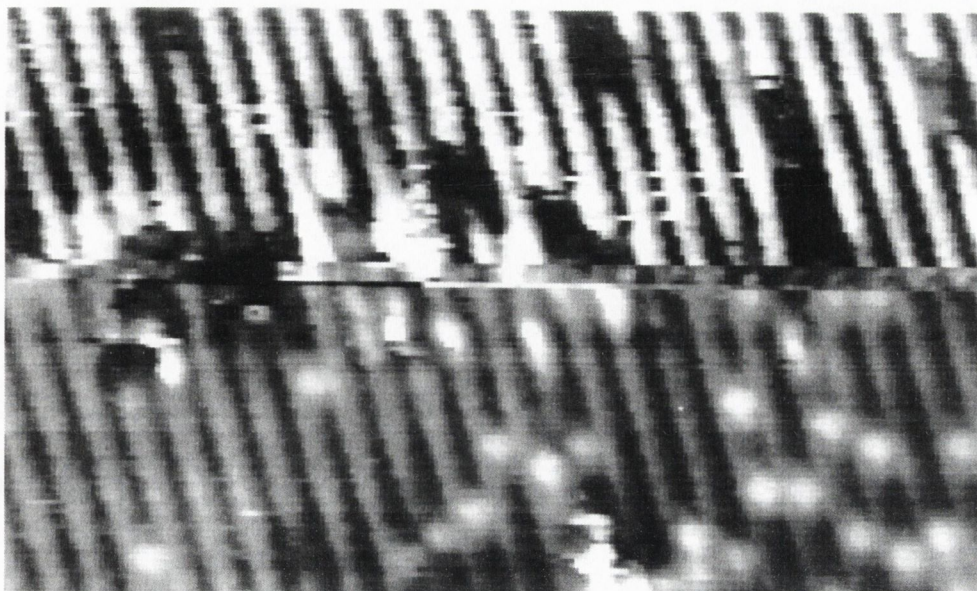


Figure 1.16: STM image ($200 \times 120 \text{ \AA}$) of the $\text{TiO}_2(110)-(1 \times 1)$ surface showing a tip change. Before the tip change all defects appear as bright objects between bright rows and after the change the defects appear as dark objects between dark rows (from Diebold *et al* 1998).

water molecules and in particular their interaction with defects. In 2001 both Brookes *et al* [113] and Schaub *et al* [114] presented STM studies on the dissociation of water on the defective $\text{TiO}_2(110)-(1 \times 1)$ surface.

Although there was some disagreement over the assignment of defects on the surface [113, 115, 116] they were generally categorised as either vacancies or hydroxyl groups adsorbed at vacancy sites due to the dissociation of water at the surface. The observed bright atomic scale features on the surface were grouped according to their height in STM topographs and labeled on this basis. Further studies from Schaub *et al* showed evidence of the effect of molecular oxygen on the diffusion of defects on the surface [115]. Bikondoa *et al* presented a detailed STM study of the modification of surface defects by high-voltage and observing their reaction with dosed water [116]. The authors labeled

the defects based on their reactivity with the adsorbed water as observed with STM.

Atomic resolution of the surface was also achieved using frequency modulation atomic force microscopy (FM-AFM) by Fukui and co-workers [117]. In their constant frequency-shift topographs the defects appear as depressions on bright rows. These defects were assumed to be related to oxygen vacancies. In a constant frequency shift topograph the appearance of a feature as a depression means that the feedback electronics moved the tip towards the surface in order to maintain a constant frequency shift value (Δf). Given that the setpoint in a FM-AFM experiment is on the negative slope of the frequency shift versus distance curve then it can be said that a depression shows that the tip-sample force gradient is less attractive over that area (this is described in more detail in Section 1.3).

Efforts to combine STM and AFM in the study of the $\text{TiO}_2(110)-(1\times 1)$ surface has been attempted by some. Ashino *et al.* used both techniques in isolation [118] and in combination [119] to study the structure of the reduced surface. The large oscillation amplitudes used mean that truly simultaneous STM and AFM was not possible. Pang and co-workers presented a FM-AFM study where they also monitored the time averaged current as well as frequency shift [120]. Again, due to the large oscillation amplitudes used ($\sim 70 \text{ \AA}$) truly simultaneous STM and force gradient measurement were not possible. Their measurement of current differs from STM in that what is measured is the time-averaged current integrated over the oscillation cycle of the tip. In this study they attempted to identify the products of water dissociation on the surface by comparison of the two channels. The authors noted that there are two distinct contrast mechanisms in frequency shift, one where the defects appeared as dark objects between dark rows and one where they appeared as bright objects between bright rows. The

authors proposed that a change in the electrostatic polarity at the tip apex could have resulted in the drastic change in AFM topography. They also presented an image of simultaneously acquired FM topography along with the time-averaged tunneling current. By comparing the two channels they observed that the bright rows in the time-averaged tunneling current image were out of phase with those in the FM topography image. However based on the contrast of some of the observed defects in the FM topography image the authors claim to be imaging the Ti rows as bright in FM topography and so the tunneling current appears to be brighter over the bridging-O rows which is in contrast with the orthodox picture from STM. The authors mention two studies which have shown such contrast in STM [121, 111] neither of which they claim are comparable to their study. The authors then attempt to explain the observed contrast in the current channel by considering an error contribution due to the fact that the tip trajectory in their experiment is determined by the frequency-shift feedback.

Lauritsen and co-workers presented an FM-AFM study of the defects on $\text{TiO}_2(110)-(1 \times 1)$ [122]. In this study they observed that there are at least two different contrast modes for defects on the surface. As in the work by Pang and co-workers they explained this by considering the polarity of the electrostatic charge at the apex of the imaging tip. By comparing with atomistic simulations of the interaction of an MgO cube (representing the tip) with a $(6 \times 3 \times 3)$ unit cell of the $\text{TiO}_2(110)-(1 \times 1)$ surface the authors claim to be able to unambiguously identify the surface defects.

From the above it can be seen that there is a discrepancy between AFM and STM in considering the role of the tip structure in determining the observed contrast. Thus far experiments and theoretical modeling of STM assume a featureless point-like tip which simplifies the interpretation of images by considering only the surface geometry and the

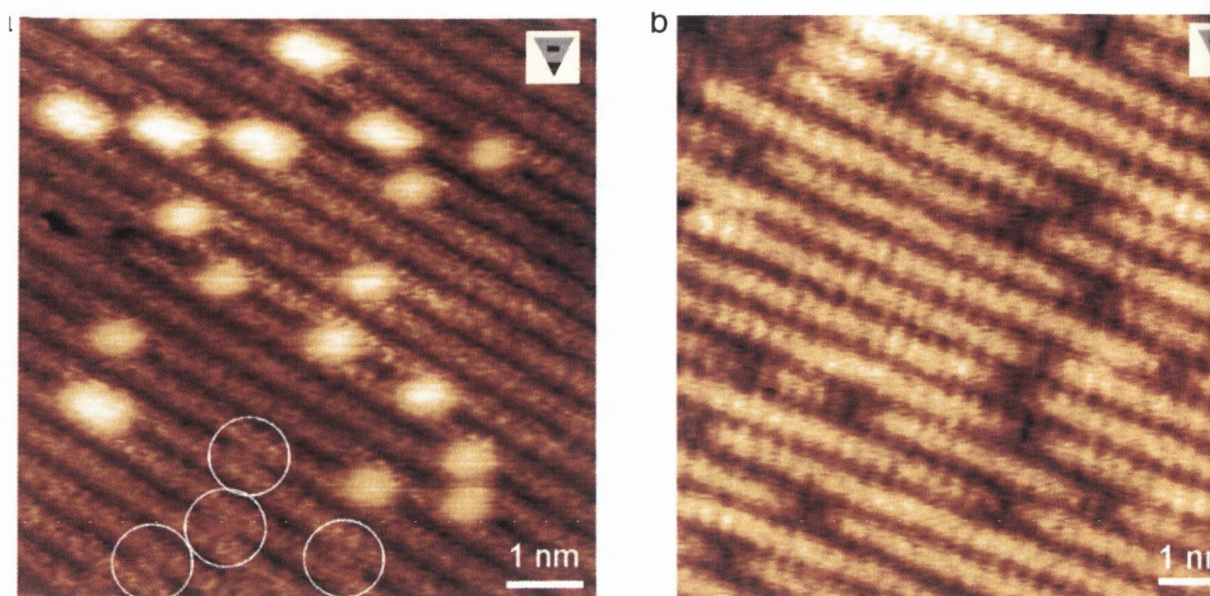


Figure 1.17: Non-contact AFM images ($100 \times 100 \text{ \AA}$) of defect on the $\text{TiO}_2(110)-(1 \times 1)$ surface showing two different contrast regimes (from Lauritsen *et al* 2006).

local density of states as in the simple Tersoff and Hamann model of STM (Section 1.2). On the other hand, in AFM it has been shown that the tip electronic structure can have a drastic effect on what is observed. Considering that these techniques share a common basic experimental setup (i.e. a sharp tip in close proximity to a flat surface) this is inconsistent. It is also clear from the summary just presented that the direct identification of surface defects based solely on their apparent topography in constant current STM images may not be valid. Complimentary data on these atomic scale defects from other scanning probe techniques should lead to a more complete picture but used in isolation these are not directly comparable due to the influence of the tip apex structure on the data acquired.

Chapter 2

Experimental background

2.1 Low-amplitude non-contact atomic force microscopy

In dynamic atomic force microscopy, if the oscillation amplitude is small compared to the length scale of the interaction then the force gradient is constant over the entire oscillation cycle. In this case the cantilever may be considered as a simple harmonic oscillator.

In low-amplitude off-resonance dynamic AFM a dither of amplitude A_d is applied to a cantilever at a fixed frequency well below the resonance [123, 124, 125]. This dither results in an oscillation at the tip-end of the lever of amplitude A_0 which in the case of $\omega \ll \omega_0$ is approximately equal to A_d . The changes in the the oscillation amplitude due to the tip-sample interaction are measured.

In the absence of a tip-sample interaction, and assuming no damping the equation of motion of the cantilever can be written as

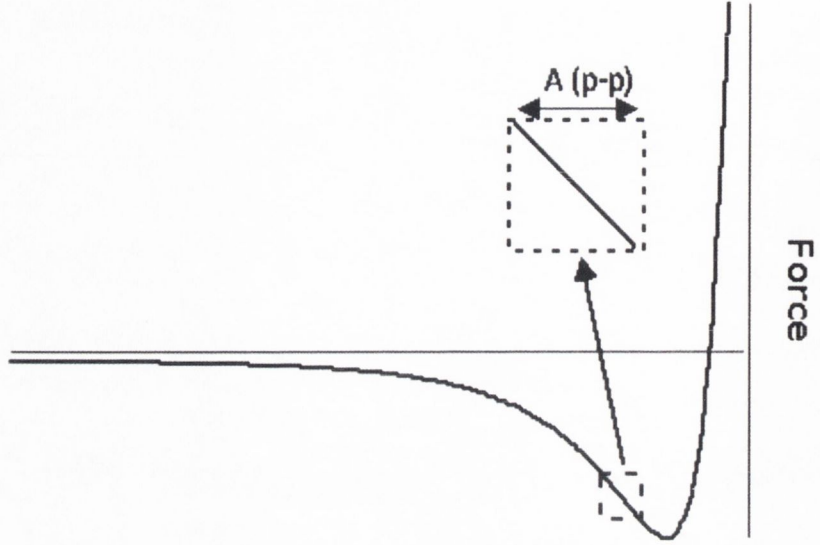


Figure 2.1: Plot to illustrate the use of very low-amplitudes in dynamic force microscopy. If the amplitude is sufficiently small then the variation in force over an oscillation period is linear i.e. the force gradient is constant.

$$m \frac{\partial^2 z}{\partial t^2} + k_0 z = F_0 \cos(\omega t) \quad (2.1)$$

where m is the effective mass, k_0 is the lever stiffness and F_0 is the force associated with a displacement of the tip from its equilibrium position by distance A_d . This has a solution of the form

$$z = A_0 \cos(\omega t) \quad (2.2)$$

so given that

$$\omega_0 = \sqrt{\frac{k}{m}} \quad (2.3)$$

$$A_0 = \frac{k_0 A_d}{m(\omega_0^2 - \omega^2)} = \frac{k_0 A_d}{m\omega_0^2(1 - \omega^2/\omega_0^2)} = \frac{A_d}{(1 - \omega^2/\omega_0^2)} \quad (2.4)$$

If we now do the same for the case where a tip-sample interaction exists then the equation of motion is

$$m \frac{\partial^2 z}{\partial t^2} + (k_0 + k_{int})z = F_0 \cos(\omega t) \quad (2.5)$$

Solving again for A at the shifted resonance frequency (ω'_0) we obtain

$$A = \frac{k_0 A_d}{m(\omega_0'^2 - \omega^2)} \quad (2.6)$$

Taking the ratio of the amplitudes in both cases

$$\frac{A_0}{A} = \frac{\omega_0'^2 - \omega^2}{\omega_0^2 - \omega^2} = 1 + \frac{k_{int}}{k_0(1 - \omega^2/\omega_0^2)} \quad (2.7)$$

which can be rearranged to give

$$k_{int} = -\frac{\partial F_{int}}{\partial z} = k_0 \left(1 - \frac{\omega^2}{\omega_0^2}\right) \left(\frac{A_0}{A} - 1\right) \quad (2.8)$$

which, if $\omega \ll \omega_0$ reduces to

$$k_{int} \sim k_0 \left(\frac{A_0}{A} - 1\right) \quad (2.9)$$

This equation is based on the case where the damping due to energy dissipation in the system is neglected. Damping contributions are likely from the lever to its environment and as a result of the tip-sample interaction.

A damped driven harmonic oscillator is described by the equation

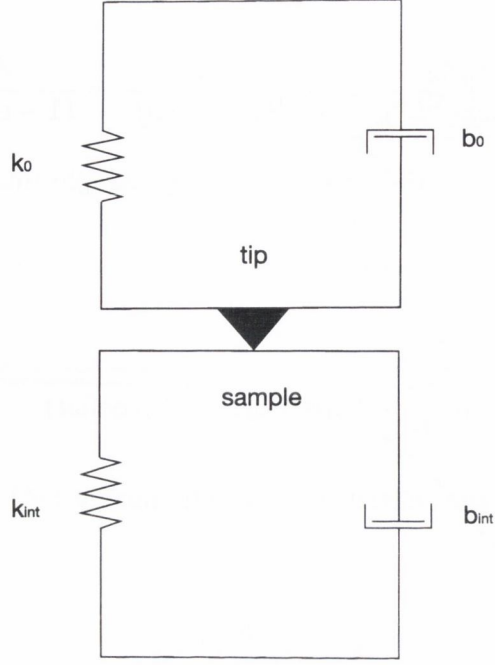


Figure 2.2: Schematic of the tip-sample system which can be described as a damped harmonic oscillator.

$$m \frac{\partial^2 z}{\partial t^2} + b \frac{\partial z}{\partial t} + (k_0 + k_{int}) = F_0 \cos(\omega t) \quad (2.10)$$

which has a solution of the form

$$z = A \cos(\omega t - \theta), \tan \theta = \frac{\omega b}{m(\omega_0'^2 - \omega^2)} \quad (2.11)$$

where

$$A = \frac{F_0}{\sqrt{m^2(\omega_0'^2 - \omega^2)^2 + \omega^2 b^2}} = \frac{F_0 \cos \theta}{m(\omega_0'^2 - \omega^2)} \quad (2.12)$$

which leads once more to the expression

$$k_{int} = -\frac{\partial F_{int}}{\partial z} = k_0 \left(1 - \frac{\omega^2}{\omega_0'^2}\right) \left(\frac{A_0}{A} \cos \theta - 1\right) \quad (2.13)$$

which reduces to

$$k_{int} = k_0 \left(\frac{A_0}{A} \cos \theta - 1 \right) \quad (2.14)$$

This value θ is a measure of the phase difference between the driving oscillation and the oscillation of the cantilever and is related to the overall damping in the system. The measured value of the phase may be used to calculate the energy loss and damping in the system [126].

2.1.1 Simultaneous multi-parameter SPM imaging

One of the long standing problems in STM and AFM is how to interpret atomic resolution data and identify what is actually being imaged. Very few techniques exist which can provide information on the same scale as STM or AFM so acquiring complementary data is difficult. One possible way of doing this is to collect more information using other scanning probe techniques [118]. Unfortunately, due to the sensitivity of the data to the imaging tip it is not possible to directly compare STM and AFM data on the same surface where the techniques are used in isolation. One solution to this problem is to measure multiple parameters simultaneously with the same tip. Achieving this is however technically difficult. While the basic experimental arrangement in STM and AFM are the same (a sharp tip in close proximity to a flat surface) the operating conditions can be quite different. In most standard atomic resolution UHV-AFM studies the oscillation amplitude used are of the order of ~ 10 nm. This makes it impossible to directly measure a simultaneous tunneling current.

By reducing the oscillation amplitude to < 1 Å it is possible to simultaneously measure other parameters such as tunneling current and barrier height (see Section

3.1.1). As mentioned in the previous section (Section 2.1), using small amplitudes well below resonance also simplifies the quantification of the amplitude data in terms of force gradient [127]. Oral and coworkers have presented work on quantitative force gradient measurement on the Si(111) (7×7) surface using STM constant current feedback [124]. In this study the authors found that their measured force gradients over corner holes were more attractive than over the adatoms. These results were the inverse of what was predicted by the calculations of Perez and co-workers [128]. The authors explained this by taking into account the effect of variation in the contribution of long-range forces due to the tip trajectory in constant current feedback in their experiment (the theoretical calculations assume a flat tip-trajectory) which, once accounted for, could result in an inversion of the observed contrast.

The technique was later applied to the Cu(100) surface [37]. There the authors demonstrate that even during flat STM scans (i.e. flat tip-trajectory) there were signifi-

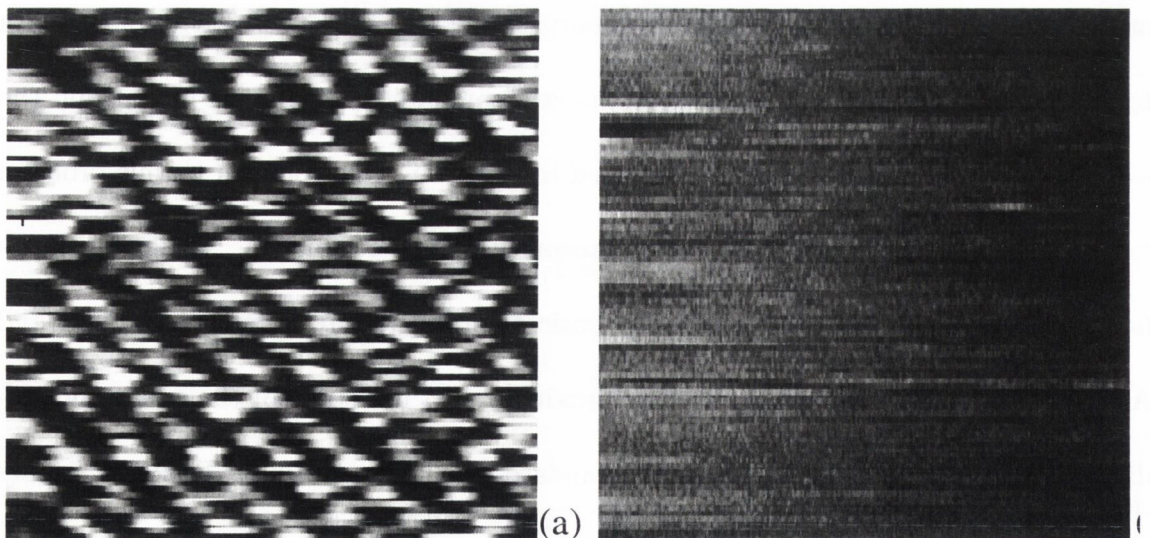


Figure 2.3: Flat-trajectory force gradient (left) with simultaneously acquired STM image (right) of the Cu(100) surface. $28 \text{ \AA} \times 28 \text{ \AA}$, 9.1 nA/20 mV (from Özer *et. al.* 2004).

cant variations in the measured tip-sample force gradient giving rise to atomic resolution (see Fig.2.3). This demonstrated that even when the STM tip is behaving in a way that would be described as a Tersoff-Hamann type tip (i.e. reflecting the local density of states at the surface) there are still force interactions which could affect measured tunneling values due to tip relaxations.

While this technique has important advantages over other large-amplitude techniques it does suffer from a number of drawbacks. Firstly, the use of such low-amplitudes requires a very sensitive detection system and is therefore susceptible to noise. Secondly, the slow scan speeds required to achieve a reasonable force gradient image are comparatively slow and thirdly, so far the implementation of the technique has relied on using tunneling current as a feedback signal which can introduce cross-talk between the STM topography and force gradient image.

In 2005 Herz *et al* reported the use of a q-plus sensor to combine force gradient, barrier-height and tunneling current measurement on Si(111) [129]. This study proved that the simultaneous measurement was feasible but required oscillation amplitudes of less than 1 Å for proper measurement of barrier-heights. A number of other groups are also making efforts to combine techniques within a single microscope in order to extend the capabilities of scanning probe microscopy [120, 130, 131, 132].

Chapter 3

Experimental procedures

The use of very low oscillation amplitudes presented significant technical challenges. Amplitudes which are lower than 1 Å mean that the restoring force on the cantilever is much lower than in large-amplitude experiments and therefore instabilities due to jump-to-contact are more likely. To avoid this problem stiffer cantilevers may be used however this presents yet another problem i.e. the loss of sensitivity. The detection of such small deflections in very stiff cantilevers requires a highly sensitive detection system and a low noise floor.

In this chapter I describe the customised AFM/STM which we built and that was used for most of the experiments presented here. Also detailed experimental procedures such as sample preparation, tip/cantilever fabrication, lever calibration and water dosing are described.

3.1 Customised room-temperature AFM/STM

A heavily customised Omicron RT-SPM system was used to perform the AFM/STM experiments described here. The original optical beam deflection detection system was entirely removed and replaced. The replacement detection system was based on a Fabry-Perot type optical fiber interferometer. The optical cavity of the interferometer is formed between the end of the optical fiber and the back of the cantilever. The optical signal is provided by an IR laser diode ($\lambda = 1320$ nm). The light is passed along the fiber and through a 2x2 3dB coupler, one output of which is to a reference photodiode to monitor the power of the laser diode (see Fig. 3.1). The other output of the coupler passes the light to the cantilever. A major challenge in the development of this instrument was noise and how to reduce it within the system. To this end many different optical components within the interferometer were replaced and different laser diodes were tried. Applying a RF modulation of some 270 MHz to the laser diode power supply and reducing the laser power to a value below the threshold for mode-hopping provided the largest reduction in noise in the system. This technique has previously been applied by Fukuma *et. al.* in the development of a low-noise AFM with an optical beam deflection detection system [133]. The modulation of the laser diode power supply reduces the coherence length of the beam which in turn decreases the effect of back reflections in the laser diode. The result was a noise floor of $20 \text{ fm}/\sqrt{\text{Hz}}$ which is an order of magnitude from the shot noise limit (see Fig. 3.2).

A schematic of our optical fiber interferometer cavity is shown below (Fig. 3.3). On reaching the end of the optical fiber the light is both transmitted onto the back of the cantilever and reflected back up the fiber. The reflected portion becomes the reference

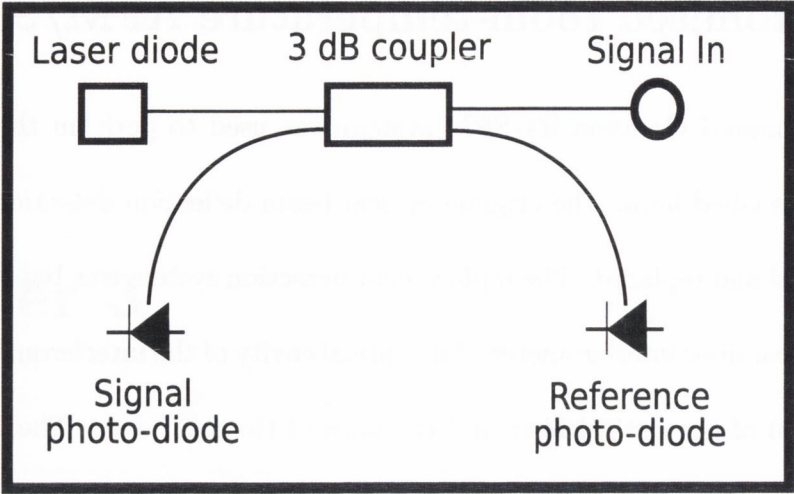


Figure 3.1: Schematic of the interferometer.

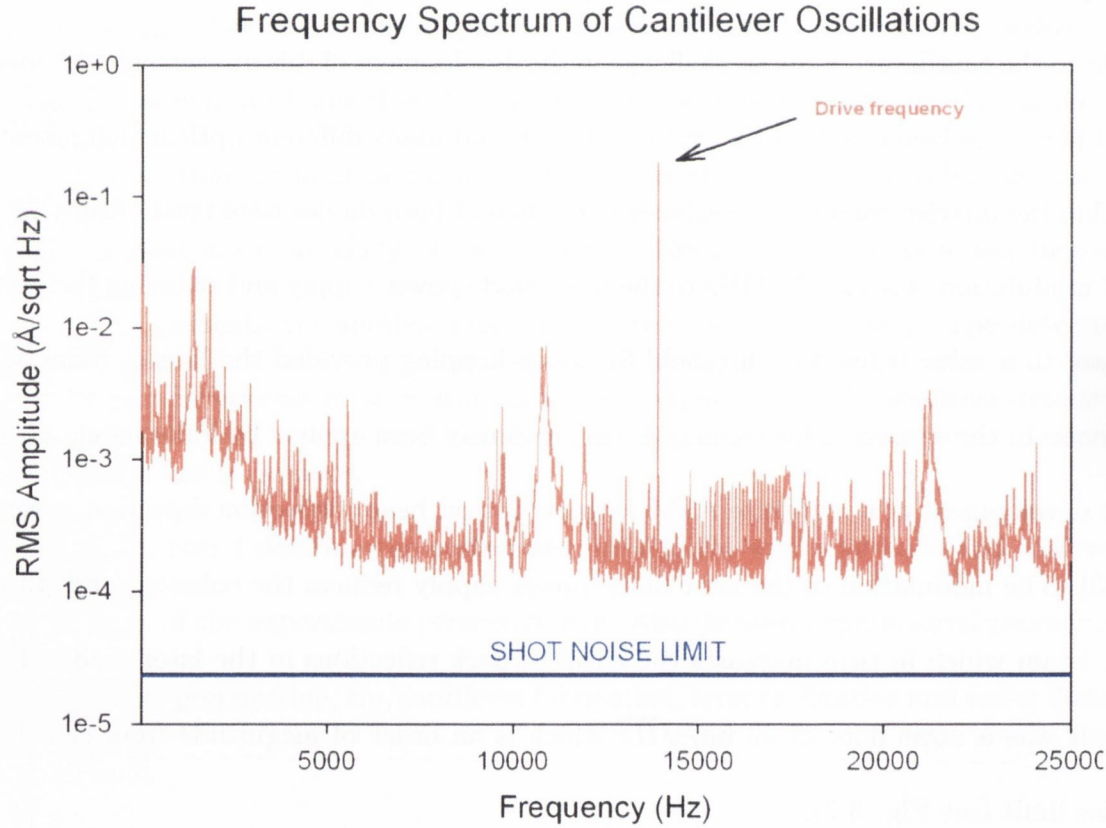


Figure 3.2: Frequency spectrum of a silicon cantilever showing the drive frequency and the noise level of the instrument.

beam. The transmitted portion travels on to the back of the cantilever where it may undergo multiple reflections in the cavity between the mirror surfaces of the optical cavity formed by the cantilever and the end of the fiber before finally being transmitted back up the fiber.

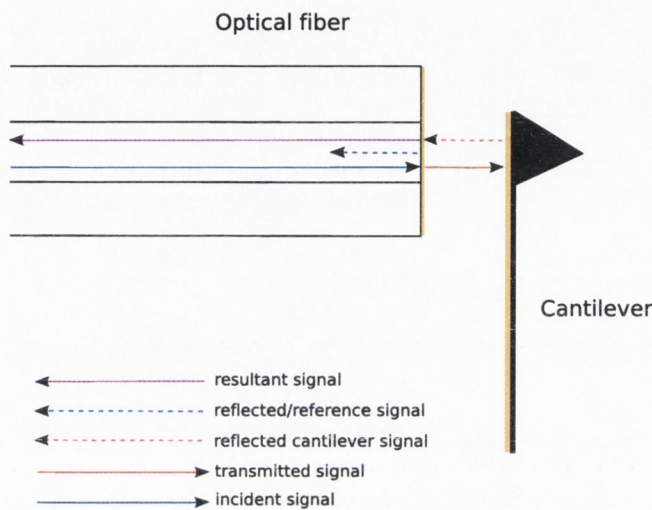


Figure 3.3: Schematic of the interferometer cavity formed between the back of the cantilever and the end of the optical fiber.

The reflectivity of both the cantilever and the end of the optical fiber are crucially important in determining the sensitivity of the detection system. In order to optimise these properties both surfaces are coated in a Edwards evaporator under high-vacuum conditions. The optical fibers were first coated with a ~ 50 nm film of silicon followed by ~ 12 nm layer of gold. The cantilevers were coated with a thin (~ 20 nm) layer of chromium and then a ~ 100 nm layer of gold. In this case the chromium is used as an adhesive layer in order to achieve a more even film of gold.

The end of the optical fiber (diameter $\sim 50 \mu\text{m}$) was accurately positioned behind the cantilever using a specially built fiber slider capable of moving the fiber in all degrees of freedom. Typically the distance between the end of the fiber and the back of the

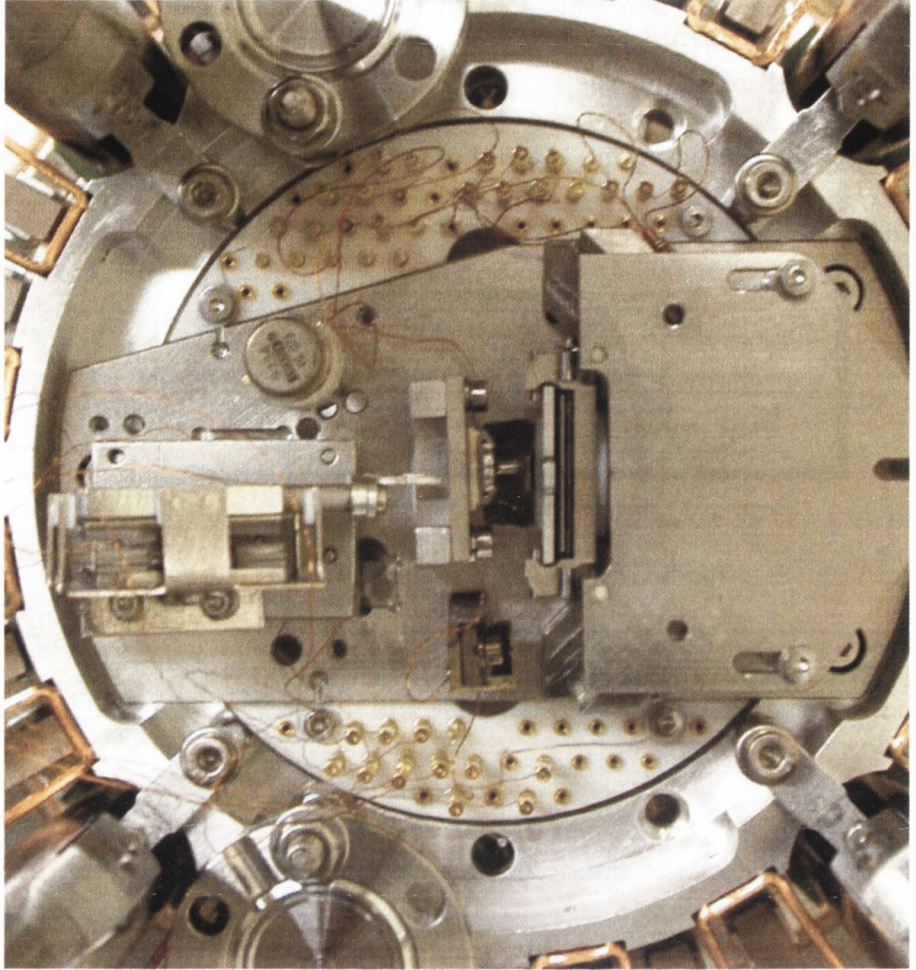


Figure 3.4: Top-down view photograph of the customised room-temperature AFM/STM microscope stage.

cantilever after alignment was $\sim 1 \mu\text{m}$. The cantilevers were mounted on Omicron stainless steel cantilever holders. These holders are tilted by 15° in order to ensure that it is the tip which contacts the sample first and not another part of the cantilever or cantilever holder. This tilt is a standard feature of SPM systems. As a consequence of this tilt, in order to make precise alignment of the fiber behind the cantilever easier the fiber slider was also mounted on a slope of 15° . Other adjustments made to help with alignment included shortening the cantilever holders and mounting the levers off-centre

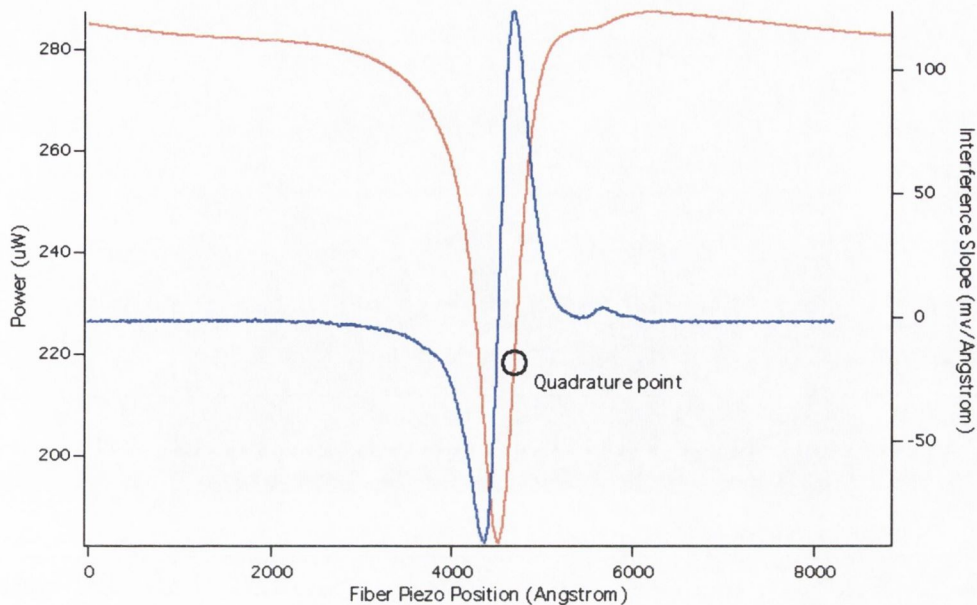


Figure 3.5: Graph of interference pattern obtained for lever ls52. The red curve is the power at the signal photodiode. The blue curve is the slope of the red curve. The maximum of the slope of the signal power gives the maximum signal for a change in distance between the fiber end and the back of the cantilever and is chosen as the quadrature lock point

in order that the useful range of motion of the fiber slider was maximised. The cantilever was actuated using a dither piezo at the base of the cantilever mounting.

Once the end of the fiber had been aligned with the back of the cantilever an interference pattern like the one shown in Fig. 3.5 was obtained. This pattern is obtained as a result of multiple reflections within the interferometer cavity. From Fig. 3.5 it can be seen that the quadrature point was the point at which the slope of the interference is at a maximum. This gave the maximum sensitivity for detecting a change in the length of the interferometer cavity i.e the fiber-lever separation. From the pattern in Fig. 3.5 it can be seen that the maximum slope is $\sim 125 \text{ mV}/\text{\AA}$ although slopes as high as ~ 500

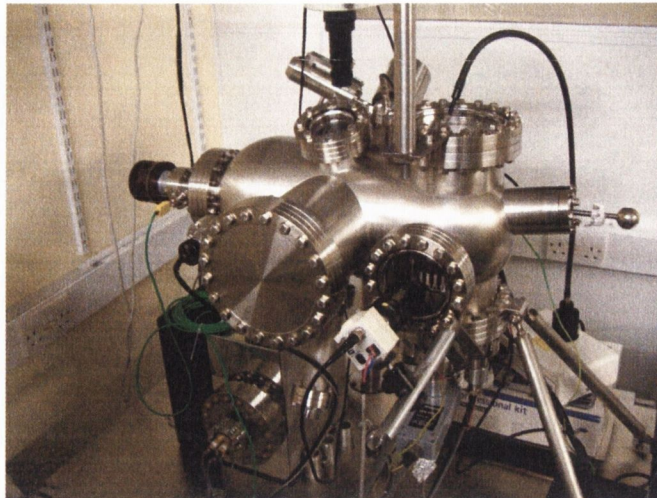


Figure 3.6: Photograph of the customised room-temperature AFM/STM system.

mV/Å were achieved during these studies which gave excellent sensitivity but made it more difficult for the software routine to maintain quadrature.

The microscope was situated in an ultra-high vacuum (UHV) chamber which was pumped by a Varian ion getter pump (see Fig. 3.4 and Fig. 3.6). Typical base pressures after a 24 hour bake at 120°C were $\sim 3 \times 10^{-11}$ mbar. The system was equipped with a simple gas admission system and ion gun for *in-situ* sample cleaning. The gas admission system was also used for dosing small amounts of water. The fast-entry lock sample transfer system consisted of a magnetic transfer arm, which could access the chamber via a Viton sealed gate valve. The fast-entry lock transfer system was pumped by a Varian turbomolecular pump.

3.1.1 Measurement setup

During measurement the microscope operated somewhat like a standard STM in that the tip-sample distance was regulated by a constant-current feedback loop. Unlike a standard STM however, simultaneous measurements were also made of a number of other parameters such as the change in the amplitude of the tip oscillation as it was following the constant-current trajectory across the surface (see Fig. 3.7).

The experimental measurement setup is detailed in Fig. 3.8. This setup consists of a pair of digital lock-in amplifiers, the main control electronics, a desktop computer to run the control software and a digital oscilloscope for monitoring various parameters. The cantilever was driven at a fixed frequency (f_{exc}) and the tunneling current (I_t), the STM topography (V_z), the change in amplitude (V_{ext}), the phase (ϕ), variation in tunneling current over oscillation cycle (dI) and the static deflection of the cantilever (V_{pd}) were recorded.

The control electronics were built by Nanomagnetics Instruments (Oxford) and comprise a number of individual control cards. These included a controller card, an interferometer card, a slider card, a scan piezo card and a spare analog-to-digital card (ADC). The controller card contained the control electronics for the STM feedback and applied bias. The spare ADC card was used to input the ϕ , dI and V_{pd} .

The first lock-in amplifier (Signal Recovery 7280 DSP) supplied a voltage (V_{exc}) at a fixed frequency (f_{exc}) to the dither piezo at the base of the cantilever holder. The resultant motion at the end of the cantilever was detected as a change in the intensity at the photodiode (V_{pd}) in the interferometer and recorded on the channel Spare 3 of the Spare ADC. This signal was also passed to the signal input of the lock-in amplifier where the amplitude at the dither frequency (V_{ext}) was monitored. The lock-in amplifier also

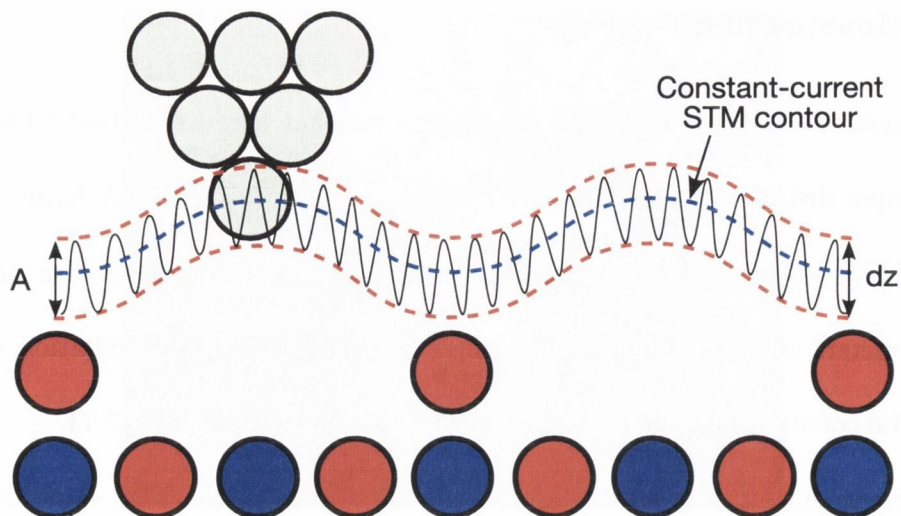


Figure 3.7: Schematic visualisation of the tip trajectory over the $\text{TiO}_2(110)$ surface. While following the STM constant current contour the tip is oscillated at a frequency much higher than the cut-off of the STM feedback electronics. The variation in amplitude A is monitored and also provides the dz value for measuring $\frac{dI}{dz}$.

monitored the phase difference between the dither applied at the base of the cantilever and the oscillation at the end of the cantilever. This phase signal (ϕ) was passed to channel 1 of the Spare ADC card.

The second lock-in amplifier (EG&G Instruments 7260 DSP) took as its reference signal the signal output of the first lock-in (V_{exc}) and I_t as its signal input. This meant that the variation in I_t at the reference frequency was monitored. This signal (dI) was then passed to channel 2 of the Spare ADC card. Care was taken in noting the time constants used in both lock-in amplifiers as these cause relative shifts between different channels of a single image.

The excitation frequency (f_{exc}) was set according to a number of criteria. Firstly it had to be far below the resonance frequency of the cantilever (i.e. $f_{exc} \ll f_0$, see section 2.1). Secondly, f_{exc} was set in a region of the lever vibrational spectrum which was

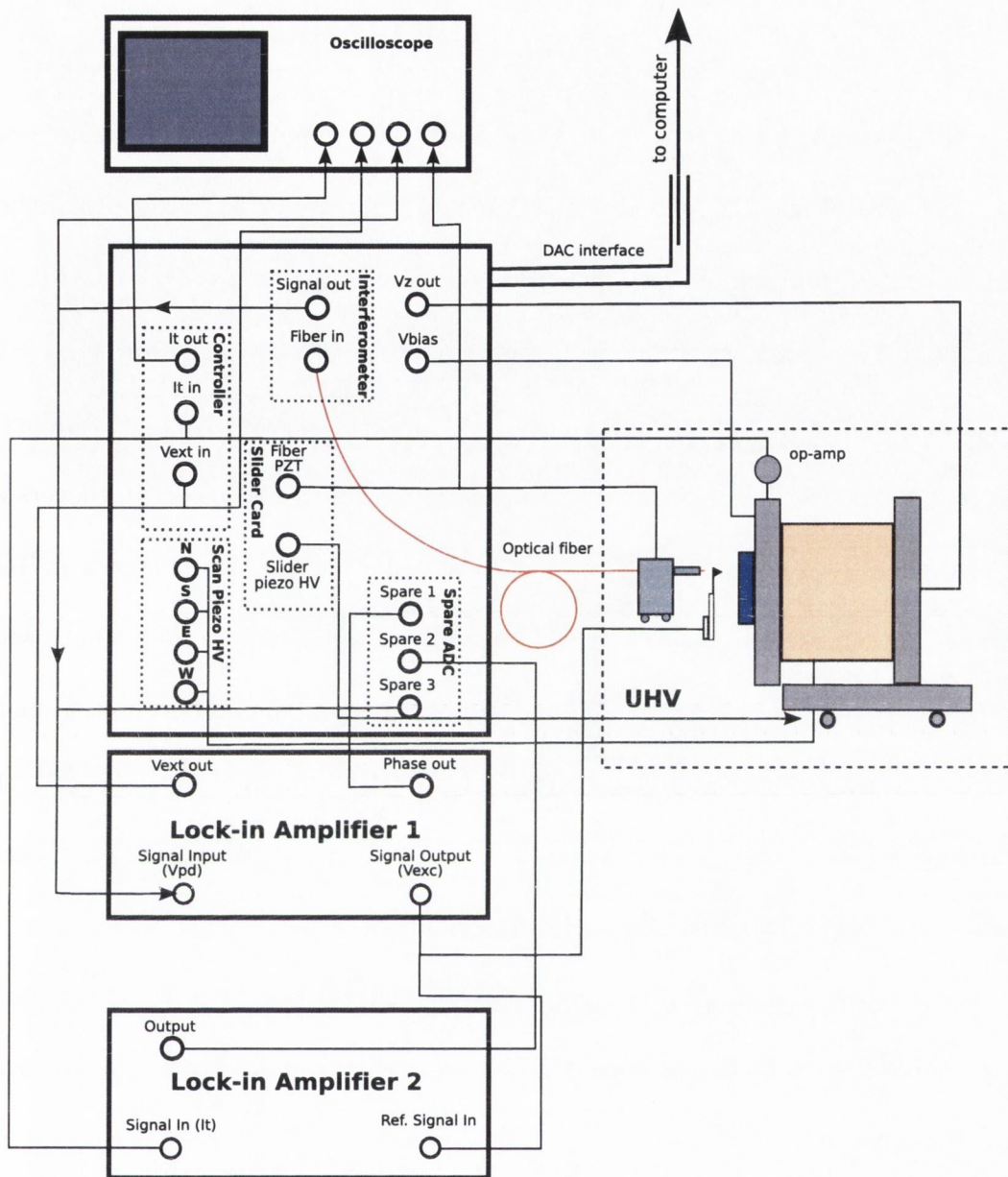


Figure 3.8: Schematic showing the experimental measurement setup.

relatively free of spurious resonances which might affect the measured amplitude should these shift due to the tip-sample interaction. Thirdly, care was taken to avoid f_{exc} values around half the value of the main resonance peak since we have shown in low-amplitude AFM that this enhances the measured dissipation due to possible coupling with higher harmonics of the cantilever [134].

3.2 Cantilevers for low-amplitude AFM

For these experiments two types of cantilever were used. The first were homemade solid tungsten cantilevers and the second were commercial Nanosensors PPP-NCLPt silicon cantilevers coated front and back with a thin film of PtIr to enhance conductivity. The tungsten cantilevers were preferred since good conductivity is essential for stable STM feedback and this was more difficult to achieve with silicon levers where the conductive coating may be damaged and delaminate from the tip. Each of the silicon cantilevers was supplied with its own data sheet. Typical values for both varieties are shown in Table 3.1. These cantilevers were chosen for their conductive coating and for their length which made them easier to use in the geometry of our microscope with its fiber interferometer. Standard silicon cantilevers with force constants of ~ 40 N/m are typically only ~ 125 μm in length. Given that the end of the fiber in our detection system had a radius of the same order this would have made accurate positioning more difficult.

The tungsten levers were made using 50 μm diameter polycrystalline 99.9 % purity tungsten wire. Firstly the wires were flattened between two polished tungsten carbide

Material	Polycrystalline Si	Polycrystalline W wire
Length	$\sim 225 \mu\text{m}$	500 - 700 μm
Width	$\sim 38 \mu\text{m}$	60 - 90 μm
Thickness	$\sim 7 \mu\text{m}$	15 - 25 μm
Resonance frequency	~ 190 kHz	14 - 25 kHz
Stiffness	~ 50 N/m	150 - 300 N/m

Table 3.1: Typical specification values for the PPP-NCLPt (levers coated both sides with ~ 20 nm of PtIr) and the home-made tungsten cantilevers.

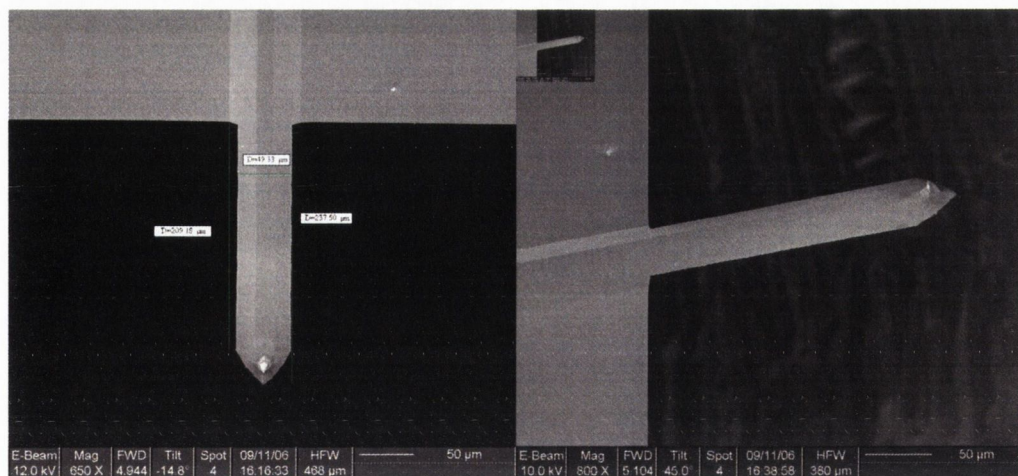


Figure 3.9: Scanning electron microscope images of a commercial silicon Nanosensors cantilever.

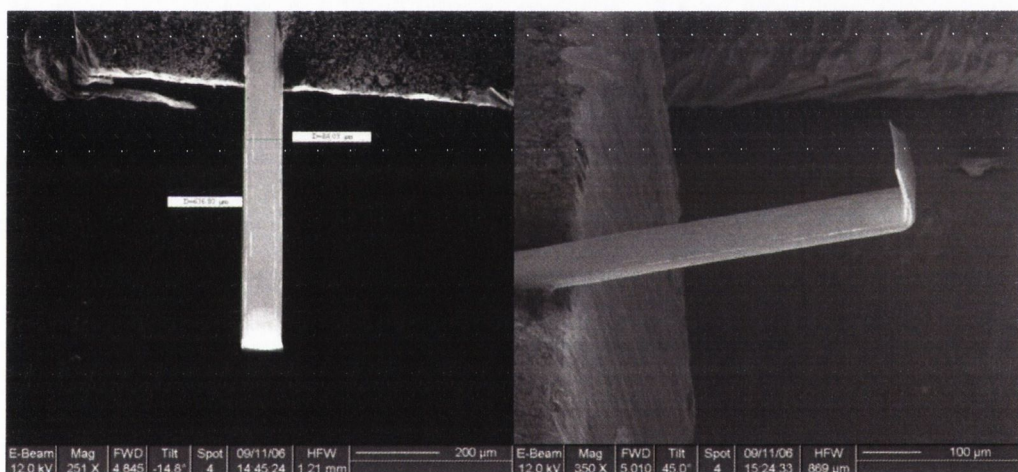


Figure 3.10: Scanning electron microscope images of a tungsten cantilever.

plates. These flattened wires were then electrochemically polished by applying a dc-voltage between the wire and a graphite anode while both were immersed in a beaker of Ilford Multigrade paper developer. After polishing, the wires were rinsed in HPLC grade acetone followed HPLC isopropanol and finally rinsed in de-ionised water. The flattened

Wire	ϕ 50 μ m polycrystalline tungsten wire
Etching solution	5 Mol/l NaOH
Etching voltage	$\sim$ 2.6 V
Insertion depth	$\sim$ 1.5 mm
Threshold current	$\sim$ 0.9 mA
Initial current	$\sim$ 8 - 10 mA
Typical etch time	120 - 180 sec

Table 3.2: Tungsten cantilever tip etching parameters.

polished wires were then bent into the shape of a cantilever with a long section for the lever and a shorter section, at 90° to the lever section, as the tip. An Omicron W-Tek tip-etching tool was used to etch atomically sharp tips on the tip section. Typically the flattened wire was inserted to a depth of $\sim$ 1.5 mm. The etching solution used was NaOH 20 % wv. During etching a bias was applied between the lever and a circular stainless steel electrode placed just below the surface of the etching fluid. This was found to minimise the creation of small bubbles in the electrolyte which could disturb the meniscus around the wire. The wire was etched until a pre-set threshold current limit was reached and the applied bias removed. Typical etching parameters used are listed in Table 3.2.

Once etched, the tip was rinsed in high purity acetone and isopropanol followed by de-ionised water. As with the STM tips, the sharpness of the tip apex was inspected using an Olympus optical microscope with $\times$ 100 magnification. The cantilever was then cut to the required length using a pair of tungsten carbide edged wire cutters and mounted on steel cantilever carriers from Omicron which had been shortened to suit

the configuration of our microscope. These cantilever holders had a 15° angle which is common in commercial microscope systems. The cantilevers were mounted using a UHV compatible conducting epoxy H20E or H21D which was supplied by Epo-Tek UK. Once mounted the epoxy was cured in an oven at 120°C for 1 hour. Following curing the levers were then transferred to an Edwards vacuum evaporator and coated with a $\sim 30\text{ nm}$ layer of chromium followed by a $\sim 120\text{ nm}$ thick layer of gold in order to optimise the reflectivity of the backs of the levers. The chromium layer was added to improve the quality of the gold film on the surface of the cantilever by acting as an adhesion layer. In order to reduce contamination of the surface with material from the tungsten evaporation boat, care was taken to make sure that not all the gold present in the boat was evaporated. Typically the vacuum coater was able to achieve base pressures better than $1 \times 10^{-6}\text{ mbar}$. Further processing of the levers was sometimes carried out in a FEI Strata focussed ion-beam system (see Section 3.2.1).

3.2.1 Focussed ion beam milling of tips

In some cases the tips of our silicon and tungsten levers were milled using a focussed ion beam. This was applied to levers which showed favourable reflectivity and vibrational properties but had suffered tip damage during measurement. The focussed ion beam system made it possible for us to sharpen blunt or damaged tips and thereby extend the useful life of the cantilever.

The system used was a FEI Strata dual-beam focussed ion beam and scanning electron microscope. As the name suggests, the system combines a focussed ion beam column and a scanning electron microscope in a single high vacuum chamber. The focussed ion beam is generated using a gallium liquid metal ion source which heats a

crucible of gallium until it is liquid. The gallium then wets a sharp tungsten needle to which a high voltage has been applied. The high electric field at the needle tip ionises the gallium atoms and these ions are then field emitted from the tip. These are extracted and focussed, using a series of electrostatic lenses, on to the sample. The secondary electrons generated by the ions interacting with the surface are detected and used to form an image of the sample. During imaging the ion beam etches the sample surface and this is utilised for the precision machining and patterning of samples down to a few nanometers.

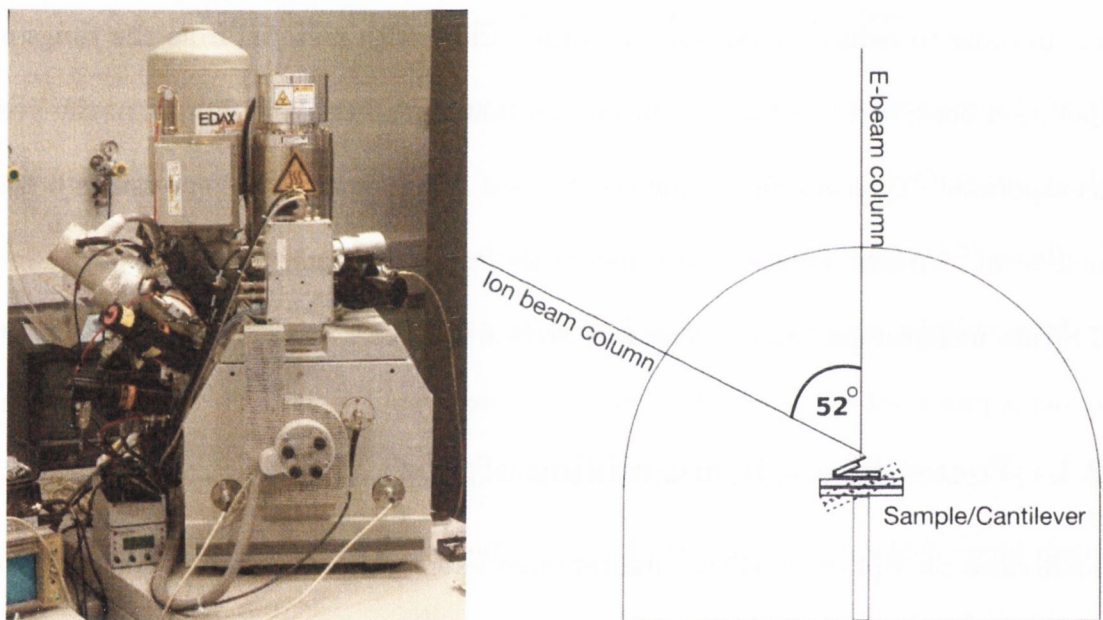


Figure 3.11: A photograph of the FEI Strata Dual-Beam FIB/SEM used. Schematic showing the geometry used when milling tips in the FEI STRATA dual-beam system. The sample stage could moved in 5 degrees of freedom so a tilt was applied to compensate for the 15° tilt of the cantilever holder.

The combination of the SEM and the FIB columns meant that it was possible to monitor the milling of the tips by the FIB by using the SEM. For milling, the tip was

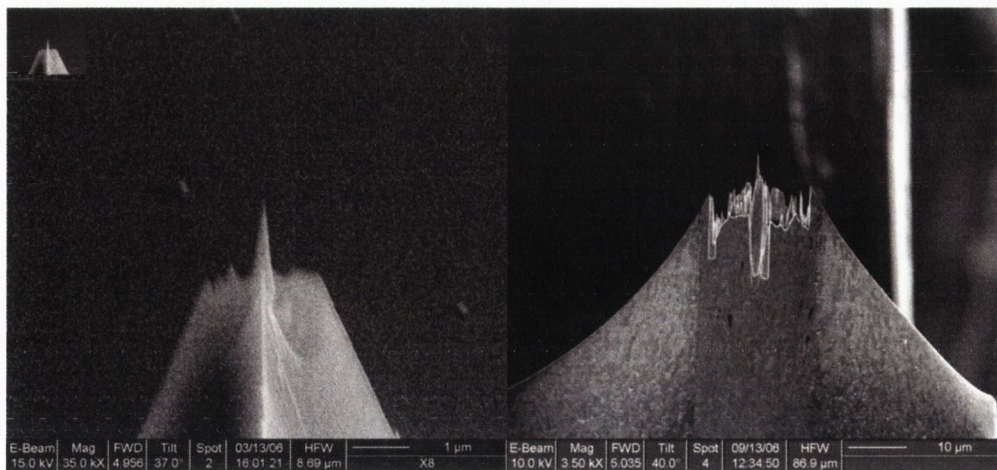


Figure 3.12: SEM images of a silicon (left) and a tungsten (right) tip during machining using the focussed-ion beam.

aligned so that it pointed directly into the ion-beam whilst the SEM was imaging the tip in profile. The control software allowed us to etch a pattern of two concentric circles. During etching the FIB removes material between the two circles thereby etching a cylinder into the sample. By using a small value for the inner radius the etch was beyond the limits of its resolution and therefore what should have been a column was etched as a sharp needle with a parabolic shape (see Fig. 3.12).

Milling was performed on both commercial silicon and tungsten levers. Silicon levers were much easier to mill primarily because of the higher ionic cross-section of the material and that the Strata FIB is designed with the purpose of precision etching of silicon for the semiconductor industry. The milling of tungsten tips was more difficult due to the materials lower ionic cross-section and also its polycrystalline structure which often made milling uneven and require further tidying after the initial milling.

This technique was never used for anything other than refurbishment of levers which had already been used. It was found that the time and effort taken to machine a tip

in the FIB/SEM was not justified unless the reflectivity or other characteristics of the lever made it particularly desirable to re-use.

3.2.2 Calibration of cantilevers

In order to obtain quantitative information from our experimental data it is necessary to obtain a value for the stiffness of the cantilever. A combination of direct and indirect methods were used in these experiments. One method of calculating the stiffness of a rectangular beam cantilever uses the following formula

$$k = \frac{E}{4} w \left(\frac{t}{l} \right)^3 \quad (3.1)$$

where w , t and l are the width, thickness and length of the cantilever beam and E is the Young's modulus of the lever material. The lever dimensions were measured using a scanning electron microscope.

From the SEM images shown in Fig.3.10 the dimensions of the cantilever were determined to be $l = 636.8\mu m$, $w = 84.0\mu m$ and $t = 19.3\mu m$. Taking a value of 4.1×10^{11} Pa for the Youngs modulus of tungsten Eq.3.1 gives us a lever stiffness value of 239.49 N/m. This method was prone to error due to the difficulty in obtaining an accurate measurement of the lever thickness.

Another method used the thermal oscillations of the cantilever to determine the stiffness. Using a spectrum analyser a vibrational spectrum of the cantilever due to thermal oscillation could be recorded.

Fitting a curve to the thermal resonance curve gives a value for the thermal energy of the oscillations. This can be related to the mechanical energy by

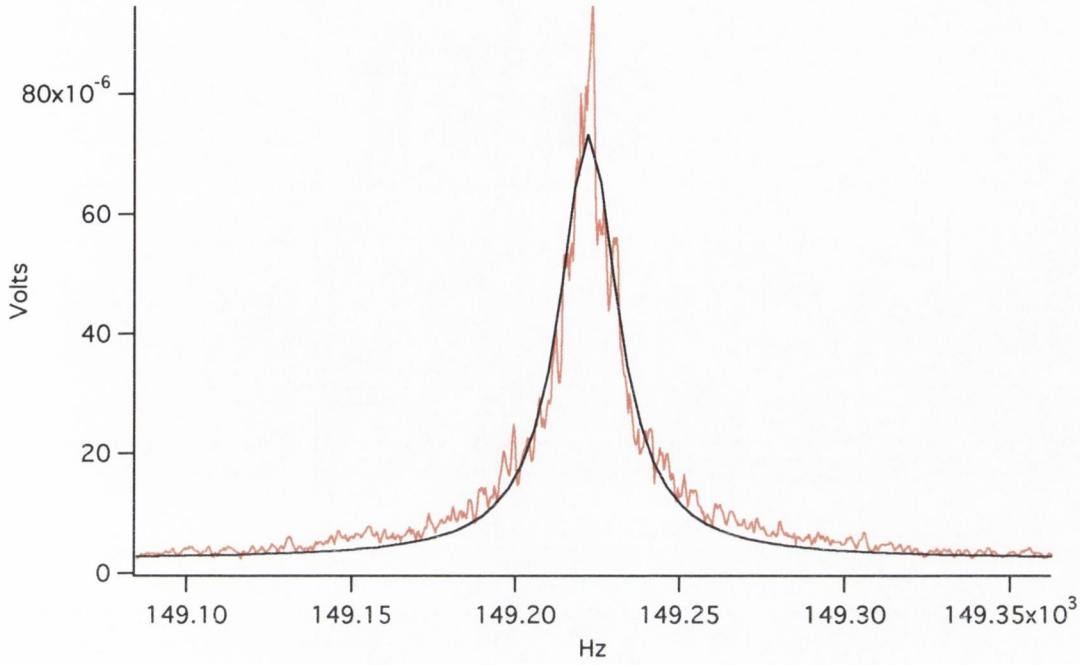


Figure 3.13: Thermal vibrational spectrum recorded around the first resonance peak of a Nanosensors silicon lever Inscb5. The black curve is a Lorentzian function fit to the raw data.

$$\frac{1}{2}k\langle z \rangle^2 = \frac{1}{2}k_B T \quad (3.2)$$

where $\langle z \rangle$ is the rms amplitude, k_B is the Boltzmann constant and T is the temperature in Kelvin. For example, from the vibrational spectrum of the silicon cantilever shown in Fig. 3.13 a value of 34.5 N/m was calculated which compares with the manufacturers value of 40 N/m. Whilst the vibrational spectra of the cantilever was readily available once it was placed in the microscope the obtained stiffness value could be skewed by the presence of a secondary peak close to the cantilever resonance frequency which often resulted in over estimation of the rms amplitude of the thermal vibrations.

Finally, in order to obtain a direct measurement of the stiffness it was necessary to

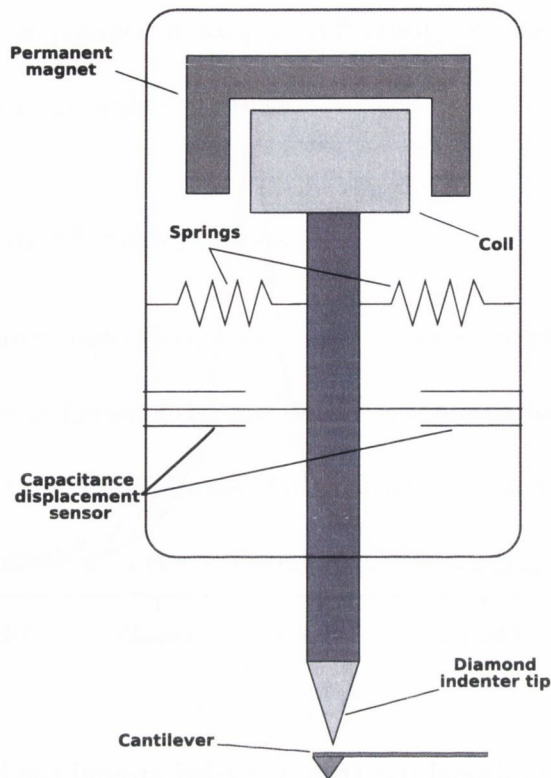


Figure 3.14: Schematic of nanoindenter setup used to determine the lever stiffnesses. A load is applied by passing a current through the coil at the base of the nanoindenter shaft. The indenter tip is made of diamond and has a known geometry. Displacement is detected by measuring the change in capacitance of sensors positioned along the shaft.

push the cantilever against a known spring and measure the deflection. This was done in a nano-indenter. The nano-indenter is a highly specialised instrument for studying the mechanical properties of small volumes of materials. It does this by applying a known load to a stiff, well characterised, indenter tip (usually diamond) in contact with a sample of the material. Compared to typical AFM cantilever spring constants, typical stiffnesses measured by the nano-indenter are very large. Our tungsten cantilevers were however very stiff, with spring constants as large as 300 N/m. This made it possible to resolve the forces required to displace the cantilevers. In determining the lever stiffness

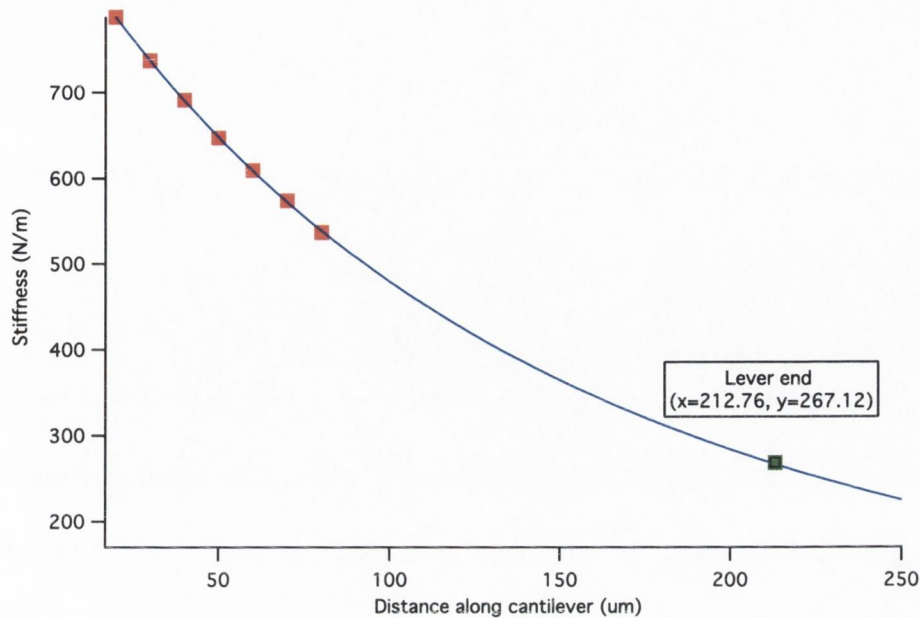


Figure 3.15: Graph of stiffness versus distance along cantilever as measured using a nanoindenter. The red squares correspond to the stiffnesses measured at seven equally spaced points along the length of the cantilever. The blue line is a fit to the experimental data which is extrapolated to the end of the lever.

the resulting displacement for a known applied force was measured at a number of evenly spaced points along the length of the cantilever. A plot of these values is shown in Fig.3.15. The fit is calculated using the inverse cube relation from Eq.3.1

By using the fit to extrapolate to the end of the cantilever the lever stiffness was determined to be 267.12 N/m. This lever is the same tungsten cantilever shown in the SEM images in Fig.3.10. This shows good agreement between the directly measured stiffness and that calculated from the measured dimensions with a difference of 8.9% in the values.

Where possible, all three of these methods were employed in the calibration of our levers. Of the three, the direct measurement of the lever stiffness using the nanoindenter

was taken as the most accurate value whenever it could be measured.

3.3 Preparation of tungsten tips for STM experiments

All STM tips were made using 0.38 mm diameter, 99.9 % purity polycrystalline tungsten wire supplied by Goodfellows Ltd UK. Sections of wire of $\sim 5\text{-}8$ mm were cleaned by sonicating in HPLC purity acetone, isopropanol and de-ionised water before being mounted on standard Omicron UHV stainless steel tip holders or Omicron VT-SPM tripod type gold tip holders depending on the experimental setup. The wires were then electrochemically etched in a 5M solution of NaOH. All etching was performed at room temperature using the Omicron W-TEK tip etching tool. Typical etching parameters for STM tips are listed in Table 3.3.

Wire	ϕ 50 μm polycrystalline tungsten wire
Etching solution	5 Mol/l NaOH
Etching voltage	$\sim 6.5\text{-}6.9$ V
Insertion depth	$\sim 1\text{-}1.5$ mm
Threshold current	$\sim 3.0\text{-}4.5$ mA
Initial current	$\sim 45 - 50$ mA
Typical etch time	5 - 7 mins

Table 3.3: Tungsten STM tip etching parameters.

Once etched, these wires were again rinsed in HPLC purity isopropanol or acetone and de-ionised water in order to remove any residues of the electrolyte. The sharpness

of the tips was assessed using an Olympus microscope with 100 times magnification. If the tip apex was of a suitable sharpness then it could not be resolved even at the highest magnification of the microscope. The tips were then transferred into the UHV system via the fast-entry load-lock. In cases where the tip-sample tunneling was unstable, treatment of the tips by field emission was performed using large voltage pulses applied between the tip and sample. After treatment the scan area would be moved some distance in order to avoid any debris caused by the field emission.

3.4 Sample preparation

3.4.1 Preparation of silicon (111) 7×7 surface

The silicon sample used was cut from a single crystal wafer of P-doped *n*-type Si supplied by Silicon Materials (Germany) [135]. This crystal was oriented to within 0.20° of the (111) plane and had a resistivity of between $0.7 - 0.9 \Omega \text{ cm}$. Once cut to size the samples were mounted on standard Omicron direct current heating sample plates and transferred to UHV. The sample underwent an overnight degas at $\sim 600^\circ\text{C}$ before flash annealing to $900 - 1100^\circ\text{C}$ for 10 - 20 seconds.

3.4.2 Preparation of titanium dioxide (110) 1×1 surface

The preparation of clean ordered oxide surfaces for study with SPM is a major challenge to experimentalists. Within the literature various preparations recipes are used for preparing clean rutile TiO_2 (110). In these studies many different sets of preparation parameters were explored, as well as different sample mountings and heating methods, in order to optimise the sample preparation.

The samples used were rutile $\text{TiO}_2(110)$ single crystals purchased from Crystal GmbH (Germany) [136]. These crystals were oriented to within $\pm 0.1^\circ$ of the (110) plane and were subject to a proprietary epi-polish. The sample dimensions were 10 mm x 3.6 mm x 1 mm. Before mounting, the samples were cleaned by sonicating in HPLC grade Acetone, Isopropanol and milli-Q ultra-pure water and blown dry with oxygen-free nitrogen. Initially the crystals were translucent and pale yellow in colour. The sample colour changed to pale blue and then dark blue as the sample bulk was reduced by annealing.

Typical cleaning cycles consisted of bombardment of the surface with argon ions ranging in energy from 0.5 - 1.0 keV for 5 to 20 minutes in order to remove the surface layers of the crystal. The argon ions were produced using a ISE5 cold-cathode ion gun mounted on one of the chamber ports [137]. This was then followed by annealing at temperatures of up to 1000 K for up to 20 mins to recover the long range order of the crystal surface. The annealing temperature was measured either with a thermocouple mounted behind the sample on a manipulator or by optical or infrared pyrometer outside the UHV chamber. If possible the long range surface order was then checked using LEED (see Fig. 3.16).

Sample preparation was carried out in both a variable-temperature (VT) UHV-SPM and a room-temperature (RT) UHV AFM/STM system. The sample mountings varied depending on the sample heating capabilities of the system being used. All sample holders were outgassed at high temperature for several hours under UHV conditions before samples were mounted on them.

Initially the samples were mounted on standard Omicron VT-SPM sample holders equipped with a pyrolytic boron nitride (PBN) ceramic plate positioned behind the

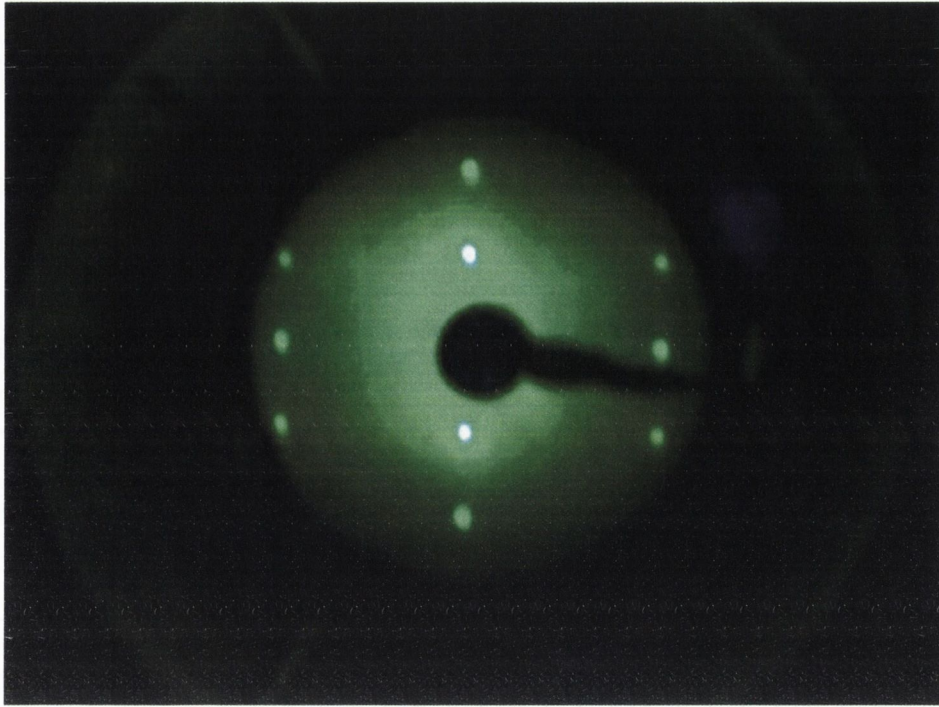


Figure 3.16: Photograph of the 1×1 LEED pattern obtained after 2 cycles of argon ion bombardment of the rutile sample and subsequent annealing to ~ 1000 K. The electron beam energy was 45 eV. Heating of the sample was done by electron bombardment of the back of the sample plate. The blurring of the LEED spots is due to a slight movement of the camera during the prolonged exposure time.

substrate for indirect radiative sample heating (Fig.3.17). The ceramic top-plate of the sample holder was coated with a thin metal film to minimise charging effects during LEED measurements. This film degraded with successive cleaning cycles and was not effective for the entire duration of the measurements. This type of holder made it possible to heat the sample while it was mounted on the SPM stage by passing a small current through the PBN heater. This sample mounting was found to perform worst out of all three configurations. Although a 1×1 LEED pattern was achieved and the imaging of large flat terraces in STM was possible using this heating method, the

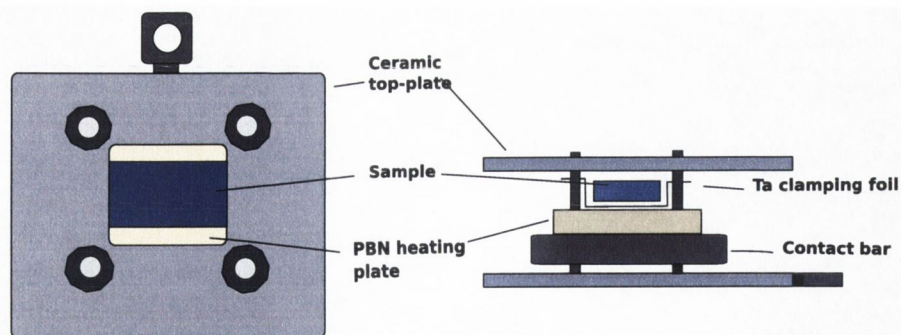


Figure 3.17: Schematic showing top view and side view of sample mounting with pyrolytic boron nitride (PBN) heating plate for radiative heating

surfaces appeared not to be atomically clean and free of contaminants (see Fig.3.18). Clear resolution of atomic features such as defects was difficult to achieve.

In the second mounting configuration the crystals were mounted on bare stainless steel or tantalum Omicron sample plates. The samples were held by Ta wires or leaf springs which were spot-welded to the sample plate (Fig.3.19). In this case the sample heating was provided by either electron bombardment of the back of the sample plate or by radiative heating of the sample plate by a resistive heater consisting of a tungsten filament located behind the sample on the sample manipulator.

It was found that the best results were achieved by sputtering for 10 mins at 1 keV followed and annealing by electron bombardment to a temperature of 973 K as measured by a thermocouple for 5-10 minutes. Typical sample currents during ion bombardment were $\sim 20 - 28 \mu A$. Using this preparation recipe it was possible to observe a clear sharp 1×1 LEED pattern (see Fig 3.16) and image (> 20 nm) clean ordered terraces with a low defect concentration with STM after as little as 2 cycles of sputtering and annealing.

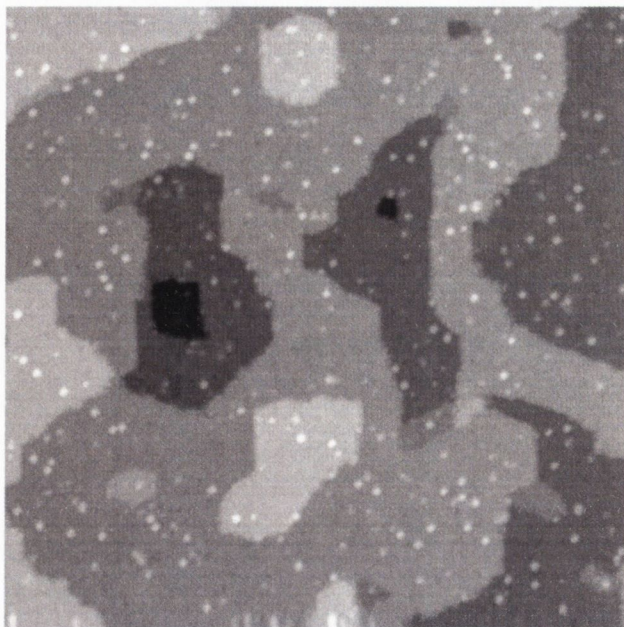


Figure 3.18: 100 nm $\times$ 100 nm scan of $\text{TiO}_2(110)$ surface after a number of cleaning cycles using PBN radiative heating

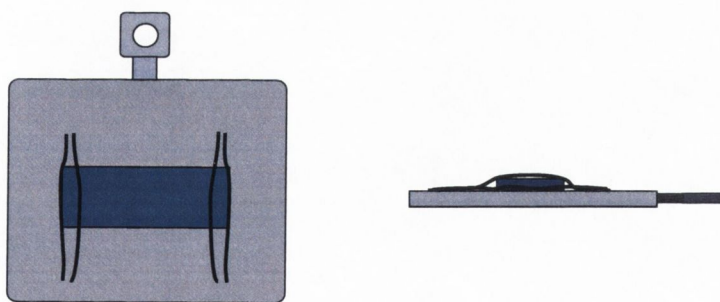


Figure 3.19: Schematic showing top view and side view of sample mounting with Ta wires for e-beam heating.

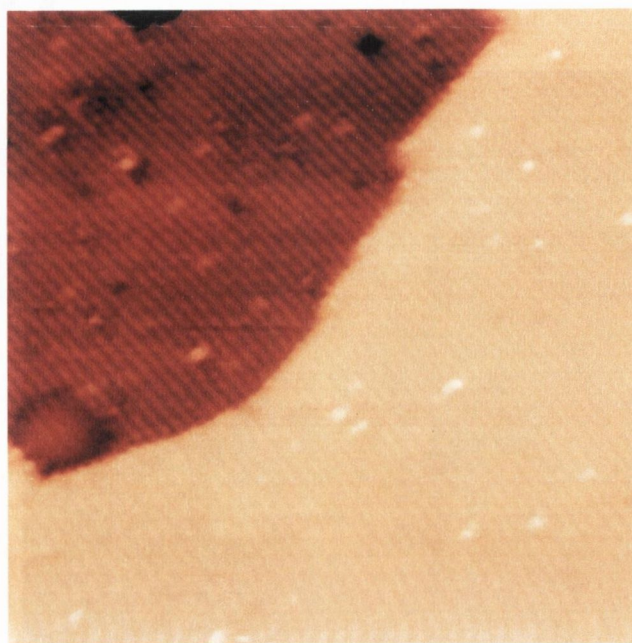


Figure 3.20: STM image showing $400 \text{ \AA} \times 400 \text{ \AA}$ area of surface prepared by two cycles of argon ion bombardment and annealing at 650 C .

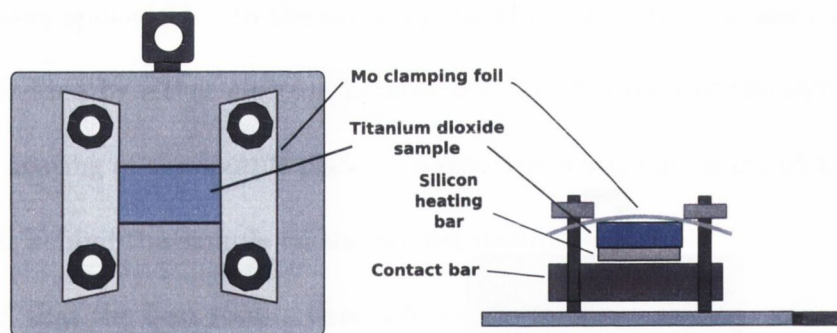


Figure 3.21: Schematic showing top-down and side view of a holder where a silicon bar and the rutile crystal sample are clamped together between the contact bars of an Omicron direct current heating plate. The rutile sample could be heated by passing a current through the silicon bar.

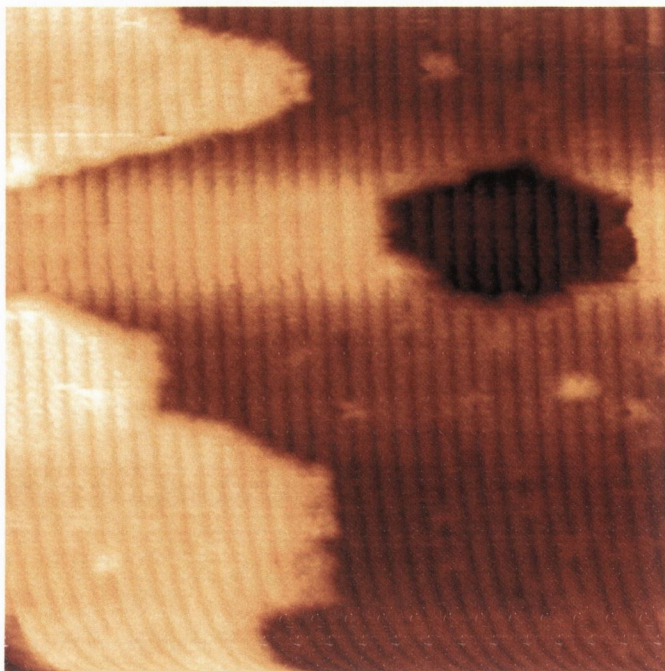


Figure 3.22: STM image of a surface prepared by annealing using a silicon heating bar.

$200 \text{ \AA} \times 200 \text{ \AA}$, $0.2 \text{ nA}/+1.2 \text{ V}$

The last sample holder configuration consisted of a rutile single crystal clamped on top of a lightly doped silicon strip on a Omicron UHV direct heating sample plate (Fig.3.21). Using this sample mounting the rutile crystal could be annealed by passing a current through the silicon bar beneath it. This heating method was used in the RT-SPM in place of the electron bombardment and was effective in reproducibly achieving clean ordered surfaces with a low concentration of defects.

There are a number of possible factors which may have contributed to the contrasting performance of the different sample preparation techniques. Firstly, it may not have been possible to achieve the desired temperature at the surface of the sample within a reasonable time using radiative heating. Bringing the main heating element to the desired temperature could be done more quickly with the Si-bar and e-beam heating

compared with the PBN heating. Also in both the e-beam and the Si-bar holders the sample was in full thermal contact with the main heating element. Secondly, the samples mounted for radiative heating may not have been as effectively sputtered as those mounted for e-beam heating. This is conceivable since the samples mounted for radiative heating were positioned below a ceramic top plate which would have occluded at least a portion of the sample during ion-bombardment and also resulted in the contamination of the surface with material sputtered from the top plate. Also, due to the removal of the thin metallic film from the top plate during sputtering, charging of the ceramic top plate may have further hindered effective ion-bombardment.

3.4.3 Dosing of water on $\text{TiO}_2(110)$

In order to study the effect of water adsorption on the rutile $\text{TiO}_2(110)$ surface small amounts of water vapour were introduced into the UHV chamber. The water used was purified using a three-stage Millipore Element system. This system combined filtration, de-ionisation and UV exposure for the removal of trace organics. The purified water was then placed in a sealed-off stainless steel to pyrex adapter with a CF16 flange. This was connected to the gas admission system of the vacuum system (Fig: 3.23)

Once connected the water was degassed by several freeze-pump-thaw cycles. The water was first frozen by immersing the water slowly in liquid nitrogen. Care was taken to expose the tube to the nitrogen vapour in order to allow it to cool before fully immersing it in the liquid nitrogen and thus avoid cracking of the pyrex due to uneven expansion of the water during freezing. The sealed off pyrex container was then pumped down using the turbo pump. After pumping down the valve between the sealed-off container of water and the turbo-pump (valve 3 in Fig.3.23) was closed and the water

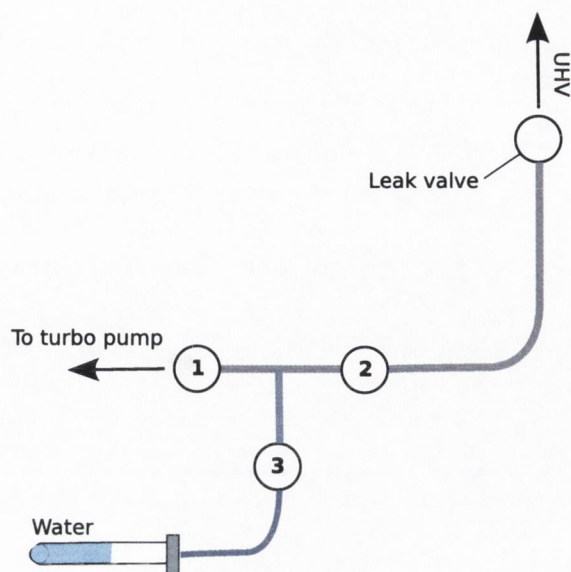


Figure 3.23: Schematic of water dosing setup. The valves between the turbo-pump, gas line and water are numbered for clarity.

was allowed to thaw. This procedure was repeated at least three times before dosing.

Prior to dosing the entire gas line was pumped with valve 3 closed (Fig.3.23) . The line was then flushed with water vapour by opening valve 3 allowing water vapour as far as valve 2. Valve 3 was then closed and valve 2 opened, allowing the water vapour to reach the leak valve. The valve to the turbo (valve 1 in Fig.3.23) was then opened and the gas line pumped until the ultimate backing line pressure was reached.This process was repeated three times before each dosing.

After flushing, the gas line was pumped again using the turbo pump. Water vapour was then allowed into the gas line as-per the procedure above. Once the water vapour was allowed to reach the leak valve, valve 2 was closed and valve 1 opened to pump the t-junction. The vacuum created in the t-junction was then used to draw more vapour in from the water container through valve 3. This vapour was then passed to the gas line via valve 2. This procedure was carried out to stagger the pressure of the water

vapour to prevent high pressures behind the leak valve which could make precise dosing of small amounts difficult.

During dosing of water the precision leak valve was opened and water vapour was introduced to the UHV chamber. Typical doses consisted of exposing the sample to 1×10^{-9} mbar of water vapour for 10 minutes while the sample cooled after annealing.

Chapter 4

Results and discussion

In this chapter the results of the application of our simultaneous multi-parameter scanning probe technique are presented and discussed. In the first section I present our results on the well established 7×7 Si(111) surface. In the second section I move on the investigation of the $\text{TiO}_2(110)$ surface which is main focus of this thesis.

4.1 Simultaneous AFM/STM of the Si(111) 7×7 reconstruction

The 7×7 reconstruction of the Si(111) surface is probably the most studied of all surfaces using scanning probe techniques. Hence it has become something of a reference for UHV-SPM studies where characterisation of the measurement technique is of more interest since the surface itself is considered so well understood. We have studied this surface using both commercial silicon and tungsten levers.

A set of simultaneously acquired STM and force gradient images are presented in Fig.4.1. The STM image shows a typical Si(111) 7×7 image. The force gradient image

in this case shows the corner holes as dark and the adatoms as bright. This indicates a larger attractive force gradient over the corner holes. Although this contrast is contrary to what is typically presented in nc-AFM experiments [138, 71, 139] some other reports of such contrast do exist. Guggisberg *et al* have presented results on frequency shift images taken using tunneling current feedback which show more negative frequency shift over corner holes [140]. Results presented by Hasegawa *et al* show similar contrast in large-amplitude STM/AFM experiments [141]. Although our low-amplitude experiments are not directly comparable to standard nc-AFM where amplitudes can be 10 nm or more it is expected that there are less attractive force gradients over corner-holes. This has also been found in theoretical modeling of the surface [128]. Such contrast in a simultaneous AFM/STM experiment was previously reported by Oral *et al* [124]. In that study the authors proposed that the unexpected contrast in force gradient may have been due to the contribution of long-range forces acting on the tip as it followed a constant current tip-trajectory which involves motion in the long-range field. Previous theoretical modeling of the surface assumes a flat tip trajectory.

To eliminate the effect of long-range forces, and the possible crosstalk between measurement parameters due to the corrugated motion of the tip during STM feedback mode, we developed a technique for flat scanning the tip. Measurements were carried out where on the forward scan the STM feedback was engaged and on the reverse scan the STM feedback was disengaged and thereby flattening the tip trajectory. In the simultaneously acquired force gradient images it was found that the force gradients remained more attractive over the corner holes regardless of the tip trajectory. In Fig.4.2 some of these data are shown. The images are arranged into two columns of three images, all of which were recorded in the same experiment with the same tip. The images in the

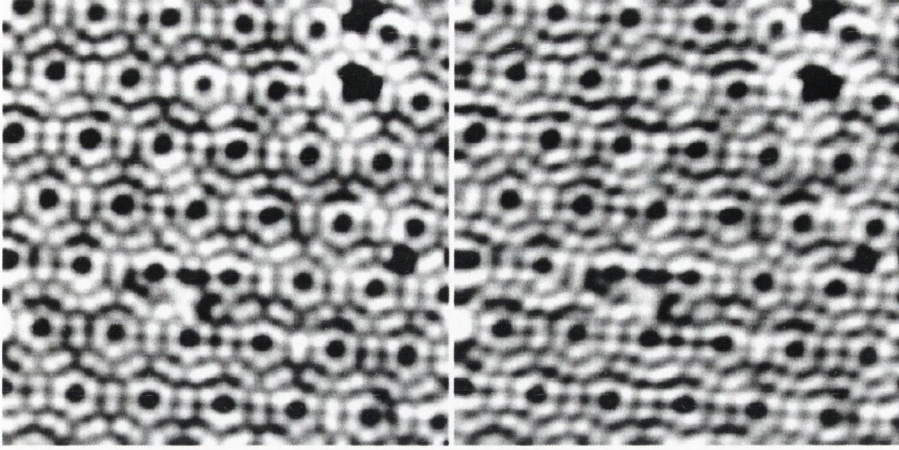


Figure 4.1: Simultaneous STM (left) and force gradient (right) images of the (7×7) reconstruction of Si(111). Scan area $150\text{\AA}\times 150\text{\AA}$, $0.25\text{ nA}/2.0\text{ V}$, $A_0 = 0.3\text{\AA}$ and $k_{\text{lever}} \sim 40\text{N/m}$.

column on the left correspond to those which were acquired in normal STM feedback mode during the forward scan while those on the left were acquired with the feedback switched off on the backward scan. The top row of images show the tunneling current image. For the forward scan the tunneling current image shows no surface structure which is to be expected as the STM feedback tries to keep the value of I_t constant. On the reverse scan the surface structure can be clearly seen in the variation of the tunneling current as the tip is scanned without feedback across the surface. In the corresponding STM topography images the surface structure can be clearly seen on the forward on not on the reverse scan. These images confirm that the flat-scanning is working as it should. In the force gradient images however, while there is a reduction in the force gradient corrugation due to the removal of the tip trajectory, there is no inversion of the contrast i.e. corner holes still appear more attractive. These surprising results showed that the influence of tip-trajectory and long range forces could not explain the contrast

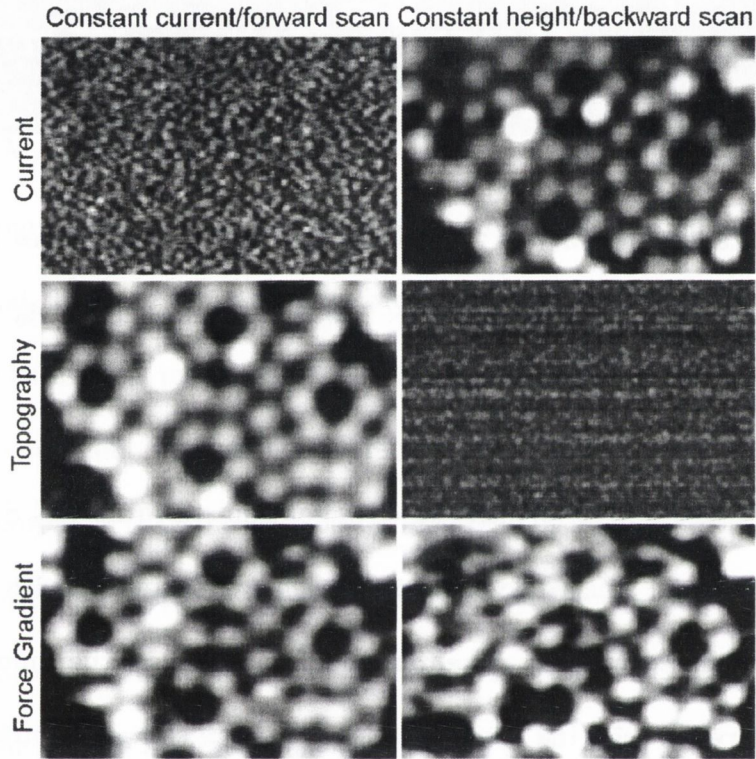


Figure 4.2: Constant-current and constant-height STM images with simultaneously acquired force gradient images of the 7×7 reconstruction of Si(111). Both show more attractive force gradients over the corner holes as opposed to the adatoms. Tungsten lever ($k_{\text{lever}} = 231 \text{ N/m}$). $A_0 = 0.5 \text{ \AA}$. I_t set-point on forward scan $0.5 \text{ nA}/2.0 \text{ V}$.

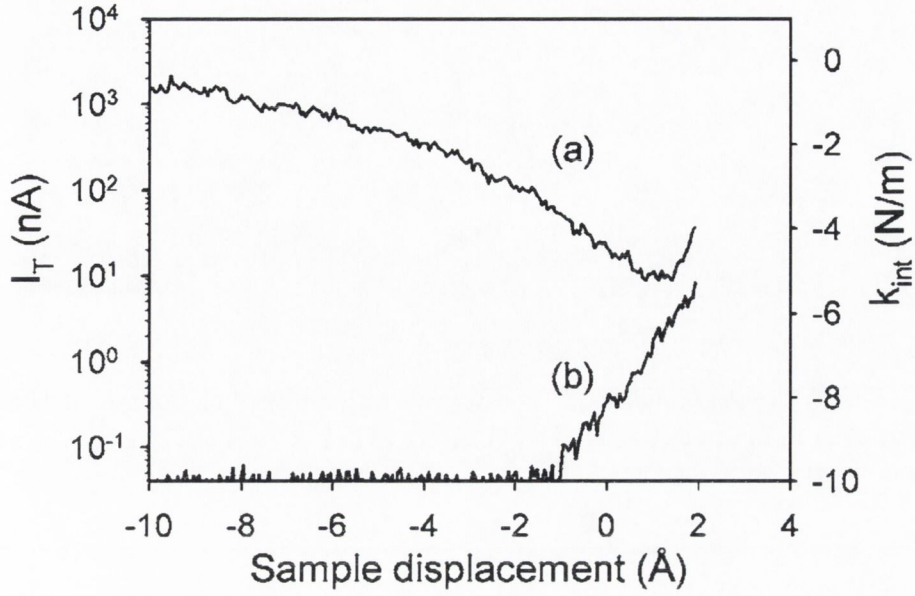


Figure 4.3: Spectroscopic data curve showing (a) force gradient/total interaction stiffness (k_{int}) and (b) tunneling current I_t vs. tip-sample displacement for a tungsten tip on the 7×7 reconstruction of Si(111). $A_0 = 0.5 \text{ \AA}$, $k_{lever} \sim 231 \text{ N/m}$. Data shown are an average of four curves.

observed.

A possible explanation for the observed contrast is that the tip is close enough to the adatoms for the interaction to be in part repulsive whereas for the corner holes the interaction is still purely attractive. There is, however, evidence that this is not the case. Firstly, numerous spectroscopic data curves were taken with the same tip over the surface. These curves are not site specific. However some are likely to have been over adatom sites. In all these curves we have seen no evidence of repulsion below ~ 5 nA, typical I_t set-point during our experiments were much less than 5 nA. Also, while imaging at 0.25 nA the I_t set-point was increased to 5 nA. This change resulted in an increase in the force gradient contrast magnitude and an increase in the overall oscillation

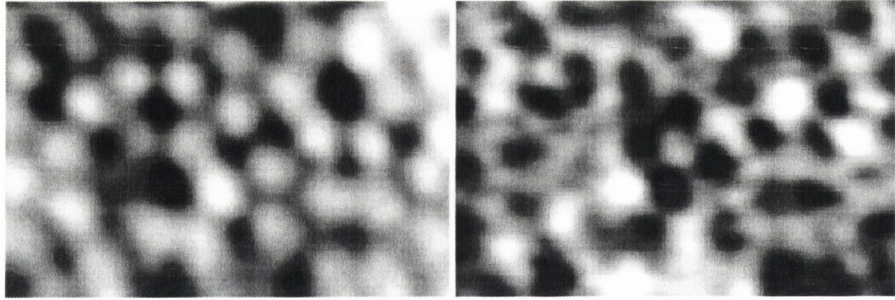


Figure 4.4: Simultaneous STM (left) and force gradient (right) images of the 7×7 reconstruction of Si(111).

amplitude which could not be possible if any part of the image were in repulsion.

During measurement commercial silicon cantilevers were also used. Silicon tips are used in the vast majority of NC-AFM experiments. We found that different contrast could be obtained with some Si tips. In about 15 % of the atomic resolution images which were acquired using silicon cantilevers contrast of the type shown in Fig.4.4 was seen i.e. showing more attractive force gradients over the adatoms compared with the corner holes. This type of contrast is consistent with what is typically reported in the literature. Note that there is no corresponding change in the STM topography and therefore no drastic change in the tip trajectory. This inversion is as a result of some (unknown) change in the tip. It might be due to a change in the polarity of the charge at the tip apex as has been suggested in the interpretation of inverted contrast of defects on $\text{TiO}_2(110)$ [122]. It should be stressed that this type of contrast was never observed with tungsten tips. This strongly implies that the tip chemical species has a key role in the image contrast and whether it inverts.

These results suggest that the observed contrast in noncontact AFM may be determined by the tip apex chemistry even on a well studied system such as Si(111) 7×7 .

This is disturbing in that the interacting tip apex is the most inaccessible part of our experimental setup and therefore the most difficult to characterise making modeling of the results, a very labour-intensive process whereby large numbers of tip configurations may have to be tried to find good agreement [84]. However, measuring more than one parameter should help narrow down the possible tip configurations which could be responsible for the observed contrast, because as we have seen above, the STM and force gradients do not change in the same way when the tip changes.

4.2 Simultaneous multi-parameter SPM of $\text{TiO}_2(110)$

4.2.1 Overview of contrast regimes in STM of $\text{TiO}_2(110)$

In this section a number of observed STM contrast regimes for the $\text{TiO}_2(110)$ (1×1) surface are introduced with examples from our measurements carried out on a standard Omicron VT-SPM [137] as well as comparison with experimental reports from the literature. These images rely on one experimentally measured parameter (I_t) so there is no other simultaneously acquired data with which to compare the registry. Due to the symmetry of the surface an image of a perfectly stoichiometric surface would look the same regardless of which surface species is being imaged since the periodicity of the rows of 5-fold coordinated Ti atoms and the 2-fold coordinated bridging O atoms is the same. For this reason the sole indication of any change in contrast is to be seen in the defects.

In the first of these STM contrast regimes the defects appear as bright objects between bright rows (see Fig.4.5). This type of contrast corresponds to what is mostly reported in the literature. From the image shown in Fig.4.5 it can be seen that there are different species of defect on the surface. These have been observed and categorised in a series of studies by the groups of Besenbacher and Thornton as bridging oxygen row defects and the products of water dissociation.

Another example of this image contrast is shown in Fig.4.6. In this image a similar distribution of defects can be seen some of which appear to be diffusing during imaging whereas others remain static.

The particular categorisation has been the source of some debate within the literature. Discrimination between defect species is based on their apparent height in STM and comparison with DFT calculations [115] and their reactivity with dosed water [116].

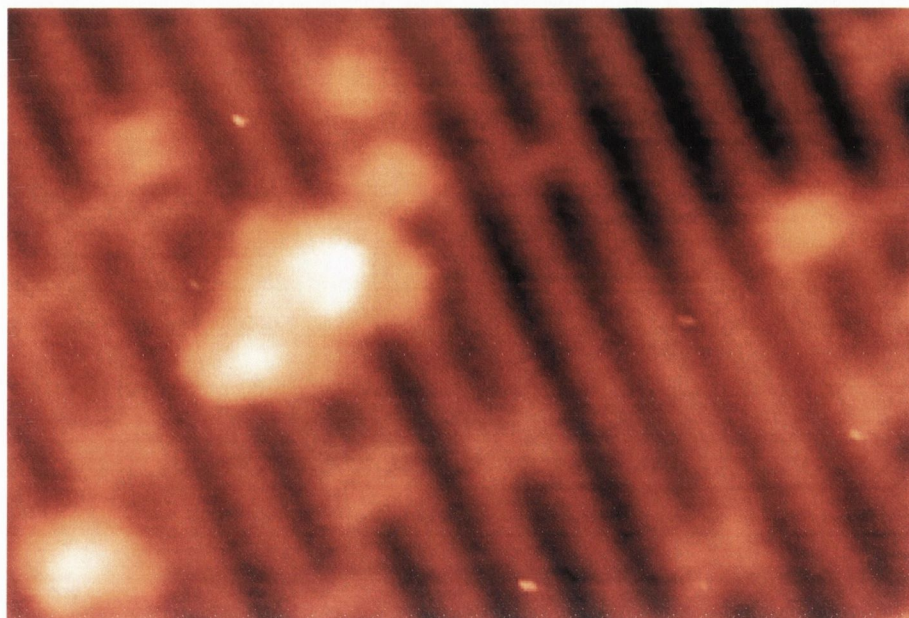


Figure 4.5: STM constant current topograph of the (1×1) $\text{TiO}_2(110)$ surface. In this image defects appear as bright objects between bright rows. Image area $95\text{\AA} \times 65\text{\AA}$, $0.12\text{ nA}/+1.29\text{ V}$.

In the second of these contrast regimes the appearance of defects is completely inverted. In this case the defects appear as dark objects between dark rows. Other examples of this type of contrast do exist [109, 111, 142, 143] (see Fig.1.13 in section 1.4.2). Fischer *et al.* [109] interpreted these dark objects as bridging oxygen row defects and therefore that the bridging O-atoms were being imaged as bright features. This type of contrast is rarely rarely seen in the literature subsequent to experiments by various groups [110, 114, 113] and the supporting theoretical work of Ng and Vanderbilt [144]

In the last of the contrast regimes we observe, the STM image appears to be made up of contributions from both atomic species, a type of contrast which was the focus of a paper by Guo *et al.* [121]. This type of contrast has also been reported by Tanner *et al.* [145] and Diebold *et al.* [111]. Their images can be seen in Fig.4.8 for comparison.

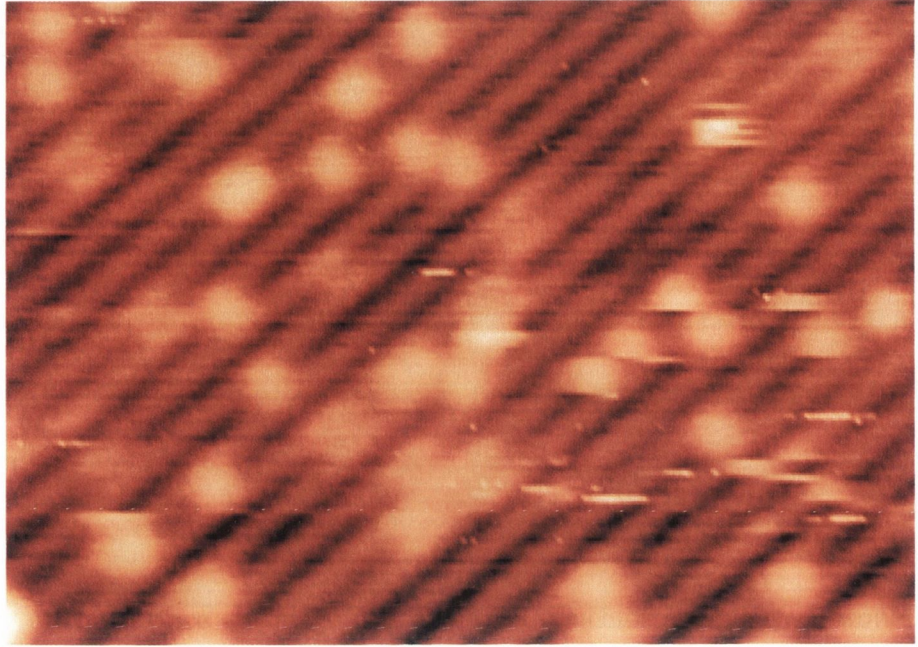


Figure 4.6: STM constant current topograph of the (1×1) $\text{TiO}_2(110)$ surface. In this image defects appear as bright objects between bright rows. Some defects can be seen to be diffusing during imaging. Image area $135 \text{ \AA} \times 95 \text{ \AA}$, $0.20 \text{ nA}/+1.50 \text{ V}$.

From the evidence presented above it can be seen that although the literature is dominated by reports where the 5-fold coordinated Ti atoms are imaged as bright and defects appear as bright objects between bright rows [146], a number of other contrast regimes have been reproducibly observed on the (1×1) $\text{TiO}_2(110)$ surface using standard STM techniques. It is important to highlight this fact when interpreting the results of our novel SPM studies, since it is evidence that the observed contrast in those results is not due to the technique itself. It can also be seen that in standard STM the assignment of which surface species is imaged as bright and which is imaged as dark relies on the observed contrast of the defects which are assumed to be the same.

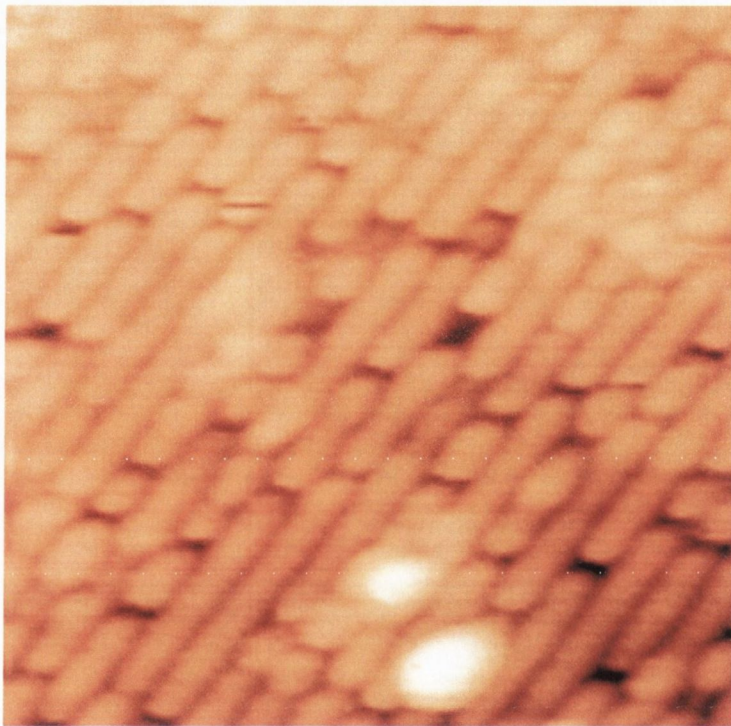


Figure 4.7: STM constant current topograph of the (1×1) $\text{TiO}_2(110)$ surface. In this image defects appear as dark objects between dark rows. Several types of defects appear on the surface which can be distinguished by their width and height (or depth in this case). Image area $100\text{\AA} \times 100\text{\AA}$, $0.19\text{ nA}/+1.51\text{ V}$.

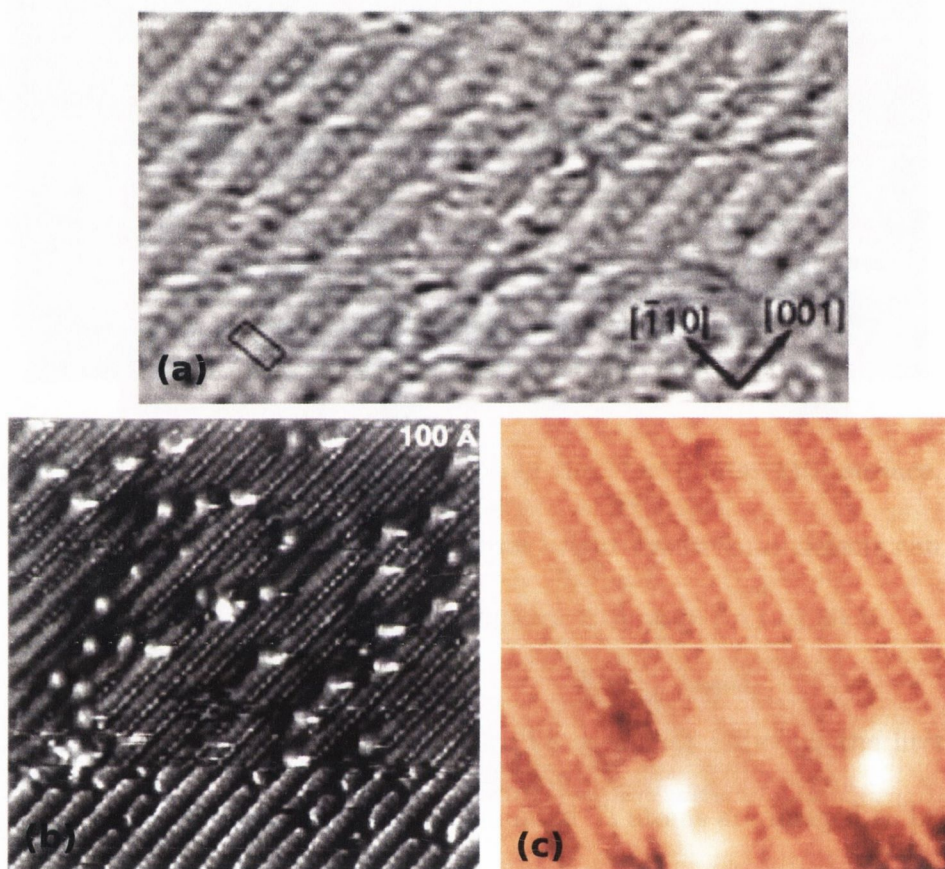


Figure 4.8: STM images of the $\text{TiO}_2(110)$ surface. Image (a) is from Tanner *et al* 1998 ($95 \text{ \AA} \times 50 \text{ \AA}$, $2.0 \text{ nA}/+0.75 \text{ V}$) (b) from Diebold *et. al.* 1998 ($100 \text{ \AA} \times 100 \text{ \AA}$, imaging parameters not available) and (c) from my own studies ($81 \text{ \AA} \times 86 \text{ \AA}$, $0.20 \text{ nA}/+1.31 \text{ V}$). These images appears to show contributions from both Ti and O atoms.

4.2.2 Spectroscopic data curves on $\text{TiO}_2(110)$

As a routine part of our measurements spectroscopic data were acquired by recording multiple parameters whilst varying the tip-sample normal separation. Data on tunneling current (I_t) amplitude (and hence $\frac{\delta I}{\delta z}$), phase, and δI were recorded. In the acquisition of a spectroscopic curve the tip is initially in tunneling range at a given set-point. Once the spectroscopic acquisition begins the tunneling feedback is disengaged and the sample is retracted a defined distance. The software then records the data for each channel as the tip-sample distance is decreased. The tip-sample distance continues to decrease until the I_t reaches a certain user-defined value. Once that limiting value of I_t is reached the sample is retracted. Data are recorded on both approach and retract. It is important to note that these data curves are *not* site specific due to the possibility of lateral drift during measurement and so must be taken as an average across the surface.

Fig.4.9 shows the variation in I_t and force gradient as the sample approaches a tungsten tip. It can be seen from the force gradient curve that there are significant long-range contributions present. The minimum of the force gradient occurs at almost the same point as the onset of tunneling. For I_t values of only 0.3 nA the interaction force gradient is already entering the repulsive regime with a possible tip crash occurring before the I_t limit of 0.5 nA has been reached. The reverse force gradient curve shows significant hysteresis due to the tip-sample interaction probably inducing some tip deformation. Virtually no hysteresis can be seen in the tunneling current however. This may be an indication that there was no adhesion between the tip and sample.

In Fig.4.10 a spectroscopic data curve for a silicon tip is shown. This tip had been sharpened using the FIB after it had been crashed in previous measurements. From the force gradient curve it can be seen that there is far less long-range contribution. This is

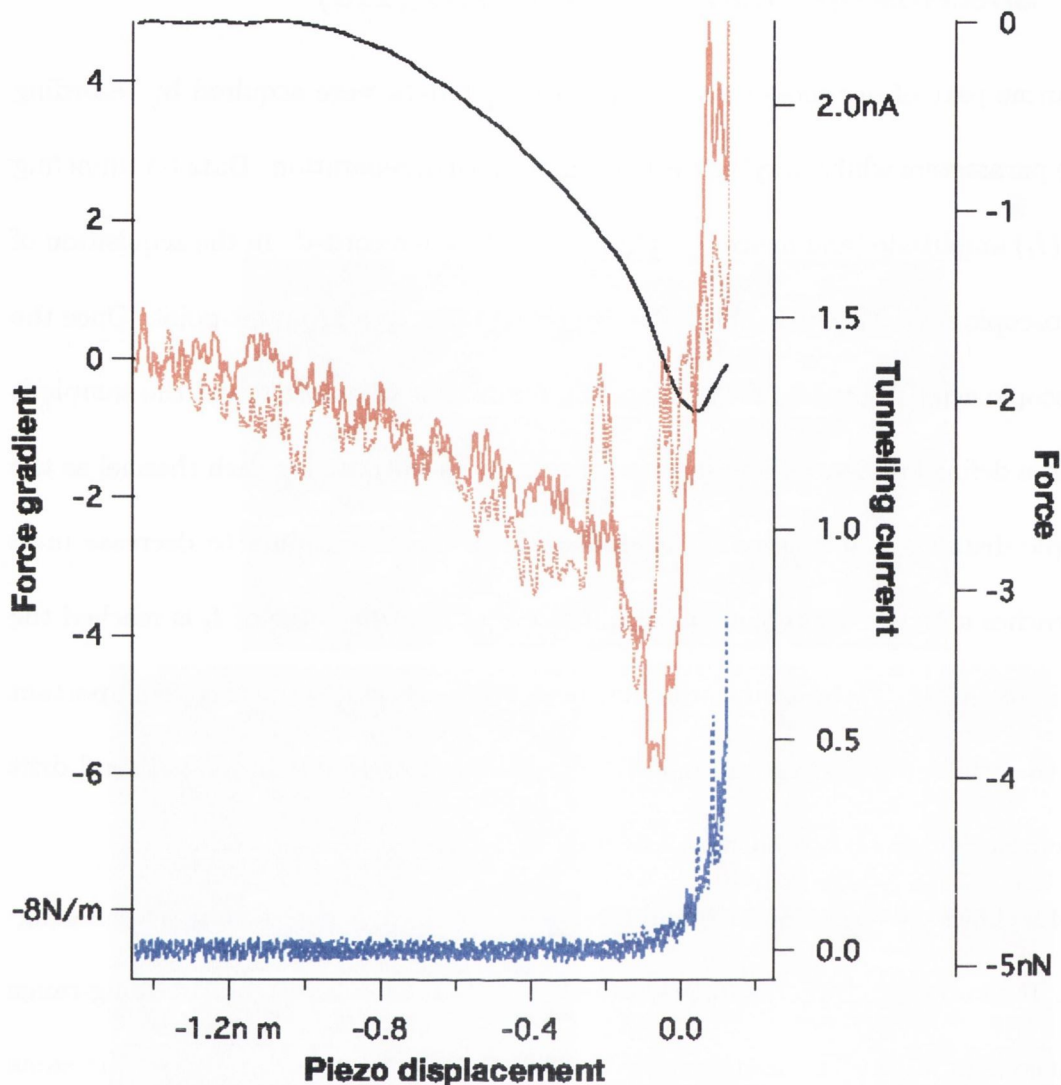


Figure 4.9: Spectroscopic data curves showing variation in I_t (blue curve), force gradient (red curve) with piezo displacement (the reverse of both are shown as dotted curves). The black curve is the force obtained by integrating the force gradient curve. The lever in this case was tungsten, $k_{\text{lever}} = 265 \text{ N/m}$ and $A_0 = 0.2 \text{ \AA}$, $V_{\text{bias}} = +1.8 \text{ V}$.

almost certainly due to a high-aspect ratio and small tip radius as a result of the FIB milling. From the force gradient curve it can be seen that the tip-sample interaction has moved further into the repulsive regime. As in Fig.4.9 the force interaction has a much longer length scale than the tunneling. Unlike Fig.4.9 the rate of increase in

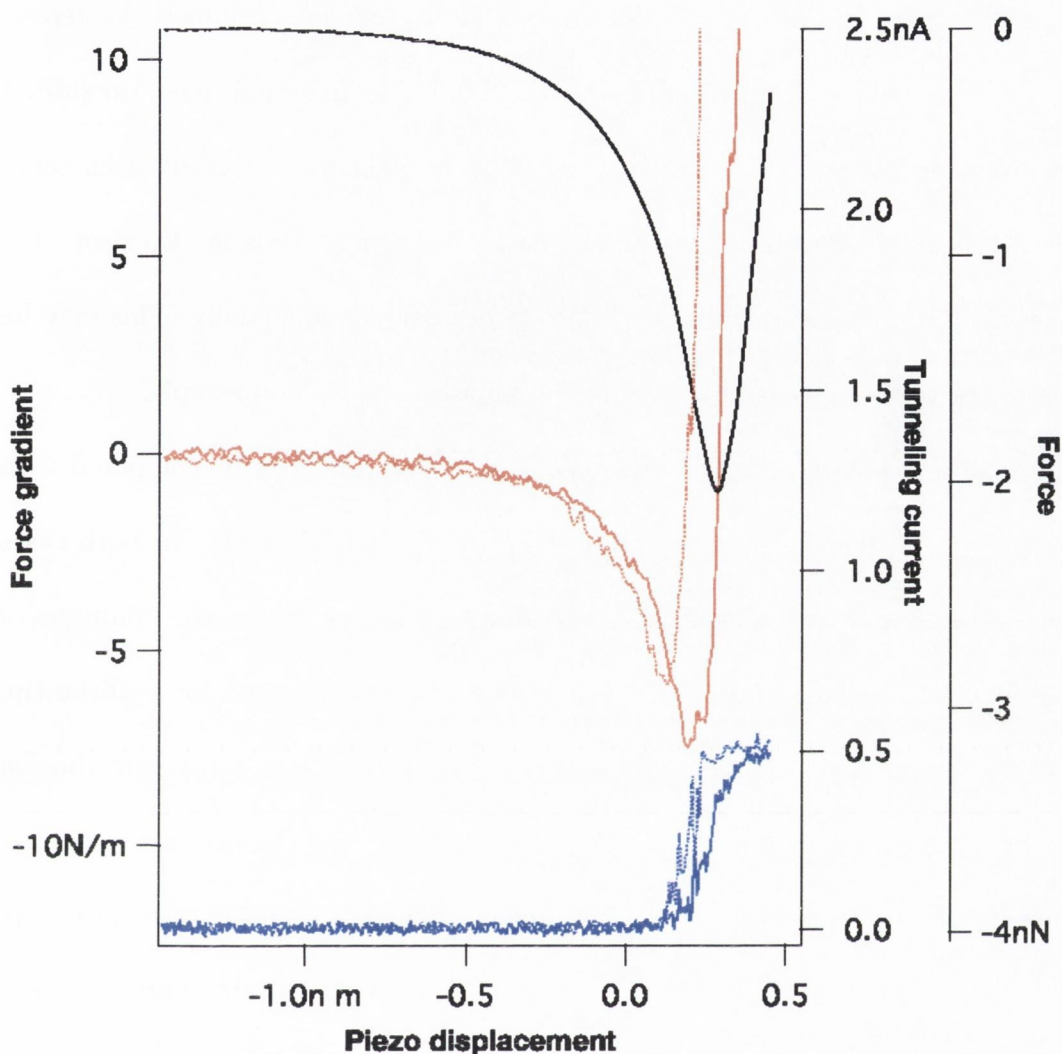


Figure 4.10: Spectroscopic data curve showing variation in I_t (blue curve), force gradient (red curve) with piezo displacement (the reverse of both are shown as dotted curves). The black curve is the force obtained by integrating the force gradient curve. The lever in this case was silicon, $k_{\text{lever}} = 40 \text{ N/m}$ and $A_0 = 0.25 \text{ \AA}$, $V_{\text{bias}} = +1.8 \text{ V}$. Tip had been milled using FIB.

I_t on approach falls off at smaller separations. This would indicate reduction in the barrier-height. The point at which the reduction in barrier-height is seen almost exactly coincides with the onset of repulsion. This reduction in barrier-height could be due to

the onset of local relaxations in the tip. The reverse force gradient curve shows hysteresis with the minimum reduced in magnitude by 1.7 N/m. The minimum has also shifted by 0.8 Å although this may be in part due to drift during the measurement, each curve taking ~ 10 seconds to acquire. In the reverse I_t curve, hysteresis is also seen. On retraction, the I_t curve plateaus for ~ 2 Å before decaying exponentially. This may be an indication of tip relaxations due to adhesion between the tip and sample.

By integrating the force gradient the force is obtained. This can be compared with the theoretically predicted values of Foster *et. al.* [147] (see Fig.4.11). In both cases shown above (i.e. for both a silicon and a tungsten tip), our values for the minimum of the force interaction agree well with the values found by Foster *et. al.* for a silicon tip. In the case of the tungsten tip there does appear to be a greater long-range contribution to the force gradient curve than is the case for the silicon tip. The actual short-range contribution may be more in line with values found by Foster for an Mg terminated tip.

In some of the force gradient curves obtained a secondary local minimum was measured. This occurred using both silicon and tungsten levers. Two examples are shown in Fig. 4.12. For the silicon tip the minima are 2.8 Å apart with the onset of the second interaction coinciding with the onset of significant variation in phase. This phase variation is indicative of energy dissipation possibly due to some atomic rearrangement of the tip. This point also coincides with the onset of tunneling. As in Fig. 4.10 (another curve taken using the same tip during the same set of measurements) a discontinuity in the force gradient curve is observed as the interaction force gradient becomes increasingly repulsive. A corresponding feature is seen in the phase variation. This point also corresponds with the collapse of the tunneling barrier. For the tungsten tip (see Fig. 4.11 (right)) the minima are 2.1 Å apart. For this tip however little phase variation is

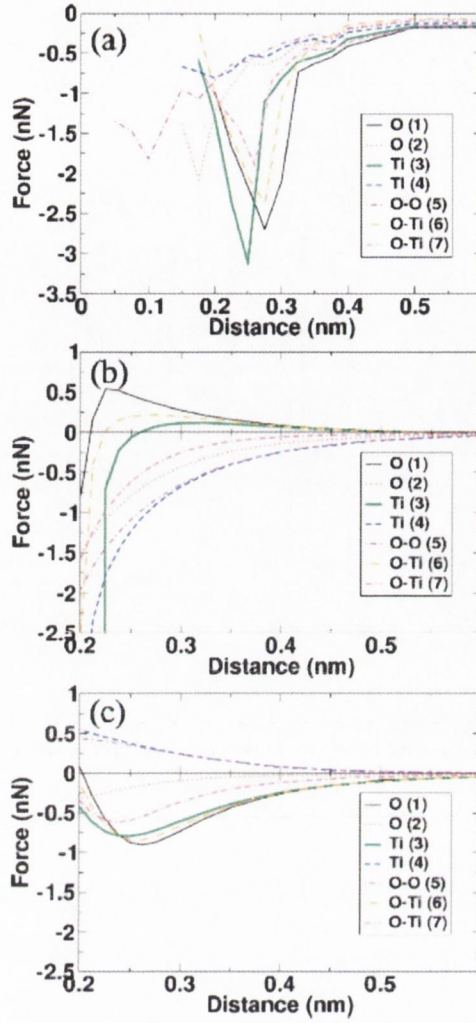


Figure 4.11: Force vs. distance curves for (a) a silicon tip, (b) an oxide tip with an oxygen atom at the apex and (c) an oxide tip with a magnesium atom at the apex over different atomic sites on the $\text{TiO}_2(100)$ surface. These curves are the result of a simulation of non-contact AFM imaging based on first principles and atomistic methods (adapted from Foster *et al.* 2003).

observed before the second local minimum is reached. This would indicate that dissipation, a sign of some energy loss perhaps due to some motion in the region of the tip apex, is more likely with silicon tips.

Such features have been reported in other studies of 3-dimensional force mapping

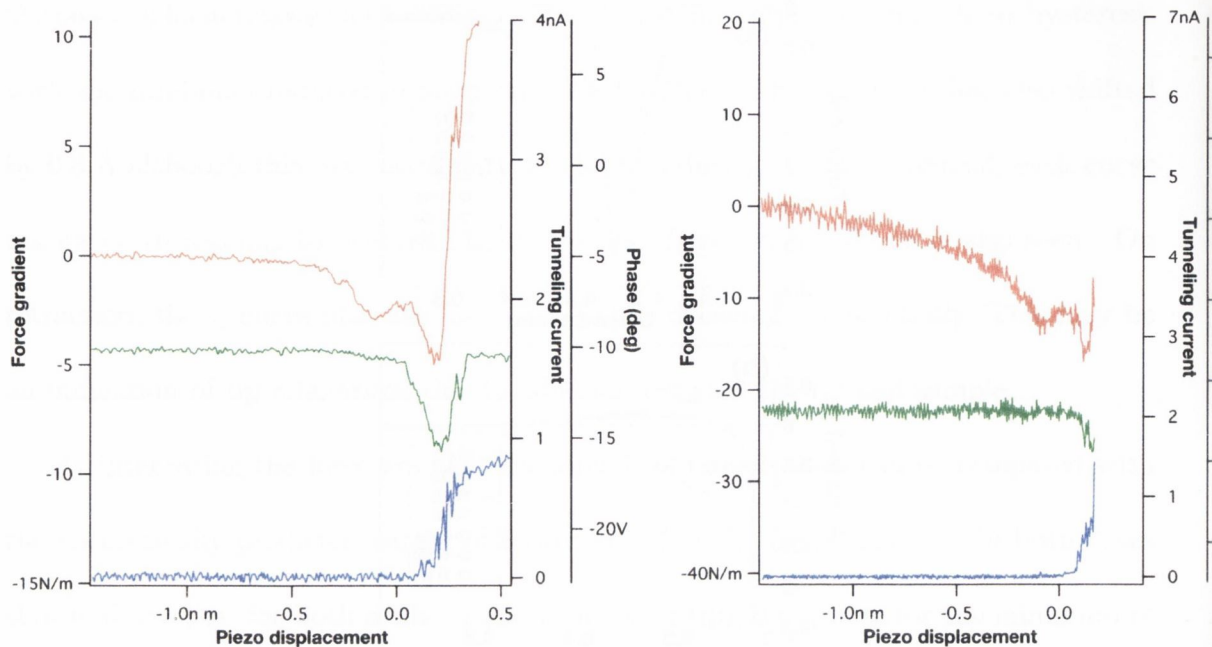


Figure 4.12: Force vs. distance curves for a silicon tip (left) and a tungsten tip (right) on the $\text{TiO}_2(110)$ surface. Both force gradient curves (red) show a secondary local minimum. These features were also seen on retraction. Also plotted are the tunneling current (blue) and phase (green).

in dynamic AFM. Schirmeisen *et al.* have observed discontinuities in spectroscopic force curves on NaCl which they explain by considering a lateral relaxation of the tip during approach [148]. Schmidt *et al.* described similar features and mechanism for 3-dimensional force mapping on NiO(001) [149]. In the case of our measurements however, perhaps due to the low-amplitudes used, these features do not appear as slight discontinuities but as more pronounced features in force spectroscopy.

4.2.3 Contrast in simultaneous multi-parameter SPM of $\text{TiO}_2(110)$

In the course of the novel multi-parameter SPM experiments some of the contrast regimes described earlier in section 4.2.1 were observed. In Fig. 4.13 a set of simultaneously acquired force gradient/STM images are presented. From the top panel it can be seen that this image would appear to be in the first STM contrast regime where the defects appear as bright objects in between bright rows. In the force gradient image the defects also appear as bright objects between bright rows. Note that this indicates a lower amplitude over the defect and hence less attractive force gradient. In the barrier-height image the defects appear as dark objects. That this indicates a drop in the apparent local barrier-height over the defect.

Reports in the literature on STM of the $\text{TiO}_2(110)$ (1×1) surface support the assignment of the bright objects in the STM topography image as bridging oxygen row defects for several reasons. The computational simulations of Ng and Vanderbilt [110] show that constant charge contours protrude further out over the 5-fold coordinated Ti rows compared with the 2-fold coordinated bridging O rows (see Fig.4.14). Therefore the Ti-rows should appear bright in a constant current STM image. Ng and Vanderbilt's calculations also predict a rise in the current density where a defect is created by the removal of a bridging O-atom, and would therefore appear as bright objects in constant current STM. Their work also shows a much shorter decay length of the current density, and therefore greater apparent local barrier-height, over the bridging O atoms compared to the in-plane Ti atoms. Their calculations also show a drop in local barrier height over a bridging O-row vacancy. All of these we observe in the images in Fig. 4.13. From this we have more evidence that the defects shown are due to bridging O-row vacancies and that the in-plane Ti rows are imaged as bright in our STM topography image.

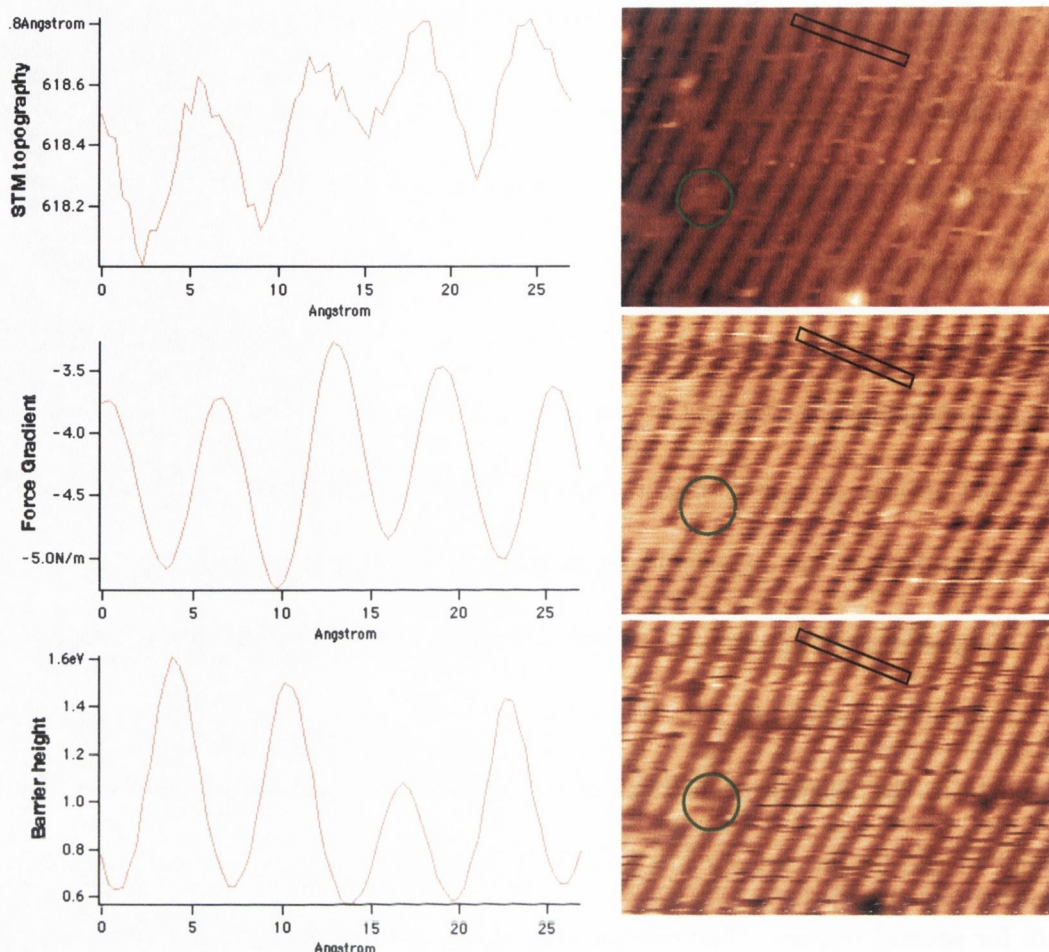


Figure 4.13: A set of simultaneously acquired SPM images. The top panel is the STM topography image, the centre image is the amplitude and the bottom image is δI . On the left of the are profiles taken from each image over the same area in each image (outlined in black on the images). The data in each profile has been used to calculate quantitative values for apparent topography ($\text{\AA}$, force gradient (N/m) and barrier-height (eV). Also circled in green is a single defect. 0.15 nA/+1.3 V (Si tip).

Based on this evidence our interpretation of the simultaneously acquired force gradient image is that there is less attraction over the bridging-O rows compared with the in-plane Ti rows. The STM topography corresponds to the overall tip trajectory so by comparing the topography and force gradient profiles in Fig.4.13 it can be seen that

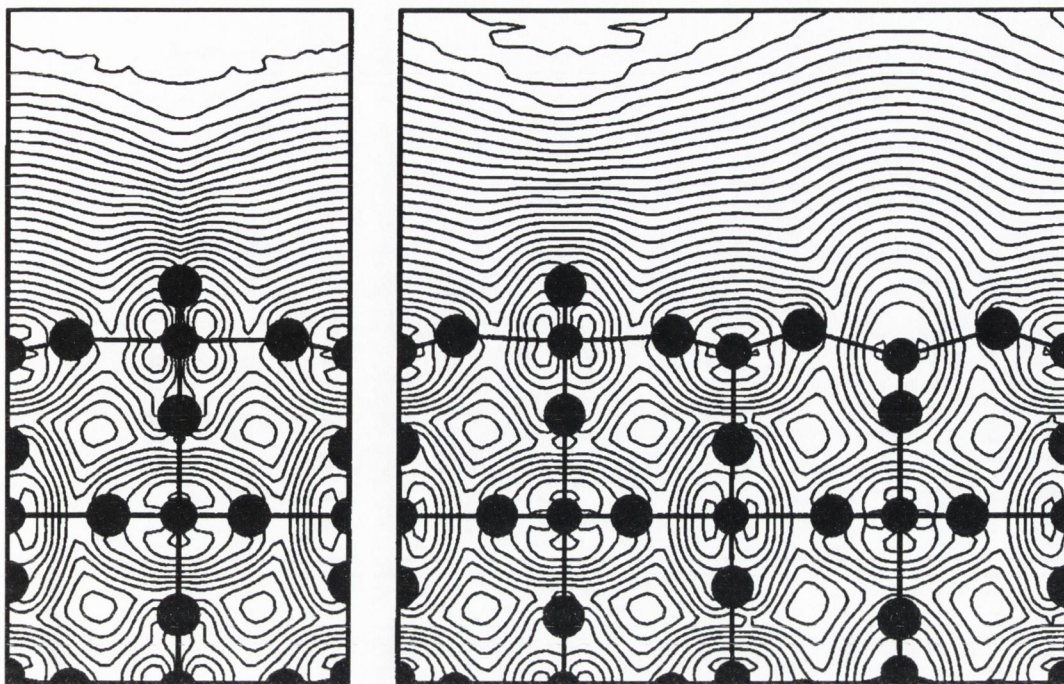


Figure 4.14: Contour plots of $[001]$ averaged charge densities associated with electron states within 2 eV of the conduction band minimum for (left) a relaxed stoichiometric (1×1) surface and (right) a relaxed oxygen deficient surface. Note the variation in the spacing of the charge contours which indicates the change in barrier-height across the surface (from Diebold et al 1996).

as the tip moves towards the surface the force gradient become more attractive. This would indicate that during imaging the tip is moving along the negative slope of the attractive force gradient. This is supported by a partial force curve taken at the end of the imaging session which produced the images shown (Fig.4.15).

If the picture of the surface electronic structure presented by Vanderbilt and co-workers [110, 144] is a fair representation of the actual surface, and our STM and barrier-height data would indicate that it is, then the dominance of electronic structure over topography in the $\text{TiO}_2(110)$ (1×1) is the result of a fine balance between those

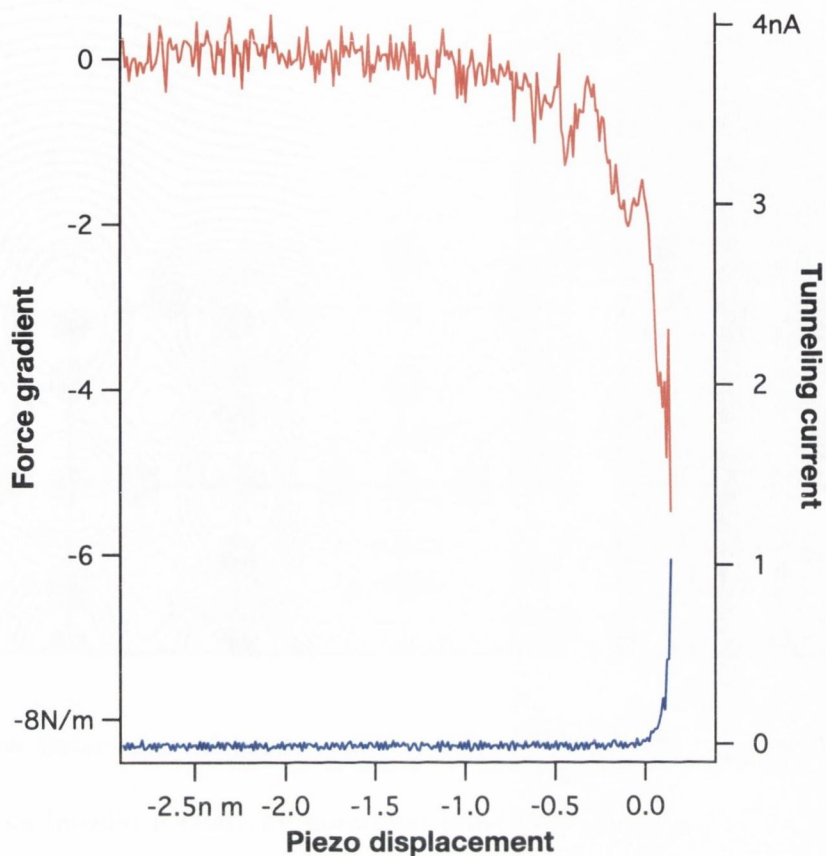


Figure 4.15: Spectroscopic curve acquired some time after recording the images in the previous figure. The graph is a plot of the variation of the interaction stiffness and tunneling current as the tip sample distance is decreased.

two competing influences. Interestingly, recent data on the structure of the $\text{TiO}_2(110)$ (1×1) surface has measured an outward relaxation of the bridging O atoms [97, 98, 96] (see chapter 1.4.2). In their study Vanderbilt and co-workers have calculated the charge density for a surface where the bridging O atoms relax a significant amount towards the surface. Hence their assumptions about the surface topography may not be an accurate reflection of the actual surface and the balance for imaging may be even finer than originally thought.

An example of the second contrast regime is shown in Fig.4.16. In the STM to-

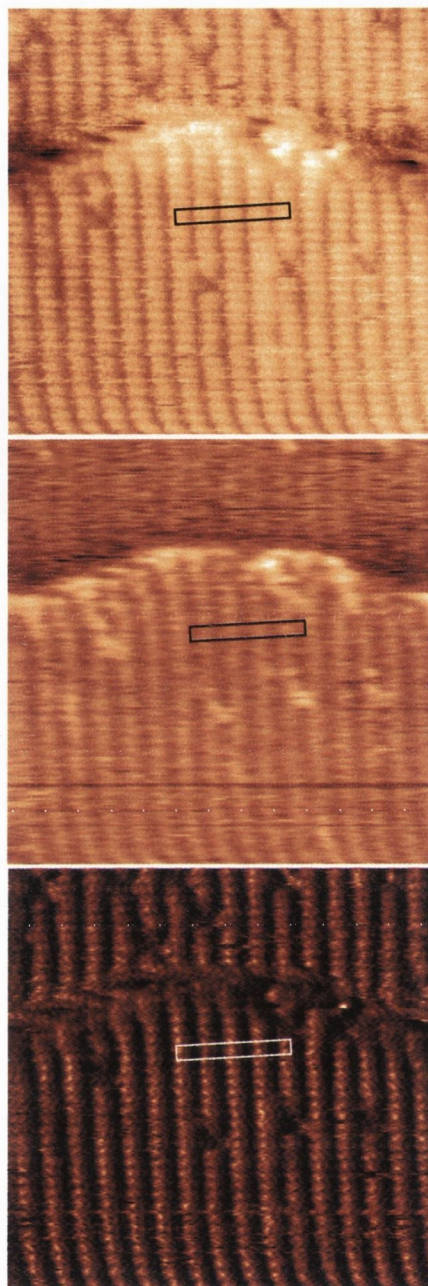
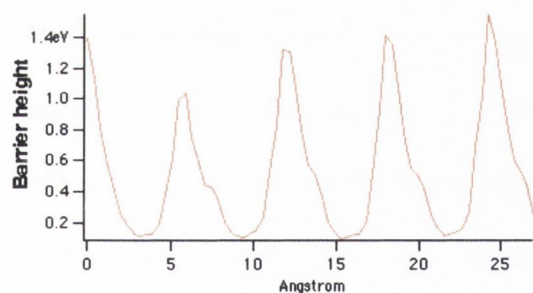
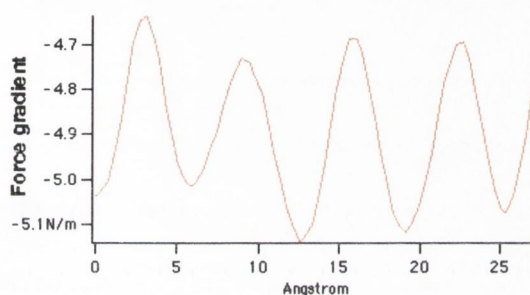
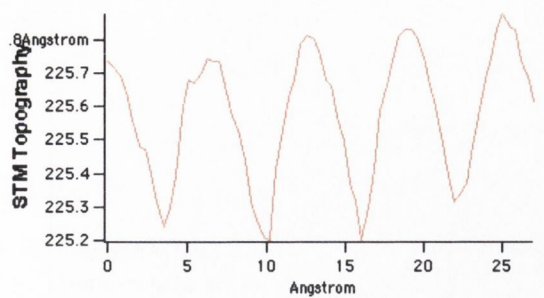


Figure 4.16: A set of simultaneously acquired SPM images. From top-bottom are the STM topography image, amplitude and δI . On the left of these are profiles the same area in each image (outlined on the images). The data in each profile has been used to calculate quantitative values for apparent topography , force gradient and barrier-height.

$100\text{\AA} \times 100\text{\AA}$

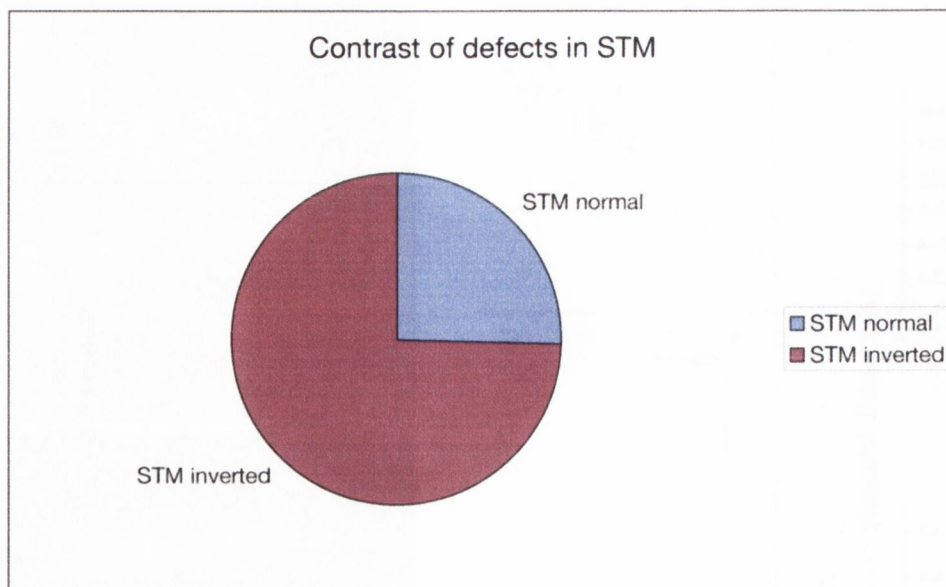


Figure 4.17: Pie chart showing the distribution of images in the two STM imaging conditions. Normal in this case means the most reported contrast regime where defects appear as bright objects between bright rows.

pography image the defects appears as dark objects between dark rows. In the force gradient image however the defects appear as bright objects between dark rows. In the barrier-height image the defects appear as dark objects between dark rows. Compared with the images shown in Fig.4.13 what has changed is that the contrast of the defects in the topography image has inverted while the other two channels have remained the same, despite the inversion of the tip trajectory. If long-range forces were dominant it would be expected that the change in trajectory would have a significant effect on force gradient image. This we do not observe, implying that long-range forces are not dominant. That the tip trajectory does not have as great an influence on the force gradient contrast is supported by our recent results on Si(111) (7×7) (see Section 4.1 and [150]).

Over a period of months over 100 images were taken at high resolution with different

tips observing different contrast regimes. Typically imaging within one contrast regime was stable and could continue for many hours without change. The STM contrast of the defects reveals that for nearly 75% of our images the defects appear as dark objects on bright rows. Therefore, what is considered normal in the majority of the literature on STM of the $\text{TiO}_2(110)$ (1×1) surface is not in fact normal in the case of our data. What the 'normal' contrast is, relies in part on the picture of charge density on the surface, as described by Vanderbilt *et al* and that this electronic effect dominates over topography. Their prediction that the electronic structure of the surface should dominate in STM assumes that the electronic structure of the surface is unaffected by the tip-surface interaction. From our images it can be seen that there are force gradients acting on the tip during imaging even at very small tunneling currents. Indeed from our spectroscopic data it can be seen that at tunneling currents of < 1 nA a repulsive force gradient may be acting on the tip. For a majority of our images these force gradients are attractive and this may induce some relaxation of the surface bridging O atoms and could be enough to tip the balance between topography and electronic structure in favour of topography [151].

The survey of the images also reveals that the contrast of the defects in the force gradient images does not vary much (see Fig.4.18) and in the majority of images appear as bright objects on bright rows.

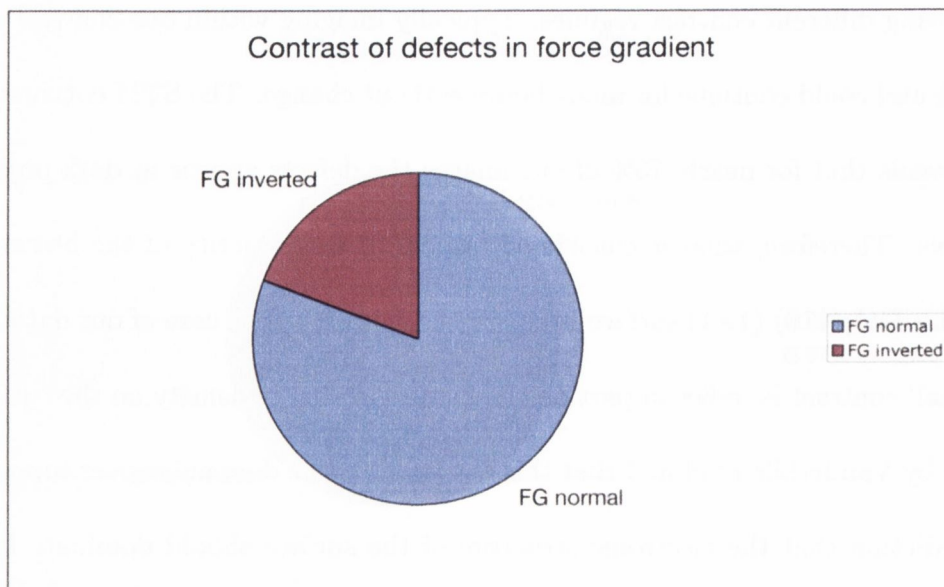


Figure 4.18: Pie chart showing the distribution of images in the two force gradient contrast on defects. Normal in this case means the defects appear as bright objects between bright rows (i.e. less attractive)

4.2.4 Controlled contrast switching

Inversions in force gradient were rare, but some instances were recorded. During measurements with a silicon cantilever it was found that the force gradient corrugation could be inverted independent of the STM topography by varying the applied bias voltage (V_{bias}) between the tip and the sample.

In Fig.4.19 an STM topograph is shown. At a point two thirds through the image the applied V_{bias} was changed from + 1.2 V to + 1.4 V. Taking a line profile across the change in the unprocessed image (Fig.4.19(a)) it can be seen that the change in V_{bias} results in a movement of the tip away from the surface of $\sim 2 \text{ \AA}$. This is a very large jump for such a small change in the applied bias. This may indicate that the applied V_{bias} is not reflected in a simple gap voltage but rather that some of the voltage

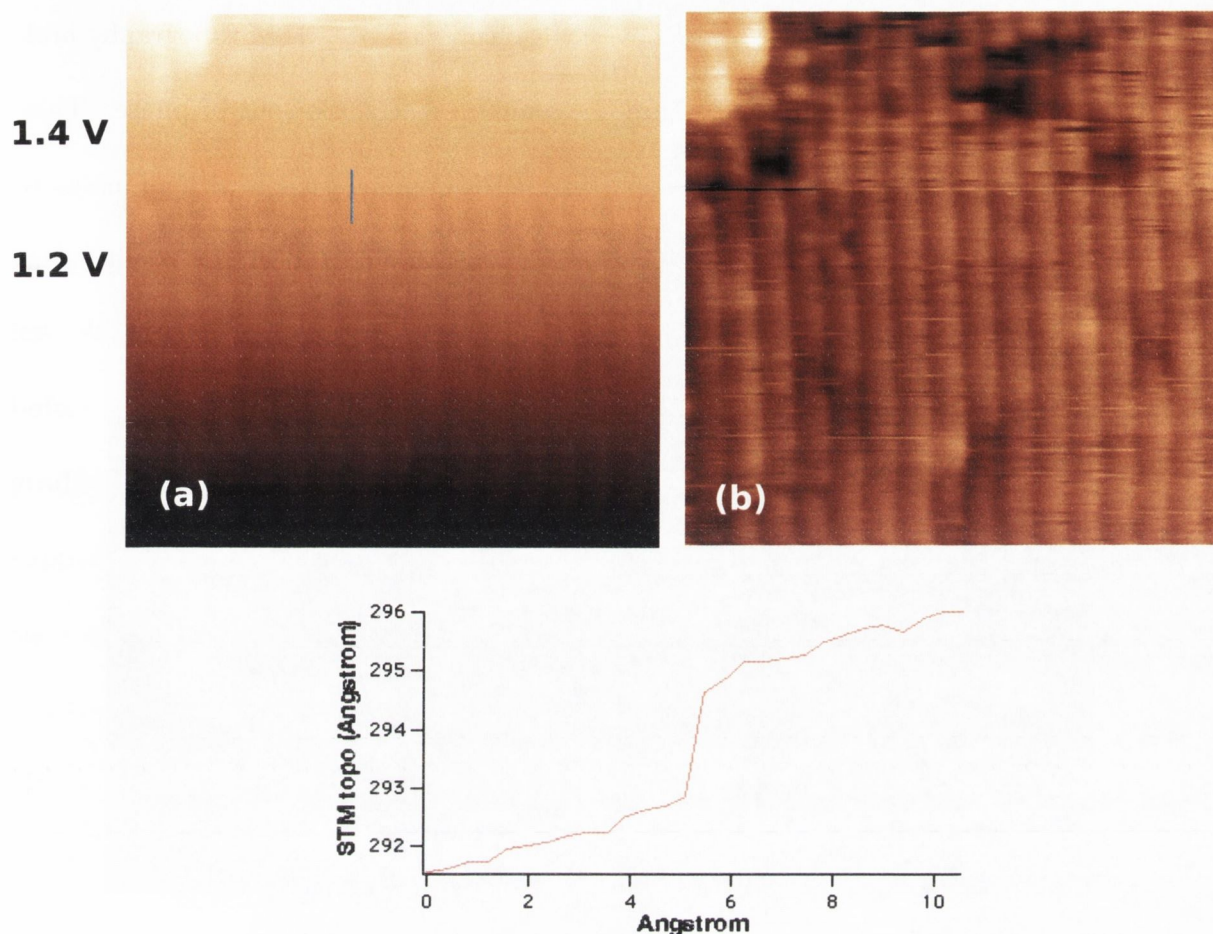


Figure 4.19: (a) STM topography image in which the V_{bias} was changed mid scan, (b) the same image equalised in the x-direction and (c) a line profile take across the switch showing the change in tip height due the change in V_{bias} ($100 \text{ \AA} \times 100 \text{ \AA}$, 0.1 nA)

is dropped over the tip. From the processed STM topography image (Fig.4.19(b))it can be seen that there is very little, if any, disturbance of the image.

In Fig.4.20 the STM topography as well as the simultaneously acquired force gradient image is shown. Line profiles were taken over the areas highlighted in both images before and after the change in V_{bias} . Looking at the force gradient image it can be clearly seen that there has been a significant change in the contrast. At the point at which the change in V_{bias} was made the corrugation in force gradient reverses. This is confirmed in

the averaged line profiles shown where before the change in V_{bias} STM topography and force gradient are in phase and afterward are almost exactly 180° out of phase. This effect was repeatable over a number of scans during the imaging session with an increase in V_{bias} resulting in the tip moving away from the surface and a decrease resulting in the tip moving towards the surface as one might expect.

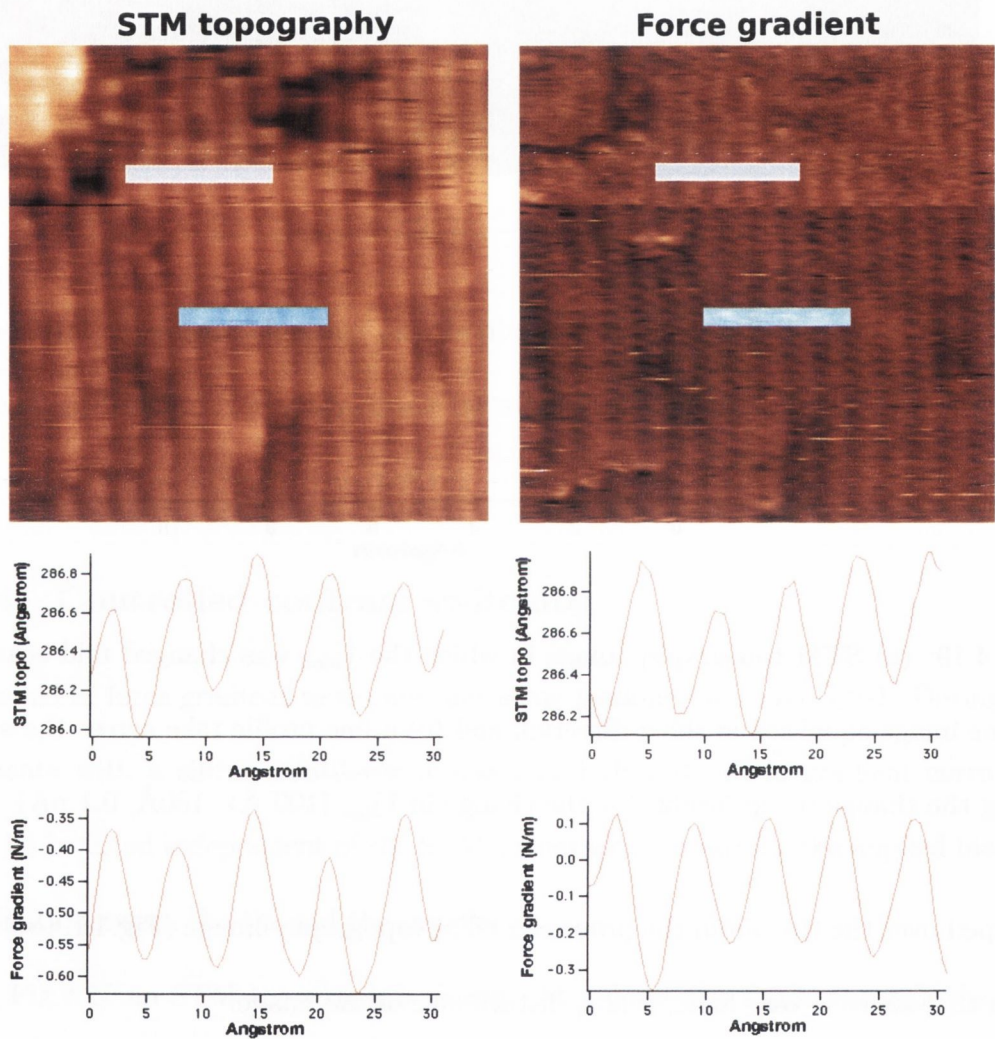


Figure 4.20: Simultaneously acquired STM topography and force gradient images. Profiles were taken over the areas shown in the images, before and after V_{bias} change ($100 \text{ \AA} \times 100 \text{ \AA}$, 0.1 nA)

This effect could be explained by considering an interaction potential with a mono-

tonic attractive component and strong repulsion closer in. Before the V_{bias} change the line-profiles show that the force gradient follows the STM topography and therefore the tip trajectory and becomes more negative (more attractive) as the tip moves toward the surface. After the V_{bias} change the opposite occurs with the force gradient becoming less attractive as the tip moves towards the surface. Intuitively this would suggest that before the V_{bias} change the tip is moving along the negative slope of the interaction force gradient and that after the V_{bias} change it is moving along the positive slope. This is supported by the quantitative values of force gradient from the line-profile taken after the switch. This profile shows the force gradient value oscillating around zero. The line profile across the switch however showed that the tip moved *away* from the surface so this would contradict the simple interaction force gradient model. This is not surprising since the argument would assume no site to site variation of the force gradient.

Looking at a spectroscopic data curve taken after the images shown above were acquired shows that indeed the interaction may not have had a simple interaction potential. The plot of I_t and force gradient against piezo displacement shows that a tip-sample force gradient was measured $\sim 4 \text{ \AA}$ before any tunnel current was measured. Once the force gradient passes through the local minimum it begins to increase before starting to decrease again. It may be that at the lower V_{bias} the tip was closer to the surface on the second negative slope and with the change to a higher V_{bias} switched to the first negative slope. Force gradient curves of this type were shown earlier in Section 4.2.2 and may be due to some rearrangement of the tip apex. From the STM topography profiles taken before and after the change in V_{bias} (see Fig. 4.20) it can be seen that the movement of the tip $\sim 2 \text{ \AA}$ away from the surface has not had any significant effect on the STM corrugation.

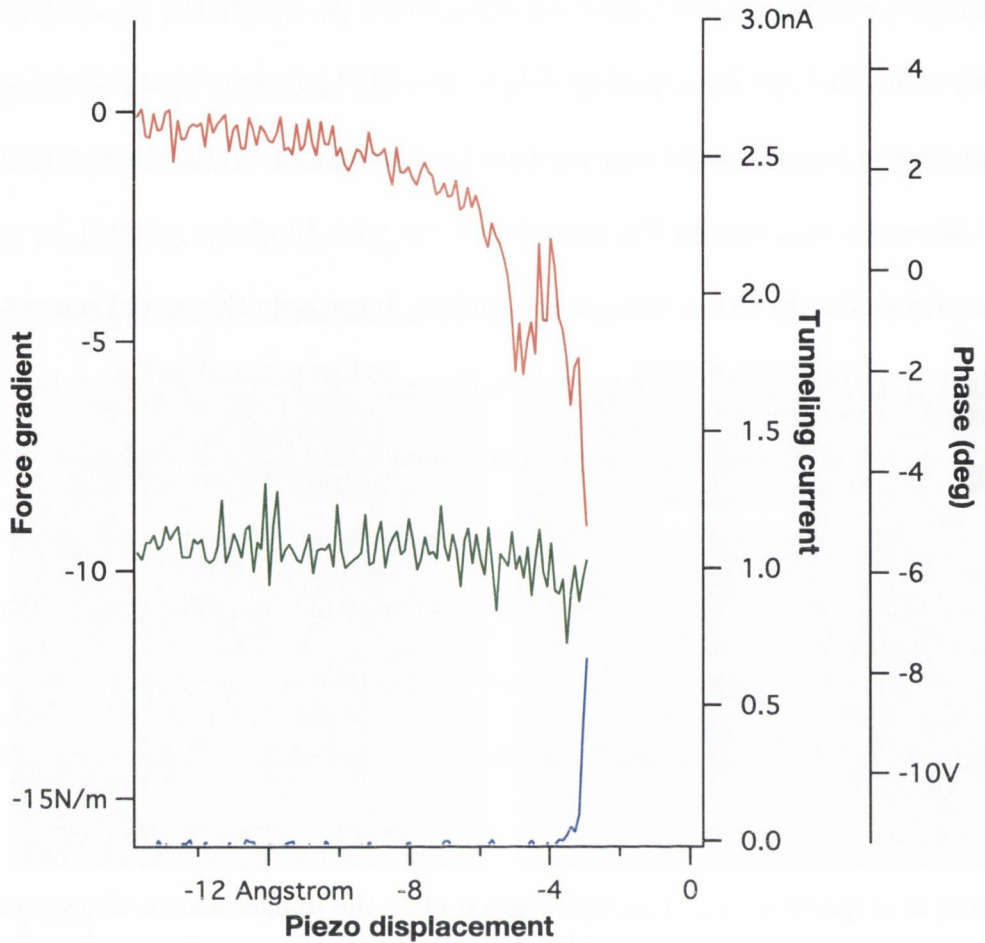


Figure 4.21: Spectroscopic data taken after the acquisition of the previous images.

Examination of some of the corresponding barrier-height images show a contrast dependence of some defects on V_{bias} . In Fig.4.22 three consecutive barrier-height images are shown. The barrier-height image in Fig.4.22 (a) belongs to the set of simultaneously acquired images shown in Fig.4.20. In these images some of the defects are seen to invert their contrast from bright to dark reversibly with varying V_{bias} . This is not true of all of the defects, which indicates that these defects are not of the same species. The change in barrier-height contrast indicates a change in the local barrier height at those defects and hence in the charge at that site. The change in force interaction may also play a role. For this set of images the bright defect contrast in barrier-height occurred

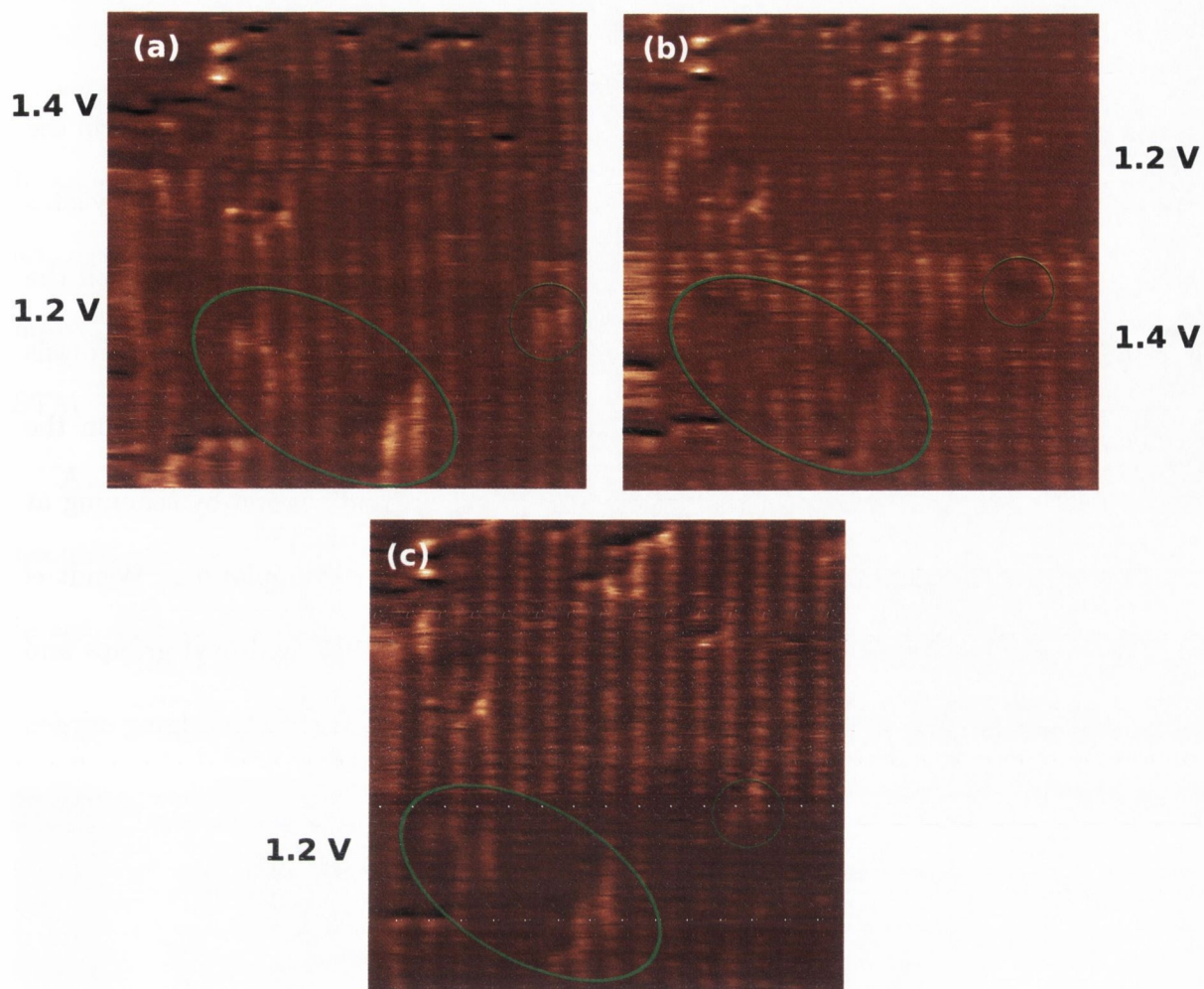


Figure 4.22: Sequence of consecutive barrier height images. During the scans the V_{bias} was varied from 1.2 V to 1.4 V and then back to 1.2 V. Circled in green are some defects whose contrast varies with the change in V_{bias} ($100 \text{ \AA} \times 100 \text{ \AA}$, 0.1 nA)

only when V_{bias} was less than 1.3 V i.e. for smaller tip-sample distances.

4.2.5 Discrimination of defects

Defects observed in STM of the rutile $\text{TiO}_2(110)$ (1×1) surface have been assigned in the literature to oxygen vacancies and the products of water dissociation at the vacancy sites i.e. hydroxyl groups and H-adatoms. The identification of these defects has been the subject of some debate in the literature, and is important for understanding hydrolysis mechanisms [115, 116]. The labeling schemes proposed in the literature rely on the apparent topographic height of the defects in STM, their modification by scanning at high voltages, the defects interaction with dosed water and DFT simulations. Wendt *et al* proposed a scheme where the defects are labeled as vacancies, hydroxyl groups and double hydroxyl groups (in ascending order of apparent topography) at bridging oxygen sites [152].

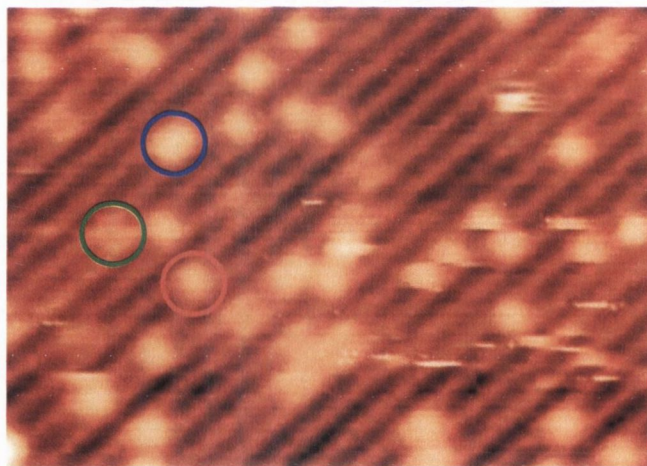


Figure 4.23: STM image of the (1×1) $\text{TiO}_2(110)$ surface. In this image defects appear as bright objects between bright rows. It can be seen that there are several different types of defect on the surface which are distinguished by their width and height. Highlighted are three species of defect; bridging oxygen vacancy (green), hydroxyl group (red), and double hydroxyl (blue). Image area $135\text{\AA}\times 95\text{\AA}$, $0.20\text{ nA}/+1.50\text{ V}$.

A similar scheme is proposed by Teobaldi *et al* which identifies four different species of defect [153]. These are (again in ascending order of STM apparent topographic height) bridging O vacancies, hydroxyl groups (and multiples thereof) and lastly molecularly adsorbed water. This type identification scheme is illustrated in Fig. 4.23 where a number of defects are labeled according to their topographic height (or brightness) in STM.

An attempt has been made to apply a similar classification scheme to our simultaneously acquired force gradient and STM data images. In Fig.4.24 an STM topography image shows a number of defects appearing as bright objects between bright rows. It

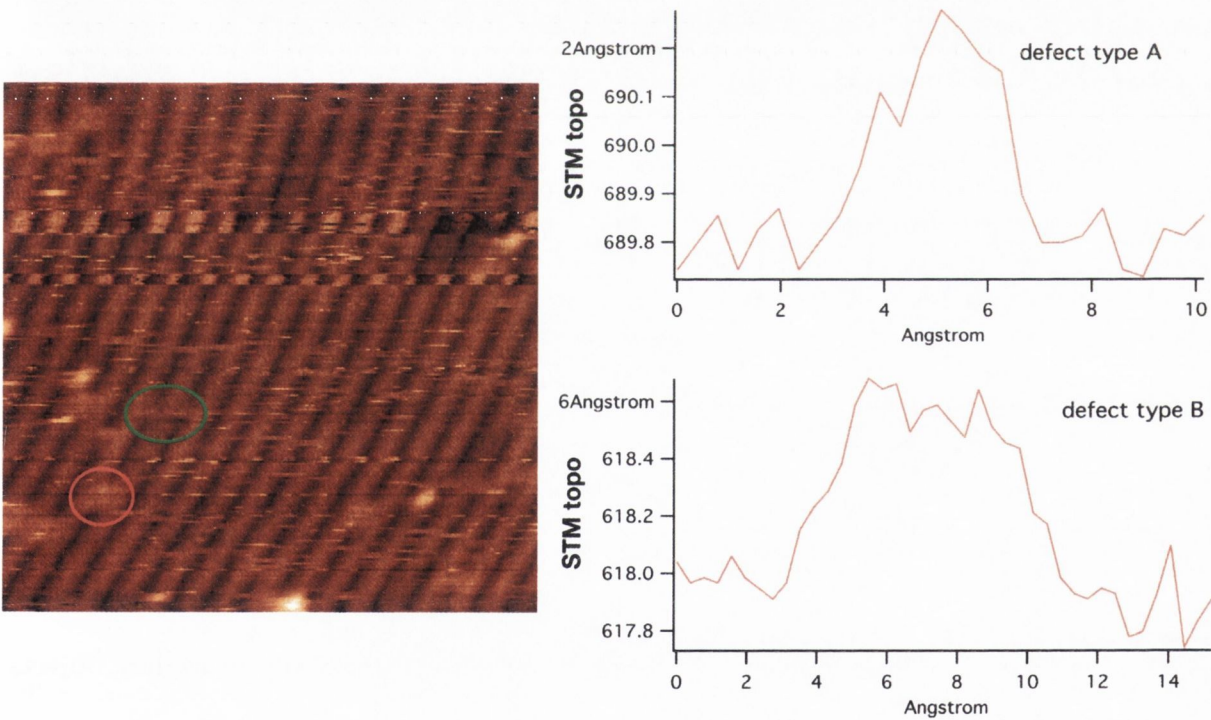


Figure 4.24: STM topography image with two types of defect highlighted, two in green (type A) and one in red (type B). On the right are averaged line profiles (taken along the rows) of the two types of defect.(100 Å× 100 Å)

can be seen that these vary in size and by taking line profiles there is a measurable difference in their apparent topographic height and width. Using the classification scheme described above we may assign the defects type A in Fig.4.24 to vacancies and type B to hydroxyl groups which are present due to the dissociation of residual water vapour in the vacuum system with bridging O defects.

Taking a look at the simultaneously acquired data on that image (Fig.4.25) it can be seen that the defects generally appear as depressions in the barrier-height image. The barrier-height images for type B defects reveals an additional internal structure which is absent from type A defects. This would indicate a difference in the barrier height which may be due to some charge at that site. In the force gradient image (Fig. 4.25 (b)), type B defects are clearly seen. The type A defects however, show little if any contrast in force gradient.

This pattern of contrasts is also present in cases where the STM contrast shows defects as dark between dark rows. Fig. 4.26 shows such a set of images. Again the hydroxyl related objects in the STM topography image are resolved in barrier height but not in force gradient. Again the different defect species may be classified according to their STM topography and features of the defects within each of the measured channels are consistent.

The final set of images again show a number of defects which appear as dark objects on bright rows (Fig. 4.27). Before imaging this surface was dosed with water and flashed briefly (10 seconds at ~ 300 °C). At least some of the defects shown are very likely the results of water adsorption and/or dissociation. While the force gradient contrast is not as clear the position and contrast of some of the defects can be discerned. Once again these defects show consistent properties across the various measured parameters. The

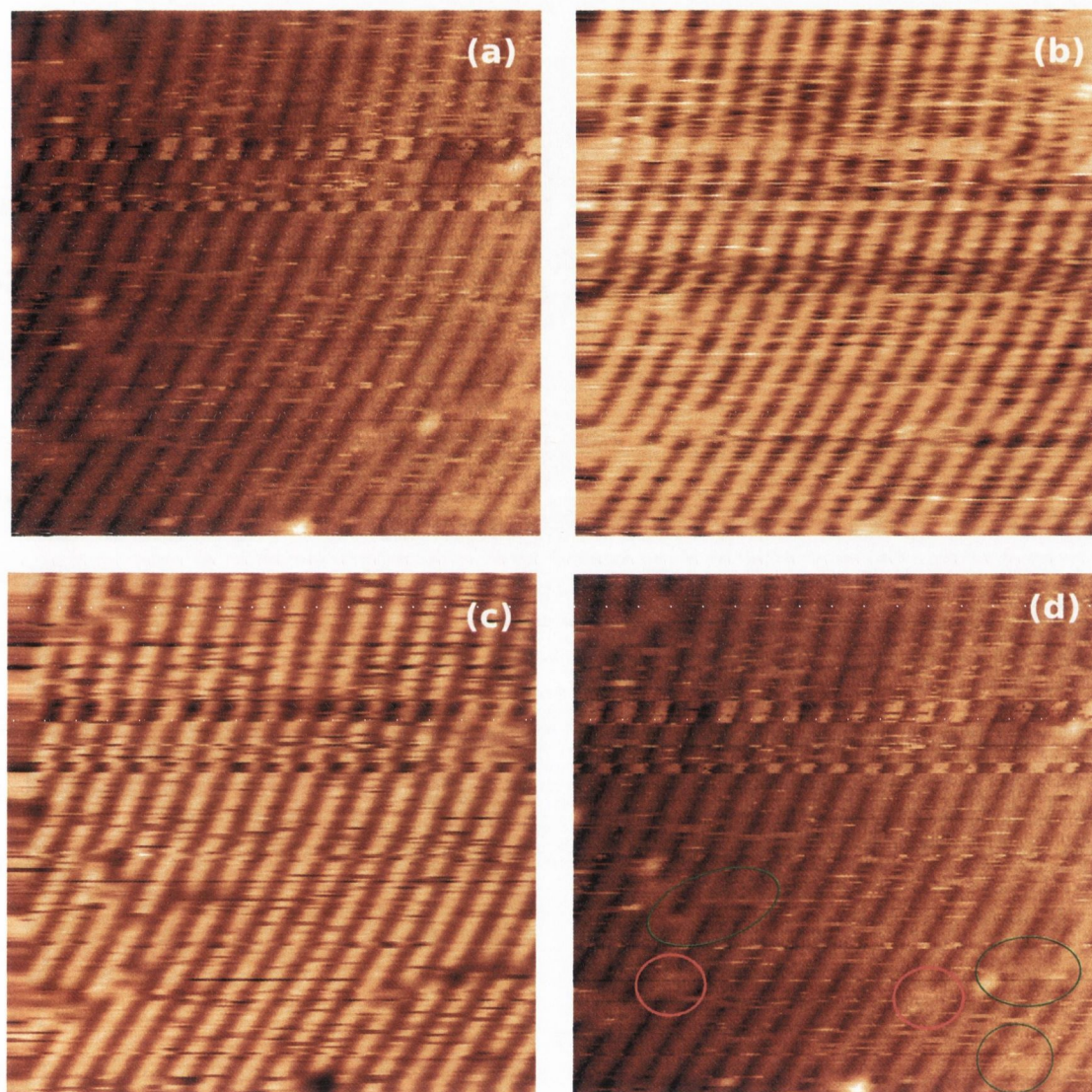


Figure 4.25: Set of simultaneously acquired images showing a variety of defects. STM topography (a), force gradient (b), barrier-height (c). Panel (d) is the same image as (a). ($100 \text{ \AA} \times 100 \text{ \AA}$)

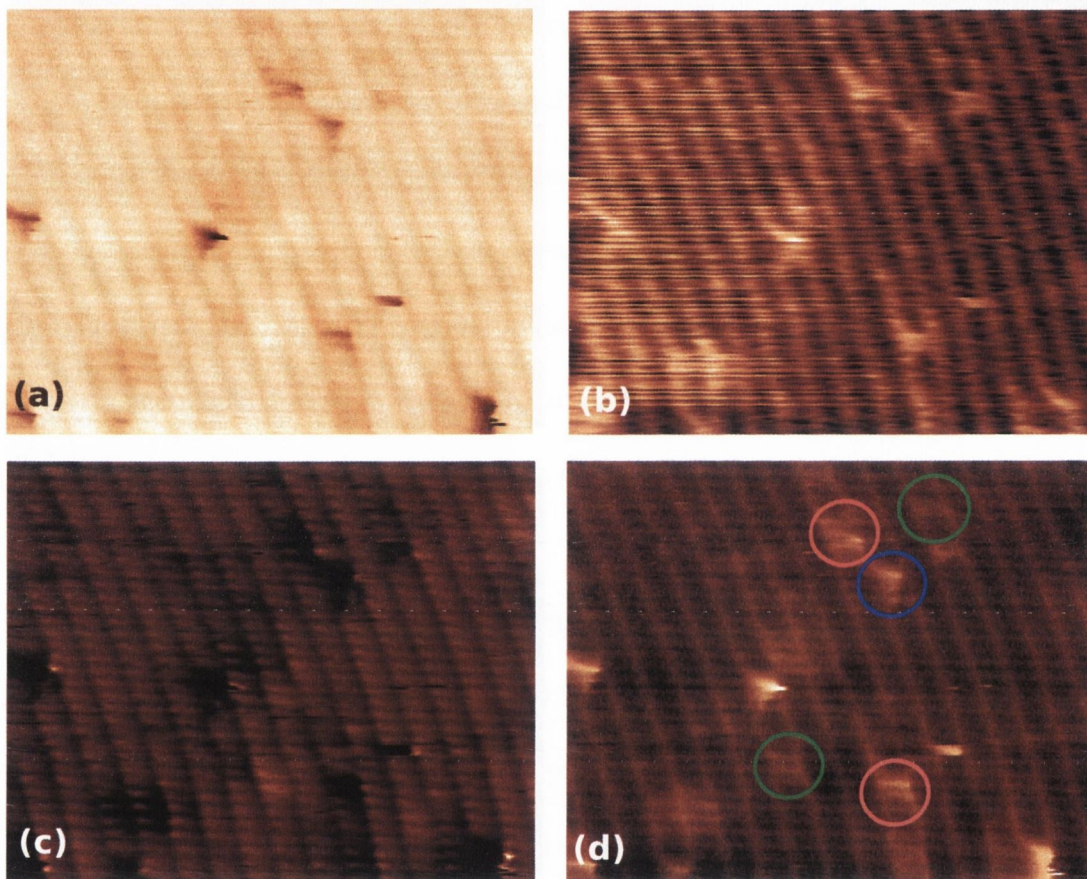


Figure 4.26: Set of simultaneously acquired images showing a variety of defects. STM topography (a), force gradient (b), barrier-height (c). Panel (d) is the same image as (a) but inverted. ($100 \text{ \AA} \times 80 \text{ \AA}$)

vacancy-type defects show very little contrast in force gradient and appear as simple depressions on bright rows in barrier-height image. Larger hydroxyl-type defects show stronger contrast in force gradient and appear as depressions with internal structure in barrier-height.

It should be emphasised that the labeling scheme used here means that a certain amount of subjective judgement is employed. Just as in other studies of defects on this surface the focus is on a few types of distinguishable defects while others are ignored. In the force gradient image in Fig. 4.27(b) for instance, while the resolution is not very high it might be tempting to group a number of the defects together since they appear largely similar. Looking at the STM and barrier-height images (Fig. 4.27(a) and (c)) however reveals a much more varied 'zoo' of defects than might be assumed from just looking at the force gradient images. This demonstrates once more the importance of using multiple parameter imaging in order to discriminate between defects. Interpretation of the data with more certainty will require comparison with theoretical modeling however, the number of possible tip configurations should be narrowed down by the simultaneously acquired data.

That said, the consistency in the appearance of some of the defects in force gradient and barrier-height regardless of the STM topography would indicate that the properties measured are not dependent on the tip. This is promising evidence that progress can be made in the long-standing problem of chemical identification in SPM by monitoring more than one parameter with the same tip.

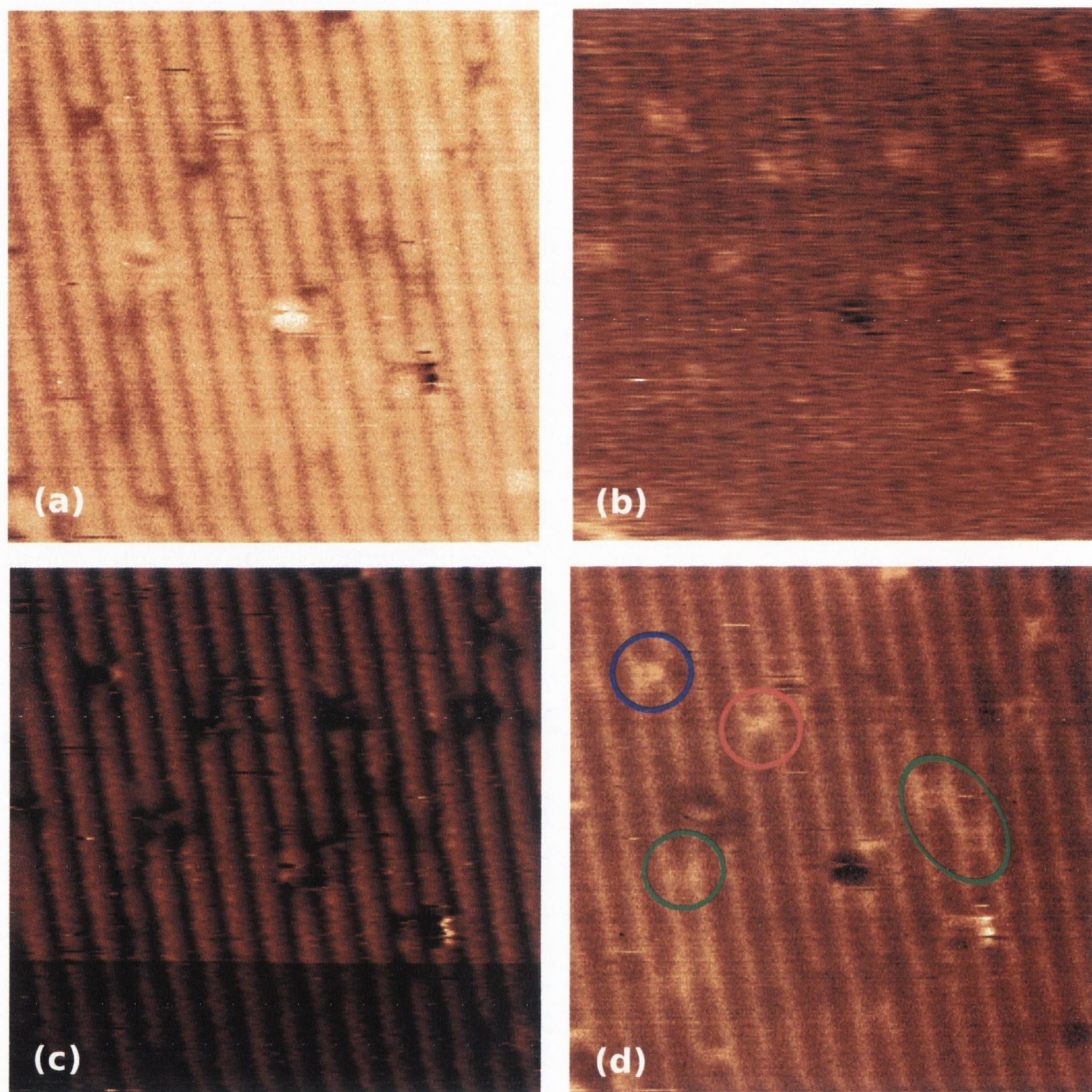


Figure 4.27: Set of simultaneously acquired images showing a variety of defects after dosing with water and briefly heating. STM topography (a), force gradient (b), barrier-height (c). Panel (d) is the same image as (a) but inverted ($100 \text{ \AA} \times 100 \text{ \AA}$)

Chapter 5

Summary and outlook

During these studies a novel scanning probe technique has been used to investigate the Si(111) (7×7) surface and the 1×1 surface of rutile TiO₂(110). A standard UHV scanning microscope was modified to include an all-fiber Fabry-Perot type interferometer. The interferometer was optimised for low-noise operation. Optimisation involved the replacement of the laser diode and the use of improved optical components such as isolators. The laser power was reduced to decrease the effect of mode hopping in the laser. The most effective reduction was achieved by applying a RF-frequency modulation to the laser diode power supply to decrease the coherence length of the laser thereby reducing back-reflections within the laser diode. The measured noise-floor of the instrument was $20 \text{ fm}/\sqrt{Hz}$.

The low-noise level of the microscope allowed for the routine use of very low oscillation amplitudes in dynamic atomic force microscopy experiments. Typical free oscillation amplitudes used were 0.4-0.8 Å peak-to-peak and these were achieved by driving the cantilever at a frequency well below its resonance. Such amplitudes are comparable to the length scale of the short-range forces acting on the tip during atomic resolution

AFM. This allowed for very straightforward interpretation of the measured amplitude data in terms of force gradient using the approximation

$$k_{int} \sim k_0 \left(\frac{A_0}{A} - 1 \right) \quad (5.1)$$

In order to achieve stable operation at low-amplitudes stiffer than usual cantilevers were required. Solid tungsten cantilevers were fabricated with spring constants of up to 300 N/m. These cantilevers were advantageous in achieving stable tunneling currents which were used as a feedback signal.

The use of such low oscillation amplitudes also allowed for the simultaneous measurement of multiple parameters with no ambiguity regarding the tip sampling each channel. Typically, simultaneous measurements were made of tunneling current (I_t), the variation of tunneling current over the oscillation cycle ($\frac{\delta I}{\delta z}$), phase and amplitude. Using this technique allowed for the investigation of the forces acting on the tip during atomic resolution STM imaging. The measurement of $\frac{\delta I}{\delta z}$ allowed for the estimation of the variation in local barrier-height across the surface using a simple equation for a 1-dimensional tunneling junction

$$\phi(eV) = \frac{\hbar^2}{2m} \left(\frac{\delta \ln I}{\delta z} \right)^2 = 0.952 \left(\frac{\delta \ln I}{\delta z} \right)^2 \quad (5.2)$$

Investigation of the well studied Si(111) (7×7) revealed that the force gradients are generally more attractive over the corner holes than over the surface adatoms. The influence of possible crosstalk with the STM topography was eliminated by performing flat-trajectory imaging with only a moderate reduction in the force gradient corrugation. Evidence of some dependence on the tip material was discovered by using silicon as well as tungsten tips. Silicon tips sometimes showed an inverted contrast (corner holes less

attractive) which was likely due to a tip change. Such contrast was never observed using tungsten tips.

From the spectroscopic data it was seen that the onset of tunneling in STM of $\text{TiO}_2(110)$ happens $\sim 2 \text{ \AA}$ after the onset of tip-sample interaction and that even for tunneling currents as low as 0.5 nA the tip-sample interaction was likely to be in the repulsive regime. That the tip is strongly interacting with the sample during typical STM imaging conditions contradicts the assumption that the tip need not be considered in the interpretation of STM data of $\text{TiO}_2(110)$.

Examination of the simultaneously recorded STM topography, force gradient and barrier height images has revealed that in the case where defects were seen as bright objects between bright rows the variation in apparent barrier-height over the defects supports the theoretical predictions of Vanderbilt and co-workers. This provided further evidence that the bright objects seen were indeed bridging oxygen row defects. These defects were shown as bright in the force gradient image indicating a less attractive force gradient. If the Vanderbilt picture of the electronic structure of the surface is representative of the surface, and some of the data presented here would show that it is, then the dominance in STM of electronic structure over topography on the $\text{TiO}_2(110)$ (1×1) surface relies on a fine balance which could be disturbed by, for example, a significant tip-sample force or by the electronic structure of the tip.

A survey of the data revealed that the STM contrast of defects in a majority of images contradicts the widely reported contrast which exists in the literature i.e. that they appear as bright defects between bright rows. In the majority of the STM images the defects appeared as dark objects between dark rows. This difference in STM topography did not appear to affect the contrast in force gradient or barrier-height. This indicated

that these defects were indeed the same as those seen in the standard contrast regime.

The results suggest that the reasons for assigning one particular contrast regime as normal are worth revisiting since in both standard STM and novel SPM measurements during this work different contrast regimes have been observed. Also, recent experimental and theoretical work would indicate that the relaxed geometry of the surface which supports the dominance of electronic structure over topography in STM contrast is not actually the case. This may mean that the current literature understanding of the STM contrast on this well studied model oxide surface may be somewhat disconnected from reality.

It was found that by varying imaging parameters during imaging it was sometimes possible to vary the contrast regime in one channel independent of the others. Altering the applied bias and thereby the tip-height reveals a dramatic change in force gradient without altering the STM topography. This also affected the appearance of some of the observed defects in barrier-height imaging, reversing their contrast. This would indicate that the apparent local barrier-height (which is an average of the local work-functions of tip and sample) has been modified by the tip-sample separation and/or V_{bias} . Again, this occurred in only some of the defects and may be due to the relative differences in local barrier-height at different defect sites (and therefore the onsite charge).

Finally, it has been shown that, even though the STM topography might invert the measured apparent barrier-height and force gradient above the defect is relatively invariant. This would indicate that the measured properties are not solely dependent on the electronic structure of the tip and are more indicative of the actual defect properties. Applying a classification scheme based on STM topography shows consistent features of certain defects in both force gradient and barrier-height. Comparison of three separate

simultaneously acquired data channels on the same defects shows that while some may appear identical in one channel, examination of the other two reveal that they are not in fact the same defect. This highlights the importance of multi-parameter imaging in SPM in moving beyond the current capabilities of standard scanning probe techniques in the identification of atomic features.

Future work may include the theoretical modeling of the results on defects to see whether consistent features of the defects observed can be explained by looking at the adsorption of simple molecules at oxygen row vacancy sites and how that affects the onsite local density of states, charge, and the expected force gradient. Further development of the instrumentation would allow the use of other feedback signals rather than just tunneling current. Feedback on force gradient, whether by monitoring the amplitude or perhaps implementing frequency shift feedback would complete the instrument's capabilities as an AFM/STM. Subjects of future experiments may include other catalytically important materials such as alumina. This could be achieved by the preparation of alumina thin films on NiAl.

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