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Manipulating atoms

using

Scanning Probe Microscopy

By

Andrew Christopher Norris

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

Department of Physics,
Trinity College Dublin
2008
Declaration

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Andrew Norris

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ABSTRACT

Manipulating species using Scanning Probe Microscopy (SPM) is an important discipline in the field of bottom-up fabrication, which facilitates nano-mechanics and electron dynamics investigations. Previous low temperature manipulation highlights include the construction of quantum dots, nano-wires and quantum corrals, all of which began in 1989 with Don Eigler’s iconic writing of I-B-M using 35 xenon atoms. Since then, the field has developed, and we now push, pull, hop, excite, desorb, rotate and dissociate molecules, even managing to induce multiple different stages of a chemical reaction. Despite these successes, precise measurement of the forces, energetics, energy loss processes, coupling efficiencies, and the heating dynamics during atom manipulations, has yet to be achieved.

To address these issues and advance this field’s range of application to technologically relevant temperatures, i.e. room temperature (RT) and above, thermal energies role as a control parameter during manipulation is investigated. For the first time, controllable, repeatable and atomically precise STM manipulations have been performed at RT and above, and, using a simultaneously nc-AFM/STM operating with sub-angstrom oscillation amplitudes, the vertical component of the forces present are quantified.

By performing these manipulations in sequence, at various temperatures with equal experimental set-ups (i.e. without any tip change), the manipulation behavior is evaluated as a function of temperature. Surprisingly, the manipulation threshold and mechanisms are both found to change with temperature, thus providing for the first time, a link between thermal energy and tip-surface coupling. Furthermore, since variable temperature manipulation data allows one to plot Arrhenius-type curves under different tunneling conditions, changes to the manipulation barrier as a function of tunneling parameters are directly measured. This is the first absolute measurement of the energy required to laterally manipulate using STM.

SPM’s are thus used, as an atomic-scale laboratory to both build and test simple nano-scale structures, whose properties we can study and tune. The species
manipulated and hence under investigation in this work, are bromine atoms on Silicon (111) 7x7, Cu (100), and complex vacancy-cluster structures on Cu (100). The interaction of bromine with silicon and copper is found to be rather more complex than previously reported, and contrary to published literature, both systems prove unsuitable for lateral manipulation.

The vacancy-cluster structures on the other hand, are suitable for RT and VT manipulation. Additionally however, they represent a new and tunable building block for atomic scale surface modification. These structures display unexpectedly high structural and dynamic stability, tunable electronic properties, and can be produced and controlled in an extremely effective manner. Crucially however, their anomalous diffusion characteristics mean they are stable, yet manipulable at RT using STM. We thus have developed, a moveable, tunable structure, which is stable at room temperature, and may be used to modify the surface physical, and chemical and electronic properties.

**Keywords:**
STM, SPM, AFM, Manipulation, Temperature, Thermal Energy, Copper, Silicon, Bromine, Vacancies, Vacancy-clusters structures, Arrhenius Graph, Diffusion, potential energy landscape

**Subject Terms:**
STM Manipulation, simultaneous nc-AFM/STM, Temperature dependent manipulation, Tip-influenced diffusion, vacancy diffusion, vacancy dynamics,
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**Figure 3-1** Schematic of the Omicron variable-temperature, ultra high vacuum, scanning tunnelling microscope (VT-UHV-STM) system used for low temperature (circa 30-70 K), room temperature (300 K) and high temperature (300-500 K) STM manipulation experiments. The chamber is connected to a roughing and turbo molecular pump, which pre-pumps the chamber to pressures in the $10^{-4}$ mbar and $10^{-8}$ mbar regimes, respectively. An ion getter pump is then utilised to reduce the pressure further. When the rate of outgassing and pumping speeds are equal, i.e. there is no improvement in the pressure anymore, the entire chamber is baked to $\approx 200^\circ$ C for about 48 hours, which reduces the water vapour contained within the chambers walls, and hence reduces outgassing. This reduction in outgassing, means the same pumps can now achieve ultra high vacuum (circa $10^{-10}$-$10^{-11}$ mbar) pressures. The main chambers
(Preparation and Microscope), and the load lock area and gas lines, may be independently pumped, permitting the input of gasses, tips and samples, without breaking vacuum. The system has two main chambers, the preparation and microscope chamber. Samples are sputtered, annealed, dosed, and analysed using LEED, in the preparation chamber. STM is performed in the microscope chamber.

Figure 3-2 Photograph of the microscope stage which sits inside the microscope chamber. This chamber is isolated from the "outside world" via two different damping systems. The first is the spring suspension system (i), and the second is the eddy current magnetic damping system (ii). Once the microscope stage is decoupled from the noise and vibrations of the outside world, the tip is transported close to the surface using piezo motors (not shown). Once atomically close, the piezo tube scanner (iii), raster scans the tip with sub-atomic precision. The sample is held inside a sample holder (not shown) upside down, and inside the sample stage (iv). If the sample needs to be cooled to perform low temperature scanning, the cooling block is lowered and locked in place (v). It is connected with copper braids to a liquid Helium or Nitrogen flow cryostat.

The last pump we use to produce UHV is the TSP. A large current (= 50 A) is passed through a titanium coated tungsten filament, heating it, and subliming the coating of reactive titanium onto the chamber walls. The reactive species then traps gaseous molecules as they collide with the chamber walls, immobilising them, and thus reducing the chamber pressure. The effectiveness of this pump is reduced with time as the surface layer is fully reacted, so TSP's are used at regular intervals of approximately four hours. It also inhibits outgassing from Figure 3-3 Electrochemically etched tungsten tips observed using an electron microscope. The tips are prepared by electrochemical etching at the meniscus metal interface. This leads to a directed thinning of the metal just above the liquid etchant level. The metal piece below the liquid etchant surface, then stretches the wire, thinning it, until it breaks. With careful control, this procedure leads to atomically sharp STM tips.

Figure 3-4 Schematic illustrating the basic set-up of an STM. The tunnel current is used to control the tip-sample distance z via a feedback circuit. The distance z is recorded by a computer as a function of scanned coordinate x and y. A high voltage amplifier is required to drive the piezoelectric scanner. Good vibration isolation of the microscope is a necessity for high-resolution imaging.

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Figure 3-6 Typical power spectrum of vibrational noise for a typical STM tip-sample gap. This data was acquired at RT by focussing the optical fibre interferometer normally used for AFM cantilever deflections, onto a dummy sample. The power spectrum then corresponds to the analysis of this interference pattern in a frequency spectrum analyser. Integrating over 2.5 kHz, gave 70 pm rms.

Figure 3-7 A simple current-voltage converter for an STM. It consists of an operational amplifier (op-amp) with high speed, low noise, and low input bias current, as well as a feedback resistor (typical impedance $R \approx 10^6 \Omega$) that has low parasitic capacitance $C_R$. With careful design $C_R$ should be less than 0.5 pF. There is also an inevitable parasitic input capacitance $C_{in}$. The parasitic capacitance, the thermal noise of the feedback resistor, and the characteristics of the op-amp are the limiting factors of the $I$-$V$ converter.

Figure 3-8 Tunnel current as a function of a distance on the copper (100) surface and the relationship between current noise $\delta I_T$ and the vertical noise $\delta z$. In typical STMs the tunneling current is of the order of $I_T \approx 100$ pA and is measured with an acquisition bandwidth of $B \approx 1$ kHz, where $B$ is roughly determined by the spatial frequency of features that are to be scanned times the scanning speed. Thus, for a spatial frequency of 4 atoms/nm and a scanning speed of 250 nm/s, a bandwidth of $B = 1$ kHz is sufficient to map each atom as a single sinusoidal wave. With a gain of $V/I = R 100 \text{ M}\Omega$ and $T = 300 \text{ K}$, the rms voltage noise is $v_{\text{rms}} = \sqrt{4k_B T R A f}$ 40 $\mu$V at RT, corresponding to a noise of $\delta I_T = 0.4$ pA. If the tunnel current is given by $I_T(z) = I_0 e^{2k_T z^2}$, where $I_0$ is a function of the applied voltage and the density of states in both tip and sample, and $k_T = \sqrt{2m_0 \phi \over h}$, the vertical noise may be given by $\delta z_{I_T} \approx \sqrt{4k_B T B / R \over 2k_T I_T}$ which amounts to a $z$ noise of 0.2 pm. Thus in STM the main electrical noise in the tunneling current is not critical, because it is much smaller than the required resolution.

Figure 3-9 Schematic of all-fibre Fabry-Perot interferometer deflection-detection system. (a) The optical signal is provided by a single-frequency laser diode coupled to a single mode optical-fibre. Laser light ($I/R$) travels along the fibre passing through a 2 x 2 3 dB coupler with one output terminating at a reference photodiode to monitor laser power fluctuations and the second output passing light to the back of the cantilever. The resulting interference signal is filtered and processed to detect dynamic changes of the lever reflecting changing tip-surface interactions. (b) Schematic illustrating the homemade Fabry-Perot cavity. (i) The cantilever backside, one of the mirror
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**Figure 4-1** (a) Schematic illustrating the face-centred cubic crystal structure of copper. Copper is a 3d a transition metal with an interatomic spacing 3.61 Å. It is high highly conductive, and has a Young's modulus of 110-128 GPa. (b) Copper (100) surface indicating a simple 1 x 1 surface termination which is confirmed by Low energy electron
diffraction (LEED), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) data.

**Figure 4-2** Three STM topographs of the copper (100) surface illustrating the different defect types: (a) surface vacancy, (b) adatom, and (c) a step edge. Defects alter the surface potential energy corrugation in its immediate vicinity, causing defect sites to act as pinning centres, growth centres, and to generally alter the surface chemistry. The lower left of each image names the mass transport mechanism taking place in each image.

**Figure 4-3** (a) Tunneling topograph taken in the constant current mode of the copper (100) surface, indicating the 1 x 1 atom periodicity. This symmetric simplicity of the surface, and the low number of different bonding sites; i.e. two: (i) four-fold hollow and (ii) on-top sites make this surface ideal for quantitative atomic manipulation studies. (b) Current-distance spectroscopic curve taken at a single atomic site using the scanning tunneling microscope at room temperature. Plotted in blue is the current on a linear scale. Plotted in black is the current on a logarithmic scale. The red curve is a linear fit to the logarithmic data. From this curve, a barrier height 4.37 eV is calculated. This compares to the work function values mentioned in the main text, which ranged from 4.5-4.95 eV.

**Figure 4-4** (a) In response to significant alteration of the electron density in the outermost layers, atoms re-arrange their atomic positions in responses to forces generated by the redistribution. This ability of surface atoms to relax their atomic positions plays a crucial role in many, if not all, STM measurements on Cu (100) surface. The forces present due to the presence of an STM tip, can induce similar surface relaxations, which may influence the measurement of the atomic corrugation, the barrier height, electronic structure and the barriers to manipulation. (b) LEED studies show that the second and third layers also change the separations as a result of such relaxation.

**Figure 4-5** Current-voltage spectroscopy curve of the copper (100) surface taken at RT with our commercial Omicron STM. The experimental data, a near straight line (red) reflects the near uniform band structure around $E_F$. No energetically localised states are apparent, and spatially resolved $dl/dz$ maps reveal no detectable difference in the localised density of states LDOS across the surface.

**Figure 4-6** (A) Line profile along the [110] crystallographic direction of copper (100). The peak-to-peak corrugation is approximately 25 pm. This is approximately one order of magnitude larger than expected from theory. (B) Peak-to-peak corrugation as a function of tunnel current set-point. As the tip-sample gap decreases, and the tunnel current rises, there is a sharp initial rise in the corrugation amplitude, followed by more gradual decline. The voltage is maintained the same throughout. This suggests that tip-surface forces, and resultant
interactions, strongly influence the corrugation amplitude. This indicates that the manipulation barrier is both dynamic and has a complex relationship with tip-sample distance.  

**Figure 4-7** Simultaneous force gradient image and STM image of copper (100) acquired at room temperature using home made conductive tungsten cantilevers. The material choice and ultra small oscillations amplitudes, make it possible to perform both STM and AFM simultaneously. (a) Force gradient image acquired using a non-contact atomic force microscope. The cantilevers distance from the surface is regulated using tunnel current feedback. The microscope cantilever oscillates with sub-angstrom oscillations, off-resonance, with changes in oscillation amplitude from the free oscillation amplitude measured using a Fabry-Perot all-fibre interferometer. This amplitude is related to the force gradient by. (b) Because the lever is tungsten, and oscillate with sub-angstrom oscillations, tunnel current data, which is directly comparable to normal STM data may be acquired.  

**Figure 4-8** Line profiles showing the atomic corrugations in force gradient images acquired at different average tunneling currents. Note the break on the y-axis.  

**Figure 4-9** Simultaneously acquired force gradient, tunnel current and force vs distance spectroscopy curve on copper (100) at room temperature. The data is acquired by turning the feedback off and approaching the surface using piezo scanners. The tunnel current signal shows its typical exponential type dependence with distance. The interaction stiffness (red) and force (blue) indicate both attractive and repulsive force are present. The turquoise arrows indicate the force regime STM typically operates within. The cantilever is a homemade tungsten oscillated at sub-angstrom amplitudes, making the $F-d$ data directly comparable to normal STM conditions.  

**Figure 4-10 (a)** STM topograph of an atomically clean copper (100) surface prepared by repeated sputtering and anneal cycles, as outlined above. The image was acquired at RT under standard imaging conditions, (Bias voltage ($V_{Bias}$) = 0.02 volts (V), Tunnel current set-point ($I_{T\ set-point}$) 0.2 nA) Illustratively shown in red are, the fou-fold hollow sites where adsorbed bromine atoms are expected to reside, and hence produce the 2 x 2 pattern seen in the following image. (B) STM topograph of the same Copper (100) surface which has been dosed with more than a monolayer coverage of Bromine,. The surface was imaged using the same tunneling parameters. The surface shows a c-(2 x 2) reconstruction as expected if bromine atoms sit in the four-fold hollows as indicated in image (a).  

**Figure 4-11 (a)** Manipulation of bromine atoms on copper (100) at RT, as reported by Fishlock, Oral, Egdell, and Pethica. The authors report that the manipulation mechanism responsible for the atom movement was a tunnel current density mechanism causing localised heating. In
figure (a) location (i), the \( I_{T, \text{set-point}} \) is temporarily changed to 3 nA, the tunnel current threshold identified in this system for inducing the onset of adatom motion. Once sweeping occurs, the authors, could then “drop the atoms off” at will, location (ii). \( \text{(b) The key criteria in energy terms for performing these experiments were that } E_{\text{tip}, \chi} > E_B \gg k_B T \). i.e the authors unveiled a manipulation system that was stable yet manipulable. The key problem with the result however, is that considerable experimental evidence suggests the species moved are not bromine atoms\(^{[32]}\).

Figure 4-12 A sequence of STM topographs of copper (100) showing areas of equal size 5 x 5 nm. (a-d), illustrating the effects, exposing the surface to increasingly large dosages of bromine atoms has. Image (a) shows the atomically clean surface prior to dose. The surface has, as expected, a 1x1 structure, with an interatomic lattice spacing of 2.96 Å. The surface is then dosed with bromine atoms, using a homebuilt halogen cell described in section 3.7.1, image (b). No new adatoms are seen on the surface. Rather the 1 x 1 copper lattice structure is retained and the interatomic spacing remains intact at 2.96 Å. The surface is then dosed with more bromine, this time with a 2000 µAmpsec dose, image (c). Again however, the surface retains its 1 x1 structure and interatomic spacing. The final dose, 6000 µAmpsec, is found to alter the surface. The surface now reconstructs to a c-(2x2) periodicity, indicating a bromine reconstruction. The absence of any images showing isolated bromine atoms, prior to full monolayer saturation is highly indicative that the atoms are mobile at RT. This is in direct conflict with Fishlock and co-workers’ results \([32]\), but is supported by Altman’s findings\(^{[32]}\).

Figure 4-13 Line profiles of the increasingly bromine dosed copper (100) surface. The interatomic line profiles, taken along the [110] direction, for 10 consecutive atoms, indicate if an atomic rearrangement has occurred. (a) The interatomic spacing for the clean substrate copper atoms is 2.96 Å as expected. (b) and (c) Do not change as the surface is dosed with sub-monolayer coverages of bromine atoms. (d) Only when near monolayer coverages are achieved, does the surface reconstruct to form the c-(2X2) Cu:Br phase.

From a simple Arrhenius type picture of adatom diffusion, it is expected that bromine mobility on the copper (100) surface ought to be reduced logarithmically with respect to \( k_B T \). Thus, it is expected that reducing the temperature to approximately 50 K will result in the bromine species hitherto, unseen as isolated atoms, should become sufficiently immobilised to be imaged with STM. Figure 4-15, a through d, shows a sequence of images whereby an initially clean copper surface is imaged, then dosed and imaged at RT, then cooled to circa 75 K and imaged, and then allowed to reach RT where once again, it is imaged. Figure 4-15 (a) is a clean copper surface with its characteristic reconstruction displaying no particular anomalies. After dosing the surface with 2500 µAsec of Br₂, Figure 4-14 (b) mirrors...
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dosing. Without any additional treatment or dosing, the sample is
then cooled to 75 K where again, the bromine dosed surface is
imaged with STM. Now however, single white (false colour scale
where white indicates high tunnel current) protrusions are observed,
indicating that the mobility of bromine has been quenched as a result
of a reduction in thermal energy, Figure 4-15 (c). At low coverage
and low temperature, STM images confirm that molecular Br₂ does in
fact dissociatively chemisorb on the (100) surface of copper. There is
no sign of the hollows or sombrero structures seen by Fishlock and
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circles), (iii) one corner hole, and (iv) nine dimers per unit cell
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physical height difference of the surface atoms with special attention
drawn to the depth of the cornerholes. (c) STM topograph taken in
constant current mode showing the 7x7 unit-cell. The image is of the
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**Figure 5-6 (a)** 34 Å x 34 Å STM constant current topograph of a “vacancy cluster” on copper (100) at RT. The species is 3 x 3 atoms wide, 1 layer deep (b-c) Forward and backward images of the same cluster.

**Figure 5-7** Atomiically resolved line profile of a vacancy-cluster structure. The cluster depth measures 160 pm, almost exactly equal to a step height. Atoms can be ‘seen’ inside the vacancy. These are 2.9 Å apart, the typical interatomic distance of copper atoms. Furthermore, their atomic corrugation is comparable to terrace atom corrugations.

**Figure 5-8** Topographic line scan of an atom row along a clusters side-wall, dashed red line in. The image is to illustrate that the centre atom of the species appears raised in STM scans with both neighbours moderately lowered. Whether physical or electronic in origin, is unknown at this point.

**Figure 5-9 (a)** Adatom-vacancy cluster structure with an “atom” stuck in its centre. Dimensions are comparable to the vacancy-cluster structure, and the location of the central atom is noted to be slightly off centre. (b) As imaged with a blunt tip.

**Figure 5-10** Superimposed line profiles elucidating and comparing the z-dimensions of each species. The depth of the adatom-vacancy is shallower than the vacancy cluster structure. The height of the adatom inside the vacancy almost exactly equals the height of a free adatom. It is clearly seen to protrude above the lattice plane.

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Figure 5-13 I-Z Tunnelling spectroscopy curve of a copper terrace atoms (red) and the inside of a vacancy cluster (black). One would expect some leakage current to surrounding atoms when measuring inside the vacancy. This could account for the higher onset slope in the black curve. Interestingly however, tunnelling inside the cluster appears virtually identical, except the curve is shifted by 160 pm.

Figure 5-14 Current-voltage (I-V) spectroscopic curve on bare copper terrace, and inside the hollow defect structure. There are virtually no spectral features on either curve and their respective slopes are almost identical. This crudely suggests that the species inside the "black-hole" is copper.

Figure 5-15 Set of STM topographs taken in the constant current mode. Images (a-d) are taken at 3 V and 0.2 nA I$_{set-point}$ indicate that it is possible to "excite" the sombrero defects centre atom. The excitation, makes the centre atom go "bright", indicating it has become more conductive around $E_F$. A side effect of this excitation, was that the species was found to become more mobile. Once "excited", the species remained bright indefinitely. Thus, the defects properties are tuneable using an STM tip.

Figure 5-16 (a) Schematic indicating the Erhlich-Shwoebel barrier that a particle encounters when traversing a step edge. The potential energy trough at the lower terrace is often sufficient in magnitude to trap thermally diffusing particles.

Figure 5-17 (a) 37.5nm x 37.5nm STM topograph of copper (100) surface including (a) step edges, (b) islands and (c) vacancy pits. The image is poor resolution, so the objects appear as black blobs. This is a tip related convolution of the image. Nevertheless, no preference was ever observed for step sites, or defect decoration.

Figure 5-18 Ratio of sombrero to hollow defects as a function of overall defect density. This is a de- facto measurement against temperature since
defect density scales with temperature. The ratio appears to be 1:1 until a critical defect density is reached after which the sombrero density continues to increase more or less linearly with overall density. The hollow defect density begins to decline at this turning point. This process may indicate the transformation of one defect type to another. 

Figure 5-19 (a-b) STM constant current topographs of copper (100) illustrating the role of anneal temperature in overall species density. The ratio adatom-vacancy clusters to vacancy clusters also changes with increasing overall species density. In image two, the mean free path (mfp), \( \sum \frac{z_n}{n} = z_{mfp} \), of the adatoms is smaller, resulting in more frequent collision with vacancy clusters, converting them to sombreros.

Figure 5-21 Three STM topographs taken in constant current mode with standard tunnelling parameters and associated line scans through the main features of each image. The main features are defect pairs, seen with both sharp and blunt tips (see insets). The features are not a double tip artefact. These defects are said to be a pair in-plane with each other, meaning they are aligned along one axis. (a) A double hollow, (b) A sombrero-hollow mixed pair, (c) A sombrero-sombrero pair. The dimensions of each feature are shown directly to their respective rights. The key trends are (i) a decrease in the measured depths of each pair with the addition of each sombrero defect, (ii) the sombrero-hollow feature has a double bottom. The sombrero-sombrero has higher protruding centre atoms than its sombrero-hollow counterpart, (iii) the sombrero-sombrero length increases in comparison to the other two defect doubles. (iv) Most interestingly of all, is that the protruding centre atom in species (b) and (c) does not change in comparison to its singular counterpart. One may expect, especially in defect pair type (b), that the centre atom would adopt a more central role. In fact, it is never observed changing its location in these defect types.

Figure 5-22 A sequence of constant current topographs taken at room temperature of the defect cluster structures on copper (100) indicating some of the defects characteristic features. (i) When the defects add as multiples of single units they do not tend to square structures as expected for vacancy structures on copper (100). (ii) and (vi) When a sombrero and a hollow combine, the central atom does not adopt a new position which is central of the two. Rather it "stays put". (iii) When groups of sombrero type defects are combined, the mentioned raised central atom in its outer wall becomes even more prominent. This is especially noticed with a blunt tip, image (f). (vii) During motion the defect structures retain their shape and structure.

Figure 5-23 STM constant current topograph still taken from a diffusion video. A single group of defects are highlighted in this Figure. The defects
can be seen to diffuse and collide with each other, however they do not tend to stick together.

**Figure 5-24** Set of STM topographs illustrating how the defects diffuse on the copper (100) surface. Images (a) and (b) show both sombrero defects and hollow defects moving in both crystallographic directions. The species seem to move as a unit, i.e. it retains its shape. It appears to be a sort of "all-or-nothing" type movement. It is therefore believed, that a new avalanche type diffusion takes place, whereby a single atom hops into the vacancy void. When this occurs, the structure quickly attempts to re-find the super-stable 3 x 3, so all the other atoms follow suit. The distance of the centre atom from the walls of the vacancy cluster is retained even during zig-zag sliding (d)-(iv), multiple hops (c)-(iii), and single hops (a-b)-(i-ii).

**Figure 5-25** Arrhenius plot of elucidating the sombrero defect diffusion barrier on copper (100). Each data point is calculated from the hop frequency at a given temperature under standard "non-perturbing" STM conditions (0.02 nA, 0.02V). Hop frequencies are calculated as the hop/species/time (scan time).

**Figure 5-26** A measure of the hop frequency of each defect type: sombrero and hollows as a function of imaging tunnel current set-point. It is clear there is a factor of at least two in their respective diffusion rates at RT indicating that the two species are different not just in appearance but also in their measurable properties.

**Figure 6-1** 20 nm x 20 nm STM topograph demonstrating controllable RT manipulation. Using 22 nA of \( I_T \), the sombreros are deliberately slid across the surface. The hollows remained stationary in this experiment (d), but these are moveable, they just require higher \( I_T \) values to induce motion. By toggling the \( I_T \) between high (22 nA) and low (0.02 nA) \( I_T \) set-points, defect motion is controlled. With this degree of control, rudimentary structures can be created, as shown in region *.

**Figure 6-2** STM line profile from the tunnel current image from the bottom (left) to the top of image (right), indicating the change in magnitude required to induce manipulation of the clusters at RT.

**Figure 6-3** 20 nm x 20 nm STM topographs of the same area, acquired simultaneously, in the forward and backward direction illustrating z-instabilities during manipulation experiments on Cu (100) as a function of increasing tunnel current. (a) The backward scan is fine because the tunnel current is 0.26 nA  (b) The image deteriorates progressively as the tunnel current increases from 0.2, to 1, 3, and finally 6 nA until the species are eventually unidentifiable. Thus, in order to analyse manipulation events precisely, one has to perform dual imaging with different parameters in the forward and backwards scans.
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Figure 6-28 Arrhenius plots for the manipulation of the sombrero defects on copper (100) as a function tunnel current. As the interaction is “turned on” the slope of the graph changes. The slope of the graphs is a measure of \( E_{B_{\text{effective}}} \) which is \( E_B \) plus the...
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1 INTRODUCTION: MANIPULATING ATOMS AND MOLECULES USING SCANNING PROBE MICROSCOPY

1.1 Introduction

Almost 50 years ago, in December 1959, at the annual meeting of the American Physical Society, Richard Feynman delivered nano-science’s equivalent of Dr. Martin Luther King’s, "I have a dream" speech[^1]. In this visionary talk, titled, "There’s plenty of room at the bottom", Feynman conceptualised the idea of manipulating and controlling matter on a very small scale:

“I am not afraid to consider the final question as to whether, ultimately - in the great future - we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could arrange the atoms one by one the way we want them (within reason, of course; you cannot put them so that they are chemically unstable, for example). (...) What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can’t see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do”

He continues this impressive talk discussing amongst other things, the miniaturizing of computers, a series of machines of decreasing length scale in which each generation constructs the next smaller one; and predicts the development of a new, atomically resolving, electron microscope. This instrument, we now call the Scanning Tunnelling Microscope, or STM.

Feynman inculcates that seeing and controlling atoms, the very atoms:

[^1]: Greyed text denotes hyperlink to extra source materials, E.g. WebPages, STM Videos etc.
"might tell us much of great interest about the strange phenomena that occur in complex situations, and, that it ought to have an enormous number of technical applications. Why cannot, we write the entire 24 volumes of the Encyclopaedia Britannica on the head of a pin?"

Referring to complex systems and self-replication, Feynman envisages that the "marvellous biological system" might provide a useful template for nanostructure design. He continues with a myriad of prophecies, "dreaming" that:

"in principle at least, it ought to be possible for a physicist to synthesize any chemical substance that the chemist writes down. Give the orders, he says, and the physicist synthesizes it. "How? Put the atoms down where the chemist says, and so you make the substance. The problems of chemistry and biology would be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed---a development which I think cannot be avoided"

Indeed, such developments were not avoided, and in 1982 when Binnig and Rohrer invented the STM, the gulf between the macro and atomic worlds was finally bridged. Bringing a sharp metal tip atomically close to a conducting surface, electrons cross the gap through a quantum mechanical process known as tunnelling. This process decays exponentially with distance with a decay length $\lambda_T$ of the order of 0.15nm and has two control parameters; the tunnel current $I_T$ set-point and voltage (V). These parameters, control distance $I_T$, density, and the electrons energy electric field, respectively. The short decay rate results in the vast majority of the tunnelling current, i.e. > 90%, originating from the outermost tip atom, and so, if this atomic sensor is scanned in two dimensions across a surface, the tips foremost atom tunnels with, and hence "sees" or senses, atoms directly beneath the tip. The scanning tunnelling tip thus creates a 3-d atomically resolved image of the sample surface.

---


4 The gap may be a vacuum gap, an insulating layer, but, more generally speaking, a potential barrier.
During tunneling, the proximity of two materials, the electric field and the resulting tunnel current induces additional physical and electronic effects. These include tip-surface forces, localised heating, and various excitation mechanisms. These concurrent and inter-influencing processes dramatically complicate attempts at quantifying the tunnelling process; nevertheless, they also provide tuneable mechanisms for coupling energy from an STM tip into adsorbate species. If a sufficient amount of this energy is deliberately coupled into a given species, it is possible to controllably perform STM induced adsorbate manipulations.

1.2 Milestones

In 1990, Feynman’s seminal vision became a reality when Eigler and Swheizer pioneered the positioning of single atoms during the formation of three nano-sized letters, spelling I-B-M, Figure 1-1. Using an STM at low temperatures, 4 K, the authors laterally repositioned Xenon atoms, writing letters a mere 50 Å in height on a Nickel (110) surface, utilising the long-range forces as the manipulation mechanism.

Since an STM tip always exerts some force on an adsorbate, consisting in part of a Van der Waals and electrostatic contribution, the authors adjusted the position and the voltage of the tip to tune the magnitude and direction of both these forces. This allowed the authors to “drag” single atoms into any desired position. The energy barrier inhibiting lateral manipulation is the barrier to diffusion parallel to the surface.

In 1991, Eigler followed this groundbreaking experiment with an equally impressive demonstration of vertical manipulation in the now famous, atom switch experiments. Again, using an STM at 4 K, Eigler reversibly transferred Xenon atoms between a Nickel surface and the STM tip. Using tunnel currents nearing 90 nA, and applying an 800 mV pulse for 64 ms; then alternating the sign between positive and negative bias, the atom could be reversibly transferred between tip and sample in either direction. Incidentally, by reducing the tip-species distance, the authors caused the atom to spontaneously hop, or to hop to neighbouring Nickel sites if farther away whilst applying the pulse. Nevertheless, for a given fixed height, and

---

5 Whether the energy coupled is sufficient, depends on the ratio of energy input to the manipulation barrier.
6 The “IBM” paper currently has 1051 citations. Source: Scopus.
7 The atom switch paper currently has 274 citations. Source: Scopus.
Manipulating atoms at room temperature using Scanning Probe Microscopy

Figure 1-1 (a) Eigler’s iconic STM writing of IBM's logo using 34 Xe atoms on a Ni (110) surface. (b) By adjusting the position and voltage of the tip, the authors control the magnitude and direction of the both the Van der Waal's and electrostatic contribution to the force, aiding the Xe atoms attempts to overcome the lateral barrier to diffusion.[6]

Figure 1-2 (a) A sequence of three 25 Å x 25 Å STM images demonstrating the reversible transfer of Xenon from (i) the surface to (ii) the tip back to (iii) the surface. (b) (i) Schematic indicating the transfer type on application of a pulse. (ii) As a 64 ms pulse is applied to the tip, over a Xe atom, the species may be reversibly transferred in either direction. (c) (i) The time dependence of the current through the switch during operation during repeated toggles of the switch activated by the voltage pulses. (ii) the measured transfer rate as a function of tunnel current, $I_T$, during the applied pulse varies as $I_T^{4.9\pm0.2}$ for this tunnel junction. The authors suggest a heat-assisted electromigration process is consistent with the observed manipulation behaviour.[7]
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pulse voltage, the distribution of delays\(^8\) is a decaying exponential, indicating a fixed probability of transferring per unit time; i.e. there is a characteristic transfer rate. Figure 1-2 (c) (ii) shows that the transfer rate for this particular 906 KΩ junction has a power law dependence on the pulse voltage and consequently on the tunnel current, \(I_t\), according to \(I_t^{4.9±0.2}\). Based on the results available, the authors surmised that:

""the competition between electron heating and the vibrational energy to the lattice may result in the power law dependence on tunnel current, particularly if multiple scattering events are required. The observed sideways motion of the Xe atom at greater tip-sample separation is consistent with the atom being vibrationally excited. The absence of sideways motion at closer tip-sample separation may be due to increased Van der Waals attraction to the tip as the tip is brought closer to the surface."

In contrast with the lateral manipulation technique, the relevant energy barrier to vertical manipulation is the desorption energy, and not the diffusion barrier. However, it ought to be mentioned that this is only the case in the limit of large tip-surface separations, and importantly, that the barrier diminishes or decreases to zero as the tip approaches the adsorbate. This barrier to vertical manipulation is 3-10 times larger than the aforementioned lateral diffusion barrier \(^9\).

1.3 Main modes and mechanisms of atomic manipulation

By November 1991, Eigler and Stroscio took stock of the developments in what amounts to a review article discussing the new papers, and possible uses, of STM manipulation as a tool for science \(^m\). In this article, the authors classify and group the emerging mechanisms of manipulation into parallel (lateral manipulations) and perpendicular (vertical manipulation) modes, noting the goal of both processes is the purposeful rearrangement of matter on the atomic scale. They viewed these acts of rearrangement as a series of steps that results in the selective making and breaking of chemical bonds between the atoms, or equivalently, as a procedure that causes a

\(^8\) The term delay used by the authors, refers to the length of time until the species transfers.
configuration of atoms to evolve along some time-dependent potential energy hyperspace from an initial to a final configuration. The modes and mechanism outlined in this article, along with some of the new mechanisms and modes, which have since been developed, are outlined in the following sections.

1.3.1 Energy coupling mechanisms for the vertical manipulation mode

Many mechanisms of vertical manipulation exist, and as early as 1990, Becker et al. demonstrated the feasibility of using field emitted electrons from an STM tip to bring about hydrogen desorption from a Si (111) surface. Later, this technique was developed by Avouris and Walkup who theoretically and experimentally demonstrated desorption of an adsorbate via multiple vibrational excitations induced by inelastic electron tunneling. Other vertical transfer mechanisms identified included transfer-on or near-contact; and in their simplest form do not require any electric field, tunnel current or potential difference for success. These events are activated processes and extensions of these processes include field evaporation and electromigration. Electromigration is thought to have two different components, the first due to an effective charge on the defect, and the second, due to a "wind force" resulting from scattering of electrons. Ralls et al. suggested a mechanism of localised heating, where defects are heated above the lattice temperature by inelastic scattering. The vibrationally hot defects then hop to a near neighbouring site. The probability of finding the species in a high lying vibrationally excited state can have a power law dependence on current, with an exponent greater than unity if multiple scattering events are required to promote the species up a ladder of vibrational energy states. Power law calculations of this variety are widely utilised nowadays, to evaluate electron-stimulated events. Using log (I) vs log (event rate), like Figure 1-2 (c) (ii), such plots, now called activation plots, are often utilised to elucidate the nature of the excitation involved.

1.3.2 Energy coupling mechanisms for the lateral manipulation mode

Transfer mechanisms in the parallel mode identified at this early stage, included field assisted diffusion and the long range Van der Waal's and electrostatic
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Manipulation using short-range forces

Figure 1-3 (i) A measured tip height curve during pulling of a Cu atom is shown superimposed on a schematic drawing of the positions of the tip apex, the manipulated atom, and the substrate atoms along [110] direction. Indicated are the jump height (a), the lateral distance between tip apex and the manipulated Cu atom at the tip position at which a hop of the Cu atom occurs (b), and the approximate tip height during manipulation (c) assuming an initial distance of 6.5 Å. (ii) While the jump height (a) and the lateral distance (b) between tip-apex center and center of the manipulated atom at the point of its hop are strongly dependent on the tunneling resistance, the height of the tip (c) at the point of hopping is less strongly affected. The error bars denote the maximum observed deviation from the indicated means of 0.2 Å in the shown data set corresponding to experiments with a single tip apex. (iii) The left part shows tip height curves during manipulation of (a,b), a Pb atom, and (c) a CO molecule. The tip movement is from left to right, and the tunneling resistances are indicated. All tip height curves are unfiltered raw data. The vertical dotted lines correspond to fcc sites next to the step edge. The initial sites of the manipulated species are indicated by small sphere models. On the right part STM images of the different ad-particles are shown. Aspect ratio and angle of view are optimized for each adsorbate. The arrows indicate the direction of tip movement.

Processes. Since then, lateral manipulation has been extensively developed by Karl Heinze Rieder’s group who have identified and set-out guidelines, for identifying tell-tale signs of different movement types. Using detailed tip height measurements, Figure 1-3, during the manipulation of single atoms, molecules and dimers on Co [211], Rieder et al. suggest that atoms are primarily manipulated using short-range...
chemical forces. This contrasts with the long range Van der Waals and electrostatic force mechanism used in Eigler's sliding \[6\].

Rieder et al. \[19, 21-30\] reveal that both attractive and repulsive manipulation modes can occur depending on the chosen tunneling parameters. By examining the shape of the STM line curves along the manipulation direction, the authors estimate if an interaction is attractive or repulsive. Such data, Figure 1-3 (ii), has additionally been used by the authors as a measure of force gradient, assuming an undisturbed diffusion barrier. We evaluate this extrapolation in more detail in section 1.5.3.

Additional forces on an adatom can arise because of the presence of the inhomogeneous electric field produced by the STM tip. There may be an electric dipole moment at the adatom caused by charge transfer with the surface resulting from the adatom-substrate bond or the tip's electric field may induce an electric dipole moment via the adatoms polarizability. In either case, a lateral force can result from the interaction between the overall electric dipole moment and the tip's inhomogeneous electric field \[31\].

It is important to note at this time, that; the mechanisms mentioned are processes of transferring energy from an STM tip to a surface species, and although they may have first, or predominantly, been used for one manipulation mode, they may also succeed in manipulating in a different manner. A prime example of this, is the tunnel current density mechanism proposed by Fishlock et al. \[32\] to manipulate bromine atoms on Copper (100) (lateral manipulation), which is very similar to the mechanism proposed during the assessment by Eigler et al. \[7\] in their atomic switch experiments (vertical manipulation).

In summary, atoms and molecules have been shown to be manipulable using a variety of different tip-energy coupling mechanisms. Tip-assisted diffusion, long-range Van der Waal and electrostatic forces, short-range chemical forces: both attractive and repulsive, an electric field gradient and localised heating mechanisms have all moved species parallel to the surface. In addition to these, in the vertical mode, inelastic tunneling, electromigration and transfer on or near contact have been employed. It is strongly emphasized, that the potential energy barriers, discussed and controlled re: vertical manipulation, yet seldom discussed for lateral manipulation, change dynamically with tip-surface separations. Dynamically changing potential
energy barriers to manipulation which simultaneously occur in response to increased or decreased tip-energy coupling, makes the quantification process all the more difficult. On the other hand, if viewed optimistically, one may conclude that there is a rich variety of atomic scale mechanisms which are examinable if careful and well designed SPM manipulation experiments are performed.

1.3.3 Additional modes of manipulation

Adding to this already impressive list of different manipulation modes, i.e. lateral \(^9\) and vertical manipulations, achieved using SPM, are examples of molecular excitations, including but not exclusively, rotations \(^{[23]}\) and flexures \(^{[24]}\). Dissociations \(^{[28, 36]}\) can also be performed. Such processes primarily occur as a result of bond specific electronic excitations, which may be utilised to perform single bond cleaving \(^{[27]}\) and bond selective chemistry \(^{[38]}\). Furthermore, by manipulating the surrounding potential landscape, at sufficiently low temperatures, Salmeron et al. \(^{[39]}\) suggest it may be possible to deliberately influence, and hence cause, the atoms themselves to tunnel from one location to another. Stroscio et al.\(^{[40]}\) and Repp et al. \(^{[41]}\) have studied this experimentally.

Heretofore, the manipulation modes outlined and mentioned have been limited to physical (species motion) processes, irrespective of the excitation mechanism utilised. However, STMs may additionally be used to induce reversible and long-term electronic manipulations. In July 2004, Repp and co-workers \(^{[42]}\) demonstrated that the charge state of individual atoms on an insulating polar surface, could be controlled using an STM tip. By applying a voltage pulse, the authors manipulated the adsorption state of an individual Au adatom. This manipulation results in two distinct and stable electronic states, \(\text{Au}^0\) and \(\text{Au}_-\). Such state manipulation is found to alter the some of the species' physical and chemical properties.

In the \(\text{Au}^0\) state for example, adatom diffusion sets in at a temperature of about 60 K, whereas in the \(\text{Au}_-\) state, the adatoms already diffuse at the lower temperature of 40 K. Small clusters of Au adatoms may be similarly switched between different charge states. This was demonstrated in an experiment for Au dimers and trimers on

\(^9\) I have highlighted with italics, the different manipulation modes possible using an STM tip as an excitation source. In this thesis, we are primarily concerned with lateral manipulation.
NaCl films. These findings open up the possibility of switching surface catalytic reactions on and off by manipulating the charge state of individual nanometer-sized Au clusters.

In summary, I have introduced the main manipulation modes, i.e. what type of excitations can be achieved. This should not be confused with the manipulation mechanisms, i.e. how the excitation, destabilisation, or energy coupling is performed, of which there are far more varieties. Furthermore, just because a manipulation mechanism may be utilised to perform vertical manipulation, does not mean it may not be used to similarly perform different manipulation types, i.e. lateral manipulation for example. By introducing the different manipulation modes I have de-facto covered many, though by no means all, of the most important manipulation mechanisms. Despite this introduction, in chapter two of this thesis, a more detailed physical picture and examination of the manipulation mechanisms relevant to this body of work, is presented where relevant. In the meantime, however, it is important to highlight some impressive applications of STM manipulation.

1.4 Smart applications of atomic manipulation

1.4.1 Quantum engineering

Having pushed, pulled, excited desorbed, rotated, ruptured, and heated all the atoms and molecules one may think of, eventually somebody will ask, what is the point? How, can we utilise atomic and molecular manipulation to quantum engineer so we may perform truly novel experiments, with serious technological and scientific implications? Then, and only then, may we begin to realise some of Feynman’s dreams?

“I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do”

The first novel offshoot came in 1993, when Crommie, Lutz, and Eigler \(^{45}\) used a 4 K STM to assemble individual Iron adatoms on a Cu (111) surface into a discrete,
Manipulating atoms at room temperature using Scanning Probe Microscopy

Figure 1-4 Spatial image of the eigenstates of a quantum corral represented in 3-d. The image consists of 48 iron atoms repositioned on the Cu (111) surface using 4 K STM atomic manipulation. The image was taken at 0.01 V, and the spacing between neighbouring Iron adatoms ranging from 8.8 Å to 10.2 Å. The image clearly shows a strong modulation of the local density of states inside the quantum corral.

artificial, closed structure or corral. Within this ensemble; electrons are confined inside the artificial structure at nanometre length scales. When electrons are confined to length-scales approaching the de Broglie wavelength, quantum mechanical effects dominate their properties. If tunneling spectroscopy (STS) is then performed inside the corral, the STS reveals a series of discrete resonances, providing direct evidence of size quantisation. The construction of Eigler's quantum corrals thus, heralded in a new era, where atom and molecular manipulation led to direct wavefunction manipulation and control.

STM images show, that the interior of the corral's local density of states (LDOS) is dominated by an eigenstate density expected for an electron trapped in a round two-dimensional box. This facilitates both spatial and spectroscopic resolution of quantum states. In effect, the authors found a way to shape the spatial distribution of surface state electrons by using Iron atoms as scattering centres. The abilities of the STM to manipulate single atoms and molecules has facilitated corrals being used to study the Kondo effect, electron lifetime measurements for states close in energy to $E_F$, and even allowed single bits of information to be represented by a single atom or molecule. Although such information densities remains beyond the reach of real-world
Manipulating atoms at room temperature using Scanning Probe Microscopy

Figure 1-5 (a) Topograph 13.5 nm × 13.5 nm; \( I_T = 1 \) nA; \( V = -60 \) mV of a molecular hologram that encodes two pages of data at different energies in the same region of space. (b) A \( dI/dV \) map taken at \( V = -18 \) mV shows the \( S \) page. \( V_{ac} = 4 \) mVr.m.s. (c) Measuring \( dI/dV \) at \( V = -45 \) mV retrieves the \( U \) page. The molecules are unchanged. By mapping \( dI/dV \) at many voltages between -80 and 10 mV, \( \rho (r, E) \) was measured throughout the readout region. A translucent surface of constant DOS is shown. Slices through this space at the appropriate energies reveal the \( S \) and \( U \) pages. (e) The normalized cross-correlation of \( \rho (r, E) \) with each template image (insets) was computed as a function of \( r \) and \( E \). Surfaces of constant correlation (at 98% of the global maximum) are shown for each page, confirming their locations in the information cube. Contours show the maximum correlation projected in each dimension (95–99.9%) \(^{49} \).

devices, it has been assumed that the spacing between atoms in condensed matter systems sets a rigid upper limit on information density. However, this is not necessarily the case.

In recent work by Manoharan et al. \(^{46} \) it has been shown that it is possible to
exceed this limit with a holographic method that is based on electron wavefunctions rather than free space optical waves. STM manipulation, and holograms comprised of individually manipulated molecules, are used to create and detect electronically projected objects with features as small as 0.3 nm, and to achieve information densities in excess of 20 bits nm\(^2\). This electronic quantum encoding scheme involves placing tens of bits of information into a single fermionic state.

Initially, atomic manipulation is used to construct open nano-structures—molecular holograms—which can concentrate information into a medium that is free of lattice constraints: the quantum states of the two-dimensional gas of electrons. Electron waves scattered from the potential imposed by the molecules propagate into an atomically uniform area of a copper surface. Here, through coherent electron interference, the information inherent in the molecules positions is densely projected into two spatial degrees of freedom and one energy degree of freedom. Similar to optical holography, this requires the precise amplitude and phase engineering of electron wavefunctions to store pages of information volumetrically. These data are read out by mapping the energy resolved electron density of states (DOS) with an STM. As the projection and the readout are both extremely near-field, and because native quantum states rather than an external beam are used, the process is not limited by lensing or collimation. This facilitates the encoding at length scales smaller than the atomic spacing limit, thus heralding a new horizon for attainable information density.

In summary, controlling the electronic states (charging) and the electronic cloud density in ways that just been shown, offer fascinating possibilities to extend manipulation way beyond pushing and pulling. In essence, such control is effectively leading us to truly novel materials with truly revolutionary properties. A more direct approach however, is outlined below.

### 1.4.2 Atomic chemistry

Another impressive use of STM manipulation is the atomic scale chemistry Rieder et al. performed whilst inducing a multiple stages of a chemical reaction. This experimental realisation was another cornerstone, of Feynman's "dreams":

“in principle at least, it ought to be possible for a physicist to synthesize any chemical substance that the chemist writes down. Give the orders, he says, and the physicist synthesizes it. How? Put the atoms down where the chemist says, and so you make the substance.”

In April 2000, these authors induced elementary steps of a chemical reaction using an STM in a controlled step-by-step manner. Utilizing a variety of manipulation techniques, the authors initially separated iodine from iodobenzene using tunneling electrons, then, brought the two resultant phenyls together mechanically via lateral manipulation and, finally, their chemical association to form a biphenyl molecule is mediated by excitation with tunneling electrons.

This result was another impressive achievement for STM manipulation, driving us closer to the ultimate goal of new material complexes with advanced and otherwise unattainable properties, resulting from an enhanced understanding of, and ability to, manipulate and engineer at the quantum scale. Yet, new materials with drastically improved or new properties are not routinely, if at all, being developed as a result of atomic and molecular manipulation using an STM. Specifically, no new species has been produced, which can not be produced by any other means. This is because several serious barriers to progress are still present. In the next section, we examine some of these challenges.

1.5 Challenges for advancing atomic manipulation

The ability to tailor the physical and electronic properties of matter at the atomic scale, is a critical step for the understanding and fabrication of new materials and devices. In practise, two main routes lead to the construction of nanoscale objects: (i) “top down” production methods, which extend the techniques currently employed in the semiconductor industry, and, (ii) the “bottom-up” approach. Using the latter, single atoms and molecules are repositioned one-by-one using SPM’s, or, alternatively, patterns may be “grown” using self-assembly technology.

1.5.1 Mass-production

Concentrating on SPM techniques, my goal per-se is not to convince you that SPM
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Manipulation is already a viable technology for mass-producing nanostructures. It simply is not. It takes too long, is difficult and unpredictable, and relies too heavily on uncontrolled SPM tips.

Rather, my interest lies in using manipulation as a research tool to study nanomechanics, dynamics, and electronic behaviour of matter at the atomic scale. In addition to developing more efficient and intelligent methods of manipulation I attempt to elucidate the tip-surface interactions, friction and dissipation effects which affect, and occasionally dominate, SPM imaging, diffusion and manipulation results. Nevertheless, what achievements might aid manipulations development technologically?

One advantageous development would be long-range, repeatable, addressability with an STM tip. That is, the ability to move microns with atomic scale accuracy, and then perform all the manipulation processes. Other useful processes might be;

- the ability to move larger scale ensemble's of species, with atomic precision and 100% reliability, since this could speed the manipulation process and help make it up-scaleable,
- reliable SPM tips, or alternatively, a mechanism for protecting the tips, since this would improve reliability, and the,
- development of room temperature systems for improved technological relevance.

With this final requirement in mind, the focus is now shifted to the scientific challenges regarding SPM manipulation. In particular, we discuss the role of thermal energy during atomic manipulations, the challenges of high temperature manipulation experiments, and the methods currently used to elucidate the amount of energy required to move an atom.

1.5.2 Thermal energy

As shown in section 1.2, using STM as an operative tool to manipulate single atoms and molecules on surfaces is now a relatively well established procedure. Using STM, large individual molecules have been repositioned on metal surfaces with atoms and
molecules also manipulated on semiconductor surfaces through selective electronic excitations. The most exciting and complex structures however, such as Eigler’s quantum corrals, have been constructed with weakly bound atoms, stabilized by operating the STM at cryogenic temperatures. Analogous experiments at room temperature (RT) are more difficult to achieve, requiring strongly bound species that are not perturbed by thermal fluctuations. Thermally stable species however, require far larger tip-surface interactions to be moved, which is potentially hazardous for the tips structural integrity.

1.5.2.1 Room-temperature atomic manipulation

In April 2000, Fishlock and co-workers reported the successful sliding of bromine atoms across a copper (100) surface. In doing so, they provided the first stable adsorbate-metal system suitable for room temperature atomic manipulation experiments. On semiconducting surfaces, Boland and Weaver independently reported the successful hopping of atoms, including halogens on silicon surfaces at room temperature. Room temperature manipulations have also been achieved by other groups, though importantly, no structures, even simple lines, could be constructed by any of these authors.

The challenges facing room temperature manipulation can be broken into two main sections. The first challenge is fundamental and inherent to nature i.e. that there are very few species which are stable, i.e. do not diffuse, yet, are manipulable at RT.

1.5.2.2 A suitable adsorbate-substrate system: Quantum Lego

The stable adsorbate-substrate challenge, relates the barrier to manipulation to the energy coupling ability of an STM tip, to the structural destabilising energy of the SPM tip. The energy overlap of these factors determines the “energy window” in which successful manipulation can occur. Species have to be bound to the surface, with an energy that lies inside a spectrum of energy, which is reliably and stably deliverable, by a metal STM tip. As early as 1991, Eigler noted in his first iconic manipulation paper that there exists;

“a limiting class of adsorbed atoms and molecules that can be positioned (at 4K)”
But devices constructed at cryogenic temperatures are not easily adapted, or utilised for technological gain. If thermally stable species at RT are an important developmental step for application of atom-by-atom, and bond-selective engineering, the development of an adsorbate-substrate which can perform all the functions, mentioned in the highlights section above at RT, needs to be developed. That is, the adsorbate needs to be dynamically stable, moveable without breaking the STM tip, electrically tuneable, and sufficiently able to alter the surface wavefunctions for corral and holographic use, whilst organisable en-masse at room temperature.

The second main challenge for RT manipulation is procedural. For species bound to a surface at room temperature, the energies required for successful manipulation approach 0.5 eV. Such values reflect the chemisorbed nature of the bonds being broken and require large tip-surface interactions or electronic excitation processes for successful manipulation, and since the latter is only occasionally applicable, the high tip-species interactions required have a high potential for altering the STM tips atomic structure. This is potentially catastrophic, since it reduces reproducibility, and often results in one not being able to complete, or relocate a half built nano structure. One potential solution to aide in overcoming the higher manipulation barriers at room temperature is to provide an external energy source in conjunction with the tips forces. Then lower tip-surface interactions may be sufficiently able to manipulate species. An obvious source type worth trying to harness, is thermal energy.

1.5.2.3 Thermal energy as a control parameter

**Tip-down heating**

The influence of tip induced heating was first discussed in 1991 in Eigler’s atom switch experiment [7, 69]. In this publication, Eigler suggests that a localised heating-assisted electromigration phenomena is the only mechanism of manipulation accountable for the phenomena observed:

"the competition between electron heating and the vibrational energy to the lattice may result in the power law dependence on tunnel current, particularly if multiple scattering events are required"
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Such a conclusion was influenced by the suggestions of Ralls et al.\textsuperscript{[16]} who found that the dominant contribution to the electromigration-force term comes from the scattering of electrons from the impurity, which heats the impurity above the lattice temperature through inelastic electron scattering. Avouris et al.\textsuperscript{[66]} pointed out that inelastic tunnelling may play a very important role in attempts to manipulate atoms and molecules with an STM. They surmised, that the very high tunnel current densities obtainable with STM might promote a series of inelastic vibrational excitations, thus localising substantial energy in a single bond. Simply put, the vibrational mode of interest can be thought of as a harmonic oscillator, with inelastic tunnelling, promoting transitions up the oscillator levels. Relaxation of the adsorbate-substrate vibrations occurs via energy transfer to metal phonons. When Avouris et co-workers\textsuperscript{[66]} applied this to Eigler's atomic switch\textsuperscript{[7]}, they found, that Xe-surface vibration could be heated to temperatures substantially above the ambient temperature. Similar considerations of a Si-H vibration, with a frequency markedly different from the surface phonon modes, and correspondingly poor relaxation, found that the effect of the vibrational heating is dramatic (increase of 200 K) for currents over 5 nA. The critical factor determining the extent of this vibrational heating being the vibrational lifetimes. Fishlock and co-workers\textsuperscript{[32]} invoked a similar argument, stating that, if around 10 meV can be delivered to an atom from the tip, additional to room temperature energy, the hopping rate of the atom will increase to a second or so, assuming a lateral barrier of $\approx 1$ eV. With the addition of a background tip-atom repulsion, the tunnel current density mechanism is then sufficient to account for the manipulation observed.

In summary, tunnelling electrons can, through a variety of mechanism locally heat adsorbates and specific bonds. Thus, the process can be utilised as a parameter to control manipulation rates. There are however, some key points which are worth mentioning: (i) only relatively low energies are deliverable ($< 10$'s of meV); (ii), relaxation rates determine the rate of localised energy dissipation, i.e. heating; and (iii), the mechanisms outlined heretofore, represent different types of tip-induced localised heating. An altogether different issue however, is the influence the surface temperature has on manipulation processes.
Bottom-up heating

The influence of surface temperature on STM energy-coupling/manipulation mechanisms is currently vague. Eigler et al. stated that the process of sliding is fundamentally temperature independent. Yet, Avouris and co-workers, found that the decreasing the temperature increases the H-Si vibrational relaxation time, resulting in a higher effective adsorbate temperature; and, that lowering the substrate temperature decreases the dephasing rate of the H-Si modes which then, reduces the rate of incoherent (Förster) vibrational energy transfer away from the Stark shifted H-Si mode under the tip. This increases the localisation of the vibrational energy and enhances the probability for multiple vibrational excitations and desorption. Thirstrup et al. reported similar findings.

On the other hand, since an increase in surface temperature increases the thermal energy of the adsorbate ($k_B T$) through phononic coupling, the adsorbate, on average has greater vibrational energy. Thus, the effective size of the diffusion barrier is reduced. One may then expect the STM tip-coupled energy required for manipulation to be reduced at elevated temperatures. Such uncertainty and potential usefulness of thermal energy as an external aide to manipulation, validates the following investigation in Chapter 5 of this thesis, of the role of surface temperature during STM manipulation of atoms.

1.5.3 The energetics and forces required to manipulate species

Another major challenge for STM manipulation is the reliable quantification of the energy input, and the forces present, during atomic manipulation. Measuring the exact energy, or force, required to move species from one location to another, or from one state to another, can reveal information regarding bond energetics, excitation mechanisms, the tip-adsorbate coupling efficiency, friction and dissipation effects, and many fundamental atomic processes. Despite this, and the obvious importance of measuring the exact amount of energy required to manipulate adsorbates, such quantification has proved illusive.

Irrespective of the manipulation mechanism responsible for delivering energy from the tunneling tip to the adsorbate, a force is always required to provide directionality and control during manipulation. Again, however, reliable and direct quantification of
the forces present during manipulation has not been demonstrated. Simply put, STM is incapable of directly measuring forces or energies involved in manipulation. With this in mind, recent successes by Morita et co-workers [68-70] in manipulating atoms using an atomic force microscope (AFM), with which STM manipulation is comparable, had provided hope.

1.5.3.1 Manipulating atoms using non-contact atomic force microscopy

The atomic force microscope, akin to its elder brother the STM, is a scanning probe, capable of atomic resolution. The property sensed however, is the force gradient. Despite the clear suitability of this instrument to measure the force to move atoms and molecules, reliable measurement of lateral forces during manipulation, has yet to be attained. Several reasons for this heretofore failure are outlined below.

Experimentally, the regulation of an AFM’s oscillation cycle, i.e. maintaining a constant force gradient, is far more complicated and less robust, than the regulation involved in maintaining an STM tip’s height above a surface. Consequently, there are serious experimental challenges in manipulating atoms, and maintaining stable oscillations, concurrently. Second, even if such hurdles are overcome as Morita et al. [68-70] have impressively shown, the measured signals, most probably a shift of the cantilevers resonance frequency is a measure of the vertical component of the manipulation force. Thus, the force to slide a species is not easily obtainable. Third, interpreting AFM data is rather complicated. Typically, there are two regulation circuits, phase changes, and the fact that the measured force related change in frequency is a convolution of different tip-surface forces. In short, though AFM can measure a property related to a force gradient, straightforward application of this to measuring the force to manipulate atoms, is not possible. Despite the limitations outlined for both STM and AFM, there have been two notable attempts at quantification during manipulation meriting some discussion.

Measuring force gradients with an STM

One attempt at quantifying the manipulation process using an STM, was by Karl Heinze Rieder’s group. By examining the shape of the STM line curves,
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Figure 1-3, along the manipulation direction, the authors first determine if the interaction is attractive or repulsive. The authors then examine a variety of measurables such as jump height, distance to sample, and lateral displacement, Figure 1-3 (i), as a function of tunnel gap resistance (effectively tip height). The jump height during manipulation is found to vary for a single tip, with gap resistance between 0.3 and 0.8 Å Figure 1-3 (ii)-(a), while the total downward displacement of the tip relative to the imaging height is in the tunnelling resistance regime between 150 and 300 kΩ a constant 3.6 ± 0.1 Å resulting in ≈ 2.9 Å distance between the tip apex and sample surface. The lateral displacement of the tip from the centre of the manipulated atom immediately before its hop varies between 1.9 and 2.4 Å Figure 1-3 (ii)-(c). From this data, a measure of force gradient, assuming an undisturbed diffusion barrier was obtained. The connection between the two values is a little vague, nevertheless and disregarding this, the validity of assuming a static barrier also merits discussion.

Since the energy barrier to surface diffusion on a metal is only a fraction of the energy with which the adatom is bound to the surface, the Van der Waals forces might suffice to move an adatom physisorbed to the surface. A more strongly bound chemisorbed adatom on the other hand, requires a stronger bond between the tip and adatom for repositioning to occur. With short-range repulsive and attractive modes identified by the authors as the manipulation mechanism, it seems large tip-surface forces are likely. With this in mind, and considering the magnitude of tip-surface forces during STM/AFM with tungsten tips and copper surfaces are approximately 1nN [71], in the short-range chemical force region, it seems extremely unlikely that the diffusion barrier remains unchanged during manipulation. Theoretical [72] and experimental tunnel current versus distance [73] data, all indicate a change in surface corrugation, and hence diffusion barrier, as a function of tip-sample distance. Hence, the validity of such an approach to the measure of the tip-energy coupling may require re-evaluation.

The force to move an atom?
By far, the most impressive effort at quantifying the force needed to move an atom on a surface to date, has been performed by Ternes and co-workers [74]. In this work, the
authors derive the vertical and lateral forces present during manipulation from a direct measurement of $\Delta f$, "roughly proportional vertical interaction stiffness", as a function of distance. The vertical force is determined by integrating $k_z$ along $z$ the frequency shift and hence $k_z$ is an average of the tip-surface interaction over one oscillation cycle of the tip, with deconvolution utilised to reduce vertical blurring. The authors interpret $F_z$ as being the sum of two components: a background force $F_b$ and the force $F_z^*$ due to the presence of the adsorbate. The background force is in large part due to long-range Van der Waals force and increases as the tip approaches the surface, but does not depend on the lateral position. The vertical force $F_z^*$ due to the adsorbate grows rapidly, doubling in magnitude as $z$ is changed by only 15 pm near the move threshold, indicating the short-range nature of the force. Surmising that the tip-sample interaction was non-dissipative, the authors then calculated the tip-sample interaction potential $U$ by integration of $F_z$ along $z$. The lateral force was then calculated by differentiation of $U$ in the $x$ direction. Thus the authors calculate forces in any direction even though only $\Delta f$ in $z$ was calculated.

With this technique the authors measure the lateral force to move a single cobalt atom on Pt (111), $F_x$, at $210 \pm 30$ pN. At the same time, $F_z^* = -1.4 \pm 0.2$ nN was much larger than the lateral force and was nearly half as large as the bond breaking force 4 nN. To understand the interplay between the vertical and horizontal force components, the authors decreased $z$ below the threshold height for hopping and continued to measure the forces. They found, that the lateral force to move the atom remained constant, whereas the vertical force varied by a large factor. For the range of heights measured, $F_z^*$ at the point where the Co atom hopped varied from $-0.45$ nN (with the tip laterally far from the atom) to $-3.0$ nN (with the tip nearly above the atom). The authors argue that the results suggest that the lateral force is the key for the manipulation of metal adsorbates on flat metal surfaces. This insensitivity to $F_z^*$ is in contrast to the mechanism mentioned by Morita et al for moving Si atoms on Si(111). There, it was found that the vertical force plays a dominant role by causing a reduction of the energy barrier between two adsorption sites as a result of relaxation of the Si adsorbate and surface.
Figure 1-6 Measuring the force to move Co on Pt (111). (A) Schematic top view of the Pt (111) surface atoms (gray) and the adsorbed Co atom (red). In the following panels, constant-height line scans in the direction of easiest adsorbate motion (x direction) were taken at successively reduced tip sample separations until the Co atom hopped to the adjacent adsorption site [red circle in (A)]. The scan speed was ~0.5 nm/s. (B) The force $F^*$ between tip apex and the Co atom can be divided into the lateral force $F_x$ and the vertical force $F_z^*$. The total vertical force $F_z$ is the sum of $F_z^*$ and the background force $F_B$. (C and D) Simultaneously measured conductance $G$ and stiffness $k_z$ (circles and gray lines). Note that these values are time-averaged over the cantilever oscillation between $z = z'$ and $z = z' + 2\Delta$. We label selected line scans with the closest approach $z'$ during the oscillation (15). (E to G) Tip-sample interaction energy $U$, vertical force $F_z$, and lateral force $F_x$ extracted from the stiffness $k_z$ data in (D). Selected line scans are labelled with the tip height $z$; here, the oscillation amplitude has been deconvoluted from the curves. The red arrows in (C) to (G) indicate the hop of the Co atom to the neighbouring binding site. Coloured lines in (C), (F), and (G) are fits with the s-wave model\textsuperscript{[16]}.

1.6 Synopsis and outlook

I have attempted to introduce both the work contained within this thesis, and the field of STM manipulation on which it is based. In doing so, some of the field’s milestones and highlights have been discussed, alongside some impressive developments, such as the quantum holographic encoding, and atomic scale chemistry. The latter’s limitations however, led the discussion onto areas, which continue to challenge STM manipulation.
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Figure 1-7 (i) Vertical and lateral forces for manipulating CO on Cu (111). Vertical (A) and lateral (B) force components when moving the tip over a CO molecule on Cu (111) for different tip heights z. The x direction corresponds to the easiest adsorbate motion from an on-top binding site to an adjacent one via a bridge site. The blue arrows mark a repulsive force $F_{z^*} = F_z - F_B$ of up to 20 pN between tip and molecule (see inset). At z = 80 pm, the molecule hopped between neighbouring site in (B) is a linear fit to the lateral force with a slope of 1.2 N/m. (ii) Tip-adsorbate energy landscape during manipulation. Two-dimensional potential landscapes of the tip-sample interaction energies during controlled manipulation of Co (A) and CO (B) on Cu (111). The energy scales of the colour-coded images are shifted so that $U = 0$ at the preferred adsorption site for Co (fcc hollow site) and CO (on-top site). The underlying Cu(111) lattice is superimposed as a ball-and-stick model. The size of each image is 550 × 480 pm².

These challenges provide much of the impetus, and effectively outline, the work carried out in this thesis.

Chapter 2 introduces tunneling, tip-surface forces and the general operation modes of each microscope. The difficulties and complications associated with quantitative analysis of STM data, e.g. forces between the tip and surface in STM, are emphasised. These complications and their potential usefulness as tip-surface energy coupling mechanisms are also addressed.

Chapter 3 introduces the instrumentation and procedures necessary to perform the experiments in this thesis.
Chapter 4 deals with the first major challenge outlined above, i.e. overlapping the energy windows of the tip-surface energy coupling ability, with the adsorbate-surface's diffusion barrier. The former is quantified using a simultaneous non-contact atomic force microscope/ scanning tunneling microscope (nc-AFM/STM) operating with a tip identical to an STM tip, making it directly comparable to standard STM manipulation data. The second key challenge addressed in this chapter is the unearthing of suitable adsorbate-substrate system for RT manipulation. Three different systems are analysed, with only one, an adatom- vacancy cluster structure having all the characteristics sought.

Chapter 5, we discuss the properties of the tuneable, stable, yet manipulable species, which offers much promise as an atomic building for the future surface engineering.

Finally, Chapter 6 describes the manipulation of atoms at RT and above. By performing variable temperature STM manipulations, Arrhenius graphs are plotted as a function of tip-sample separation. This allows the direct measurement of the energy coupled from an STM tip, the force needed to move species, the mechanism of manipulation, and the role thermal energy plays in the manipulation process.
2 SCANNING PROBE MICROSCOPY

2.1 Introduction

Scanning probe microscopy (SPM) has developed into a ubiquitous nano-science tool, with the range of phenomena studied continuing to grow. Surface properties of metal [78] and semiconductor [78] surfaces were studied first, but recently, areas as diverse as electron dynamics [77] and listening to living cells [78] have also been investigated. Such diversity and application is achieved using a family of SPM’s [79-88], sensing a variety of different tip-surface interactions on atomic length scales.

The first family member, the Scanning Tunneling Microscope, STM, was invented in 1982 by G. Binnig and H. Rohrer [85-88], who both received the 1986 physics Nobel Prize for their efforts. Their STM measures electron tunnelling between a sharp metal tip and a sample surface, and in UHV, it provides excellent atomic resolution images on a variety of conducting surfaces [89-111]. For poorly conducting substrates such as insulators and biological samples however, tunnelling is rather difficult to achieve [112-116]. To facilitate investigation of these surfaces, it was thus necessary to develop a new instrument measuring a different near-field interaction.

The first, and most important extension to the SPM family was the development of the Atomic Force Microscope, AFM, in 1986, by G. Binnig, C. Quate and C. Gerber [84]. Detecting force interactions rather than the tunnelling electrons, AFM’s opened a gateway for wide ranging multidisciplinary studies of almost any material, e.g. chocolate [117, 118]; and in almost any environment, e.g. space [119]. But that’s not it!

Using SPMs creatively, people realised very early on that STM and AFM could also be used as a tool to shape the environment in which they see [43, 54, 55, 120, 121]. Hence, a tool was created to not only see, but also to build, using single atoms and molecules as nano “building blocks”.

In the following two chapters, I introduce the experimental and theoretical aspects of ultra high vacuum Scanning Tunnelling Microscopy, (STM), and the Atomic Force Microscopy, (AFM) with particular interest and emphasis drawn to tip-surface interactions that may be exploited for manipulation of matter, at the atomic scale.
2.2 Scanning tunnelling microscopy

For an in-depth review of STM, the reader is directed to a wide variety of literature describing in detail the techniques and theory of STM\textsuperscript{[122-126]}. STMs utilise quantum tunnelling, the ability of electrons to traverse a vacuum potential barrier as its basic operating principle. During normal operation, a sharp metal tip, usually W or PtIr is positioned 0.3-3 Å from a conducting surface, so an overlap between tip and sample wave functions can occur. An electron then flows from a tip to a surface, or vice versa, before point-contact occurs. The magnitude of tunnel current increases exponentially with decreasing tip-sample distance, so even individual atoms protruding from the surface can give rise to detectable current variations. This exponential variation of tunnel current with distance is the key scientific principle for achieving atomic resolution using STM.

2.2.1 Tunneling

In the classical world, particles cannot overcome potential barriers when they have insufficient energy. In quantum mechanics however, particles like electrons tunnel through such barriers. When electron wavefunctions “tail off” at barrier boundaries rather than getting “completely confined”, they overlap with tip-wavefunctions and electrons “tunnel” through the potential barrier. Factors influencing tunnelling probabilities include;

(i) The physical, chemical and electronic structure of the tip and surface
(ii) tip-surface forces, and resulting deformations of samples and tips
(iii) the applied bias voltage
(iv) the tip and sample temperature
(v) and, of course, the tip-sample distance

The relative influence of each factor changes with distance and voltage, but despite this complexity, the tunnelling system can still be rationalized.

With the help of a one-dimensional quantum mechanical simplification, and experimental data taken in controlled, but elucidating conditions, we explain the
Figure 2-1  Idealised and simplified 1-dimensional energy diagram modelling electron tunnelling across a vacuum gap. Here both electrodes are metallic, as indicated by the constant DOS (grey area). When a difference in the two Fermi energies exists, $E_F$, bi-directional tunnelling across the vacuum gap can occur. Tunnelling may be increased using an applied voltage, which increases the potential energy available to one electrodes electrons. These electrons then have sufficient energy to traverse the tunnel gap, if, and only if, there is an empty state to receive them. Even in this simple model, the importance of each electrodes electronic structure, the tip-sample distance, and barrier shape, can clearly be seen to influence the tunnelling probability. Electrons in higher energy states have higher probabilities of tunnelling as indicated by the varying sized arrows.

The tunnelling process in a semi-quantitative manner. To provide this understanding we first consider a simplified model using metal tips and surfaces at RT. In this model, it is assumed that the tip-surface gap is rigid, and an atomically sharp and conical STM tip is used.

### 2.2.2 Single particle approach

Figure 2-1 is a single particle model based on the scattering and transmission of an electron incident on a 1-d model potential. Exactly solving the Schrödinger equation for the classically forbidden region-(ii):

$$|\psi(z)|^2 = |\psi(0)|^2 e^{-2kz}$$  \hspace{1cm} \text{Equation 2-1}
where, $\psi$ is the wavefunction, $k$ is the wavevector and $z$ is the tip-sample distance, we obtain an exponentially decaying function for the wavefunction in the barrier region. Squaring this function, gives the probability of finding the particle in that region of space. **Equation 2-1** thus demonstrates that there is a non-zero probability of finding the particle in the vacuum gap outside the metal. The transmission coefficient $T$, is a ratio of the transmitted current density, $j_t$, to the incident current density, $j_i$, which are both given by:

$$j_i = \frac{\hbar k}{m}$$  \hspace{1cm} \text{Equation 2-3}$$

Thus $T$, is given as:

$$T = \frac{j_t}{j_i} = |D|^2$$  \hspace{1cm} \text{Equation 2-4}$$

where $m$ is the mass of the electron, $\hbar$ is Planck’s constant, and $D$ is the transmission coefficient. Matching their $\psi$’s and first derivatives, $d\psi/dz$ at the discontinuities of the potential, $V(z)$, an overall wavefunction is constructed and an exact solution for $T$ may be derived. In the limit of a strongly attenuating barrier, a transmission probability is then approximated by:

$$T \approx \frac{16\hbar^2 \phi^2}{(k^2 + \phi^2)^2} \cdot \exp^{-\frac{2\phi z}{k^2}}$$  \hspace{1cm} \text{Equation 2-5}$$

where $\phi$ is the height of barrier, and $z$ is the barrier width. Using typical work function values of 4.5 eV and a decay length, $1/k \approx 0.9 \, \text{Å}$, this model correctly predicts tunnel current decay of approximately one order of magnitude per Å of tip-surface movement. This, as is shown later, is extremely close to measured $I$-$z$ curves for Cu.
Scanning probe microscopy

Figure 2-2 (a) Simplified schematic of an STM tip trajectory whilst imaging an adatom on Cu (100) in the constant current imaging mode. This gives the illusion that STM imaging simply produces topographic images of the conducting surface (100). The accuracy of the model is rather striking considering the large list of assumptions made in forming the model. Nevertheless, this model serves as a useful introduction to the tunnelling problem, indicating the exponential dependence of tunnel current with both distance, and the square root of the effective barrier. It provides a useful indication of an STMs z-resolution capabilities, whilst simultaneously suggesting that STM images are simply contours of constant surface height. Such interpretations of STM images are in fact, sufficient for operating STMs. Early models by Garcia [130-132] and Stoll [131, 135-138] were based on such ideas.

Using a corrugated surface as a model tip, with an emphasis on the geometric, rather than the electronic nature of the surface, these models are limited in practise, to free-electron like metals with constant energy surfaces. In particular, these models fail to give a correct physical understanding of the imaging process.

Correctly interpreting STM images requires a more detailed understanding of the tunnelling process, in particular, the localised density of states (LDOS) of the surface, and the applied bias potential. Figure 2-3 shows two STM topographic images simultaneously acquired in constant current mode but at different bias voltages. The images show identical real-space locations, but the images are different nevertheless.
Scanning probe microscopy

Figure 2-3 Two STM images acquired simultaneously by scanning forward and backwards at different bias voltages. The images show exactly the same real-space surface, but we "see" different states (orbital's) by imaging at different bias voltages. (a) 10 nm x 10nm STM topograph of Silicon (111)-7x7 surface taken with a potential bias of 2 V. (b) Equivalent image of same physical area, showing a different electronic structure. Such images highlight the inadequacy of considering STM topographs as simple contours of constant height.

Figure 2-3 (a) and (b) differ through the emergence of bright spots in Figure 2-3 (b). These bright spots are in fact bromine atoms, and though present in Figure 2-3 (a) they are undetected. Such results are inexplicable if STM images are considered simply as constant height topographs as our last model suggested, in Figure 2-1 or Figure 2-2. Figure 2-3 (b) differs from Figure 2-3 (a) for two main reasons: (i) the LDOS of Si (111)-7x7:Br is not linear about $E_F$, and (ii) the applied bias has changed (different energy window). Figure 2-3 (b) potential energy window increases with increasing its bias voltage. This provides its electrons with sufficient momentum $k_F+3eV$, to tunnel into 3 eV anti-bonding states otherwise inaccessible when tunnelling with 2 eV. This result highlights the influence of surface LDOS and the applied bias potential in image formation, suggesting a more comprehensive theory is required. An improved model describing in detail the electronic structure of both electrodes, the tunnel barrier region, and how wavefunctions decay within this region is required to
Figure 2-4 (a) Current voltage (I-V) scanning tunnelling spectroscopy (STS) curve of a Copper (100) surface showing an expected linear behaviour I-V. (b) Schematic illustrating tunnelling from a metal surface. As the voltage is altered, the potential energy window shifts correspondingly, but since the electrodes (both metal) have a linear LDOS around $E_f$, there is simply an increase or decrease in $I_T$.

Figure 2-5 I-V curve taken of a Silicon (111)-7x7 sample indicating the non-linear change in tunnel current as a function of voltage. With semiconductor surface having directional localised bonds, the LDOS is not linear around $E_F$. Also clearly seen is a band gap. By changing the voltage, and hence the energy window, we can tunnel into the HOMO or LUMO states, and furthermore, gain insight into bonding energies. We can thus get spatially resolved spectroscopic information.

develop an understanding of what images actually represent. For this, the Transfer Hamiltonian (T-F) approach is now considered.
2.2.3 Transfer-Hamiltonian

The most widely used theory of STM, that takes into account the electrode’s electronic structure, is the model by Tersoff and Hamann \[^{140, 141}\]. Their theory is based on the transfer Hamiltonian approach introduced by Bardeen in 1961 \[^{142}\].

In the Bardeen approach, the tip-surface interactions are considered sufficiently weak as to be neglected, and eigenstates of the entire tunnel junction are approximated by eigenstates of uncoupled electrodes. The sample and tips are modelled as ideal metals with electron states filled to the Fermi level, \((E_F)\). The electrodes are separated by a distance \(z_0\) having respective workfunctions \(\Phi_s\) and \(\Phi_t\). An applied voltage \(V_T\) causes the Fermi levels to shift by \(eV_T\) with respect to each other, forming a parameter controlled trapezoidal tunnel gap, within which the electron wavefunction decays exponentially:

\[
\psi(z) = \psi(0)e^{-kz},
\]

where,

\[
\kappa = \sqrt{\frac{m_0}{\hbar^2}(\Phi_t + \Phi_s - eV_T)}
\]

Equation 2-6

Equation 2-7

Summing over all states within an energy interval, \(E_F - eV\) at a position \(r\), the concept of local density of states (LDOS) is then introduced:

\[
\rho(r, E) = \sum \left| \psi_s(r_n) \right|^2 \delta(E_F - eV)
\]

Equation 2-8

This approach represents an approximate solution to a more precise model junction, with the tunnel current calculated using first order perturbation theory from an overlap of the \(\psi_t\) and \(\psi_s\) tails in the barrier region:

\[
I_{t-s} = \frac{4\pi e}{\hbar} \int_\infty^\infty \left[ f(E_F - eV + \epsilon) - f(E_F + \epsilon) \right] \rho_s(E_F - eV + \epsilon) \rho_t(E_F + \epsilon) |M|^2 \, d\epsilon
\]

Equation 2-9
Figure 2-6  Schematics of Tersoff and Hamann model. The tip wavefunction is approximated by an s-wave. The tunnel current is proportional to the local density of states of the sample at the Fermi level, LDOS \( (E_F) \), at the distance \( r_0 = R + s \), which corresponds to the centre of curvature of the tip.

where \( \rho_s \) and \( \rho_t \) are the density of states of the sample and the tip respectively. The Fermi distribution \( f(E) \) given by:

\[
f(E) = \frac{1}{1 + e^{(E-E_f)/k_BT}}
\]

Equation 2-10

which determines the occupancy of available states, whilst \( M_{t,s} \), the tunnelling matrix, denotes the coupling between the tip wavefunctions, \( \psi_t \), and the sample \( \psi_s \). Bardeen showed that the tunnelling matrix:

\[
M = \frac{\hbar}{2m} \int_{\text{surface}} (\psi_t^* \frac{\partial \psi_t}{\partial z} - \psi_s \frac{\partial \psi_s^*}{\partial z})
\]

Equation 2-11

could be evaluated by solving the wavefunctions separately and then solved using Equation 2-10. For low voltages, tunnelling current is then simplified to:

\[
I_{t\rightarrow s} = \frac{4\pi e^2}{\hbar} \int_0^{eV} \rho_s(E_F-eV)\rho_t(E_F+e)|M|^2 \, de
\]

Equation 2-12
The delta function in Equation 2-12, implies that electrons lose no energy during the tunnelling process (elastic tunnelling) and since the electrons in states whose energy is closest to $E_F$ experience smaller barrier heights, they have a greater contribution to the overall tunnelling current (decreasing arrow length in Figure 2-1 away from $E_F$).

Shortly after the invention of the STM, Tersoff and Hamman presented their calculation using first order perturbation theory to give an analytical result for the matrix element in a simplified system representing the STM. Assuming a simplified tunnelling tip geometry as shown in Figure 2-6, Tersoff and Hamann, (TH) found an expression for the tunnel current valid in three dimensions using the assumptions that (i) the tip wave function can be approximated by a spherical $s$-wave function, and that (ii) $\rho_s(E_F)$ is the local density of states of the sample LDOS at $E_F$ at a distance $s + R$, where $s$ is the distance between the tip apex and sample surface, and $R$ is the radius of curvature of the tip. In this case, with a constant tip LDOS:

$$I \propto V_T \sum_s \left| \psi_s(\mathbf{r}_t) \right|^2 \delta(E_F - eV)$$

Equation 2-13

The sum represents the LDOS at the sample surface near $E_F$ as evaluated at the centre of the tip $r_t$. This expression crucially shows that for an idealised tip model, STM topography may be interpreted as tracing contours of constant wave-function density evaluated at the centre of an assumed spherical tip. The model therefore achieves what prior theories had lacked, i.e. a precise physical picture of what was actually being measured.

### 2.3 Imaging

In the previous section, it was shown that the tunnel current depends exponentially with tip-sample distance. Thus, scanning the tip over the surface laterally results in a modulation of the tunnel current corresponding to the surface corrugation. However, for such small tip-sample distances, typically less than 1 nm, even a small mechanical instability can cause the tips to crash. Therefore, imaging in the constant height mode is only possible on atomically flat surfaces and on extremely small areas. To overcome this limitation the constant-current imaging mode is typically used. In the
Scanning probe microscopy

Figure 2-7 STM of exactly the same real-space surface, "showing" different states (orbital's). Both the highest occupied molecular orbital's, (HOMO) or valence band, and the lowest occupied molecular orbital's, or LUMO are imaged since we switch the voltage between positive and negative polarities during the forward and backward scans. (a) 10 nm x 10nm STM topograph of Silicon 111 (7x7) surface taken with a potential bias of -2V. (b) Equivalent image of same physical area, imaged at 2V. The change in polarity makes it possible to image both, filled and empty electron states.

constant current imaging mode, tunnel currents are kept constant by altering the tip-sample distance $z_0$ using a $P$-$I$ feedback control system. Currents are initially amplified using a logarithmic amplifier, then using the $P$-$I$ controller, an error signal is calculated. This is the difference between the chosen tunnel current set-point and the measured tunnel current. This difference, or error signal, is multiplied by the proportional gain ($P$-part) and integrated ($I$-part) with a characteristic time constant. The $P$ and $I$ parts are then added together and outputted from the feedback circuit. This output is amplified, and then fed directly to the z-piezos to alter their height. In this manner, recorded changes in $z$ as a function of $(x,y)$ give a direct image of the sample surfaces density of states at $E_F$. Figure 2-7 shows two such images simultaneously acquired at equal voltages, but at different polarities. Figure 2-7 (a) and (b), differ because altering the polarity allows one to tunnel into, or from, surface states. Hence, it is possible to image the filled (HOMO), or empty (LUMO) electronic states, of surface atoms and molecules with atomic resolution.
The geometrical shape of the tip limits the lateral resolution capability during STM imaging. If the typical tip is envisaged as a cone with an opening angle and a finite radius at the apex, images of steps for example are smeared out if the walls are steeper than the opening angle. This causes a convolution of the tip shape and surface structure in STM images. Holes in a surface for example, may not be seen if their radius is smaller than the tip radius. At the atomic level, resolution is usually determined by the atomic structure of the tip apex. This is a major and inherent problem still afflicting STM and AFM image interpretation.

Estimates of vertical resolution in STM have been put forward by Stoll and Laloyaux. The Stoll formula derives an equation for the corrugation height $\Delta z$ on simple metals, depending on the atomic periodicity $a$:

$$\Delta z = h_s \exp \left[ \frac{-\sqrt{2m(U-E)}(R+s)}{\kappa a^2} \right]$$

Equation 2-14

where $\kappa = \sqrt{2m(U-E)/\hbar}$ is the decay constant of the tunnelling current, typically $1\text{Å}^{-1}$, $h_s$ is the corrugation height of the metal surface, $d$ is the distance between the sample surface and the apex of the tip and $R$ is the radius of curvature of the tip.

### 2.4 Scanning tunnelling spectroscopy (STS)

A fascinating application of STM is its capability to obtain spectroscopic data at specific atomic sites. It has just been shown that the tunnelling current is dependent on two material properties, (a) the localised density of states, LDOS, and (b) the tip and surface work functions, $\Phi$. By performing current-voltage, $I-V$, or current-distance, $I-Z$, spectroscopy, it is also possible to measure these material properties in real space. Furthermore, until now, our simplified models have only accounted for elastic tunnelling. However using $I-V$ spectroscopy, inelastic processes may also be identified.
Figure 2-8 (a) Current imaging tunneling spectroscopy CITS data acquired by taking an I-V curve at every pixel. The feedback circuit is switched off for the duration of the I-V acquisition, after which, it is switched back on. The tip then moves to the next pixel and repeats. Images may be displayed as energy filtered images or site-specific I-V curves. Typically, each data-set takes over 40 minutes to acquire, so at room temperature it is extremely challenging to achieve high spectral resolution without drift. This limitation may be overcome using voltage modulation and lock-in detection.
2.4.1 I-V spectroscopy: LDOS

**Figure 2-3 and Figure 2-7** showed glimpses of STMs ability to energy-filter states of interest seen in STM, by an arbitrary choice of applied bias voltages. This reveals the asymmetric nature of the LDOS around $E_F$. If we assume the tunnel current matrix element changes very little when small voltages are used, and that the tunnel current is given by:

$$I_{t\rightarrow s} = \frac{4\pi e}{h} \int [f(E_F - eV + \varepsilon) - f(E_F + \varepsilon)]\rho_s(E_F - eV + \varepsilon)\rho_t(E_F + \varepsilon)|M|^2 \, d\varepsilon \quad \text{Equation 2-15}$$

From this, the first derivative of the tunnel current with respect to an applied voltage can be also calculated. Assuming the tip LDOS is constant, the derivative of the tunnel current is given by:

$$\frac{\partial I_t}{\partial V} \bigg|_{V_t} \propto \rho_t \int \rho_s(\varepsilon)\delta(\varepsilon - eV_t) \, d\varepsilon = \rho_t \rho_s(eV_t) \quad \text{Equation 2-16}$$

This derivative, $\frac{\partial I_t}{\partial V}$, provides in 2-D an experimentally obtainable quantity that is proportional to the LDOS in the sample at an energy $eV_t$.

Experimentally this is achieved by placing tips over the point of interest on the sample surface, with $V_t$ and $I_t$ controlling the tip-sample distance, $z$. The feedback loop is switched off and the voltage is ramped between two predefined values of interest. The values are then plotted with respect to each other to produce a LDOS spectrum. However, noise, drift, mechanical instabilities, and temperature related state broadening make it very difficult to obtain quantitative data room temperature. Despite this, energy filtered images may still be obtained at RT, from which chemically originating data can be derived. **Figure 2-8** is current image tunnel spectroscopy, CITS map of the Silicon 7x7:Br. The side images are energy filtered scans of the same regions in real space. Clearly the images are different. The resolution of these images and corresponding normalised conductance graphs are
relatively poor, because of drift and acquisition time problems. Nevertheless, proof of principle is clearly shown, that atomically resolved spectroscopic curves can be obtained. Resolution of the spectroscopic curves is typically improved by performing single point spectroscopy, going to milli-Kelvin temperatures, and by applying small oscillations to the tip.

2.4.2 I-z spectroscopy: barrier height imaging

Barrier height imaging is possible in exactly the same manner as outlined above. By taking the log of the variation in tunnelling current $dl$ over a distance $dz$, a measure for the local barrier height is obtained. For a 1-d barrier of height $\Phi$ the barrier height is usually expressed as:

$$\phi(eV) = \frac{h^2}{2m} \left( \frac{\partial \ln I_{\text{t}}}{\partial z} \right)^2$$

Equation 2-17

By modulating the tip height $(z)$ at a frequency beyond the cut-off frequency of the feedback loop, the variation of the tunnel current with $z$ can be recorded during STM imaging. This can provide local site-potential data.

2.5 Summary

Though beauty of STM lies in its ability to directly observe the atomic structure of the sample, however, one has to aware that the physics of image formation is far more complex than outlined above. After 25 years it still remains inaccessible in all its details. To neglect the tips LDOS, the Tersoff and Hamann model assumes an idealised spherical tip but an $s$-wave electronic tip structure is unlikely in reality.

This issue was addressed by Chen \cite{145}, who included higher angular momentum components of the tip electron wavefunctions, finding $d^z$ type orbital's enhanced resolution \cite{146}. Results from this study are often used to understand "anomalous" resolutions. On the other hand, Tersoff \cite{147} also addressed this problem and found that under various conditions, the correspondence between STM images and surface LDOS was in fact quite general. The LDOS interpretation was also independently verified by Lang et al. \cite{148} in an extension of the transfer Hamiltonian method, using
jellium electrodes and an adsorbed atom to represent the tip. It should however be remembered, that the T-H model only holds for low voltage imaging and the tunnelling barrier, heretofore assumed constant, may be altered by image potentials [149] and tip-surface interaction forces [150, 151]. A major assumption of the standard T-H model is that the STM junction is static. This is not a realistic assumption as shown in Figure 2-9 is a cartoon illustrating tip surface relaxations [152-160].

![Diagram](image)

**Figure 2-9** (a) STM topographic image of Cu (100) (b) A more realistic illustration which includes tip and surface relaxations. Since atomic sites do not relax equally, tip/surface relaxations are widely expected to enhance tunnel currents at specific sites, giving higher than expected “contrast”. (c) Line profile indicating topographic corrugation that is inconsistent with Stoll’s formula, and can only be explained by invoking tip-surface interactions and/or tip-sample deformations.

which is some cases completely dominates STM imaging [152]. This presents considerable problems for quantitative analysis of topographic data, or for precisely modelling tip-surface tunnelling. In failing to account for any tip-surface interactions [152]

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and/or any resulting tip surface relaxation effects which occur \([161-164]\), the model is severely compromised for more compliant surfaces, or in high tunnel current conditions. Such high tip surface interactions can have a massive impact on STM image contrast, and are potentially useful for atomic manipulation. It is thus clear, that a detailed understanding and measurement of tip-surface forces is required for a realistic assessment of processes occurring during imaging, and manipulation.

2.6 Forces and their measurement using nc-AFM

As early as 1986, Pethica \([105]\) proposed that interatomic forces were present and responsible for some anomalous STM results. Atomic manipulation \([19]\), anomalous corrugation amplitudes \([196]\), and the simple fact that tunneling involves the overlap of wavefunction tail ends, strongly suggests that forces are present and critical during tunneling microscopy. Though forces exist whenever a potential gradient exists, atomic resolution nc-AFM is believed to primarily occur as a result of short-range chemical forces \([167]\). As such, the atomic resolution imaging process in both STM and nc-AFM must be considered a similar sequence of making and breaking of chemical bonds, with the tip-surface interactions occurring during nc-AFM, STM and atomic manipulation inherently related \([169]\).

For a comprehensive introduction to the various force types and formalisms of interest to STM, nc-AFM, and this body of work; the reader is directed to the excellent book by Israelachvili \([169]\). For a review of nc-AFM, the reader should consider the independent reviews by either Giessibl \([170]\) or Garcia \([171]\), which are both impressive because of their depth, but also for their clarity and scope.

In nc-AFM, the tunneling tip is replaced by a force sensor and the potential energy between the tip and sample \(V_{ts}\) causes a z-component of the tip-sample force:

\[
F_{ts} = -\frac{\partial V_{ts}}{\partial z}
\]

Equation 2-18

Depending on the mode of operation, the AFM uses \(F_{ts}\), or some entity derived from \(F_{ts}\), as the imaging signal. Tunneling, as shown in section 2.2.1, has a very short range and extreme distance-dependence. This is the primary reason for its awesome
resolution capabilities and relative simplicity. $F_{ls}$ on the other hand, has both long and short-range contributions classified by their respective ranges and strengths and typically requires deconvolution techniques to separate individual force contributions. In vacuum, the forces of interest to us include the short-range chemical forces (fractions of nm); the Van der Waals forces, and the electrostatic forces, with a range of up to 100 nm.

**2.6.1 The Van der Waal’s interaction**

The Van der Waal’s interaction is a long range force caused by fluctuations in the electric dipole moment of atoms and their mutual polarization resulting from thermal and/or zero-point quantum fluctuations. The Van der Waals force between atoms and/or molecules is the sum of three different forces, that are all proportional to $1/d^6$ (where $d$ is the distance between the atoms or molecules). These are: (a) the orientation or Keesom force, (b) the induction or Debye force, and (c) the dispersion or London force. The Van der Waals force has different values in different directions, i.e. it is anisotropic. It is non-additive and it is effected by retardation effects.

If however, we assume additivity and integrate over a volume with a fixed number density of atoms, the Van der Waals interaction between macroscopic bodies can be calculated using a Hamaker approach. This approach fails to account for retardation effects and is therefore only appropriate for distances up to several hundred angstroms. For a spherical tip with radius $R$ next to a flat surface the Van der Waals potential is given by:

$$V_{vdwaals} = -\frac{A_H R}{6d}$$

Equation 2-19

where $A_H$ is the Hamaker constant which includes physico-chemical information:

$$A_H = \pi^2 C \rho_1 \rho_2$$

Equation 2-20
in which $C$, is the constant in the atom-atom pair potential, and $\rho_1$ and $\rho_2$ are the densities. The Van der Waals force for spherical tips is thus proportional to $1/d^2$, while for pyramidal and conical tips, a $1/d$ force law holds. For most interactions across a vacuum, $A_H$ is of the order of 1 eV so the Van der Waal’s interaction can approach $\approx -30$ eV for a typical etched metal tip with a radius of 100 nm at 0.5 nm from the surface. Since the corresponding force approaches -10 nN under these conditions, the Van der Waals force is a major disturbance when attempting to follow an atomic contour of short-range chemical bonds during nc-AFM.

2.6.2 The electrostatic interaction

When a tip and sample are both conductive, and have a potential difference such that $V \neq 0$, electrostatic forces are present. If the distance between a flat surface and a spherical tip is small, compared to the tip radius $R$, then the electrostatic force is approximately given by:

$$F_{\text{electrostatic}}(z) = -\frac{\pi\varepsilon_0 R^2}{d}$$

Equation 2-21

For an STM/AFM tip with dimensions equal to those already mentioned, and with a 1 V applied bias, these electrostatic interactions can induce a relatively large force of approximately -5.5 nN.

2.6.3 The chemical forces

The chemical bond is reviewed in many textbooks on quantum mechanics, each giving insight into its character. The Morse potential for example, given by Israelachvili as:

$$V_{\text{morse}} = -E_{\text{bond}} \left(2 e^{-\kappa(z-d)} - e^{-2\kappa(z-d)}\right)$$

Equation 2-22

describes a chemical bond with bonding energy $E_{\text{bond}}$, equilibrium distance $d$, and a decay length $k$. With a proper choice of $E_{\text{bond}}$, $d$, and $k$, the Morse potential is an
excellent fit for the exact solution of the $H_2^+$ problem. The Lennard-Jones potential also given by Israelachvili as:

$$V_{\text{Lennard-Jones}} = -E_{\text{bond}} \left( 2 \frac{z^6}{\sigma^6} - \frac{z^{12}}{\sigma^{12}} \right)$$

Equation 2-23

has an attractive term $\approx r^{-6}$ originating from the van der Waals interaction and a repulsive term $r^{-12}$ occurring as a result of Pauli repulsion. While the Morse potential can be used for a qualitative description of chemical forces, it lacks an important property of chemical bonds: anisotropy. Chemical bonds, especially covalent bonds, show an inherent angular dependence of the bonding strength so more complex models such as the Stillinger-Weber potential may be more appropriate for detailed and quantitative calculations and interpretations of AFM results.

2.7 Sensing the force

The central element of a force microscope consists of a flexible cantilever (typically silicon) which has a sharp tip on one end. The exact preparation methods and techniques for calibrating the lever’s force sensitivity are outlined in section 3.6.1. The precise detection of the physical or dynamic changes the cantilever experience in response to a force, is outlined in section 3.6. For a review of the material used and development of cantilever material type, stiffness values, production method, and physical dimensions, the reader is referred to a review by Giessibl.

In contrast to STM, samples in AFM set-ups are typically mounted on a piezoelectric tube (PZT) which positions the sample in the $x$, $y$ and $z$ directions. As the sample approaches the sharp tip, interactions between this tip and sample result in: (a) a deflection of the cantilever, or (b) a change in the oscillator’s dynamic properties (If dynamic AFM is performed).

2.7.1 Static AFM

Treating the cantilever as a linear spring the force can be related to the deflection by Hooke’s Law:
For sensing normal tip-sample forces, the force sensor should be rigid in two axes and relatively soft in the third axis. The properties of interest are the stiffness \( k \), the eigenfrequency \( f_0 \), the quality factor \( Q \), the variation of the eigenfrequency with temperature \( f_0 / T \), and of course the chemical and structural composition of the tip. Restrictions on useful \( k \) values apply because the deflection of the cantilever should be significantly larger than the deformation of the tip and sample.

Since typical interatomic force constants in solids range from 10 Nm\(^{-1}\) to 100 Nm\(^{-1}\) this implies working values of \( k < 10 \) Nm\(^{-1}\). The eigenfrequency \( f_0 \) needs to be significantly higher than the desired bandwidth. i.e. if ten lines per second are recorded during the imaging a width of say 100 atoms, \( f_0 \) should be at least 10 x 2 x 100 s\(^{-1}\) = 2 kHz to prevent excitation of the cantilever. The physical interpretation of data as a map of \( z(x,y, F_{ts}=constant} \), is simple, but the key experimental hurdle associated with achieving atomic resolution in static mode AFM, i.e. the difficulty in cancelling the long range attractive forces is only occasionally overcome in special conditions.

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. In order to prevent jump-to-contact, the most obvious solution is to use much stiffer levers, which would result in a loss of sensitivity. However, it turned out later that \( k \) values exceeding hundreds of N/m could also help to reduce noise and increase stability \([130]\). In order to overcome this obstacle, application of dynamic AFM techniques was required.

### 2.8 Dynamic atomic force microscopy

In the dynamic mode of operation, the cantilever is deliberately oscillated. There are two basic methods of dynamic AFM: (i) amplitude-modulation (AM) and (ii) frequency modulation (FM). For a review of the FM mode, the author is referred to many excellent books and reviews covering these techniques in detail. We now look at the low amplitude AM mode of nc-AFM used to perform experiments in this body of work.
In AM-AFM, an actuator is driven with a fixed amplitude $A_{\text{drive}}$ at a fixed frequency $f_{\text{drive}}$, where $f_{\text{drive}}$ is close to but different from $f_0$. When the tip approaches the sample, elastic and inelastic interactions cause a change in both the amplitude and phase (relative to the driving signal) of the cantilever. These changes may be used as the feedback signal. The change in amplitude in AM mode does not occur instantaneously with a change in tip-sample interaction, but on a time scale of $\tau_{\text{am}} \approx \frac{2Q}{f_0}$. With Q factors reaching 100 000 in vacuum, this AFM mode is thus very slow.

### 2.8.1 Off-resonance low amplitude nc-AFM

The problem of long-range forces was identified early by Pethica, who searched for a way to minimize them. In DFM, the contribution of various force components $F_i$ with a corresponding range $\lambda_i$ to the imaging signal is a function of the cantilever oscillation amplitude $A$. For $A > \lambda_i$, the imaging signal is proportional to $\sum F_i \sqrt{\lambda_i}$, while for $A < \lambda_i$. Thus for small amplitudes, the imaging signal is proportional to the force gradient and the weight of the short range forces is much larger than the weight of the long range forces. This has been used in our off-resonance technique originally developed by Hoffman, Oral, Grimble, Özer, Jeffrey and Pethica. In this technique, a tungsten lever ($k \approx 300$ N/m) is oscillated at a frequency far below its resonance frequency with an amplitude $A_0$ of the order of $0.5$ Å. When the cantilever comes close to the sample, the oscillation amplitude changes according to:

$$A = \frac{A_0}{1 + k_{ts} / k}$$

Equation 2-25

Where $k_{ts}$ is the tip-sample stiffness. Two other AFM challenges, namely the instability and the $1/f$ noise problem, are also solved with this technique due to the stiff lever and the dynamic mode. Lock-in detection is used to measure the amplitude which improves signal to noise ratio.
3 INSTRUMENTATION

3.1 Introduction

The basic physical principle underlying any SPM method is the interaction between the scanning probe and a sample surface. In Chapter 1, two important physical interactions were introduced; quantum tunnelling and tip-surface forces and their use for atomic manipulation was discussed. In Chapter 2, some elementary theory was presented, outlining the approximate magnitudes of each interaction type as a function of distance. Experimentally, the variation of each measurand; i.e. force $F_z(x,y)$ or tunnel current $I_t(x,y)$, has to be larger than the systems noise for successful detection. From theory, the tunnel current was found to decay exponentially; atomic forces exhibited various dependencies with distance, and a noise varies little from one atomic site to another. Despite this, atomic resolution is still difficult to achieve in practise, since extremely small surface corrugations (sub-angstrom) induce only small $\Delta F_z$, or $\Delta I_t$ variations (typically < 0.005 nA for $I_t$, and < x nNm$^{-1}$ for $\Delta F_z$). Thus, achieving atomic resolution then requires that:

- the tip is sharp enough that a foremost atom predominantly interacts with, and hence distinguishes between surface atoms
- the tip can be laterally and vertically scanned with sub-atomic precision
- there is sufficient vibration isolation
- any potential signal is successfully retrieved and treated
- finally, that the sample is atomically clean

In this chapter, I thus outline the experimental and instrumental requirements for the precise measurement, isolation, and amplification of each signal, and explain how the system set-up minimises potential sources of noise (e.g. vibration isolation). Also discussed, is the successful preparation of homemade sharp tungsten tips and
Instrumentation
cantilevers, the feedback control systems, and the different experimental set-ups employed for atomic manipulation and atomic force quantification.

Since an overarching goal of this body of work is to perform room temperature manipulations requiring strongly bound species, the production of highly electronegative halogens using a homebuilt electrochemical dosing cell is discussed in this chapter.

Finally, achieving atomic resolution requires an atomically clean surface, hence, the ultra high vacuum chamber, equipment, and procedures for producing and maintaining clean surfaces are also introduced.

3.2 Variable-temperature ultra high vacuum STM

The variable-temperature scanning tunnelling microscope (VT-STM) (Omicron-GmbH) used to perform our experiments is a commercially available and unmodified, ultra high vacuum (UHV) chamber. **Figure 3-1** is an illustration of the stainless steel system, comprising two main chambers, one for sample preparation, with the second housing the microscope. The system has a base pressure of $2 \times 10^{-11}$ mbar that can be achieved using a combination of four pumping techniques and a bakeout for 36 hours.

The preparation chamber is used to clean, modify and analyse samples, and contains all instruments used for sample preparation and treatment. Sample preparation facilities include an Ar$^+$ ion sputtering gun, precision leak valves for the introduction of high purity gases, a variety of sample heating facilities, the sample manipulator, a low-energy electron diffraction (LEED) setup, a mass spectrometer, and several halogen-dosing cells. There is an evaporator, and all of the system’s pumps are connected to this chamber. This chamber is connected to the load lock and hosts a rotating carousel used for tip and sample storage.

The second chamber houses the microscope, **Figure 3-2**. The microscope head consists of a sample stage, scanning tip, heating and cooling facilities, all of which are suspended on an eddy current damping system, necessary to provide sufficient vibration isolation for achieving atomic resolution. Atomic resolution however, requires extremely clean samples, which is achieved by maintaining an ultra clean, ultra high vacuum environment.
Figure 3-1 Schematic of the Omicron variable-temperature, ultra high vacuum, scanning tunnelling microscope (VT-UHV-STM) system used for low temperature (circa 30-70 K), room temperature (300 K) and high temperature (300-500 K) STM manipulation experiments. The chamber is connected to a roughing and turbo molecular pump, which pre-pumps the chamber to pressures in the $10^{-4}$ mbar and $10^{-3}$ mbar regimes, respectively. An ion getter pump is then utilised to reduce the pressure further. When the rate of outgassing and pumping speeds are equal, i.e. there is no improvement in the pressure anymore, the entire chamber is baked to $\approx 200^\circ$ C for about 48 hours, which reduces the water vapour contained within the chambers walls, and hence reduces outgassing. This reduction in outgassing, means the same pumps can now achieve ultra high vacuum (circa $10^{-10} - 10^{-11}$ mbar) pressures. The main chambers (Preparation and Microscope), and the load lock area and gas lines, may be independently pumped, permitting the input of gasses, tips and samples, without breaking vacuum. The system has two main chambers, the preparation and microscope chamber. Samples are sputtered, annealed, dosed, and analysed using LEED, in the preparation chamber. STM is performed in the microscope chamber.
Figure 3-2 Photograph of the microscope stage which sits inside the microscope chamber. This chamber is isolated from the “outside world” via two different damping systems. The first is the spring suspension system (i), and the second is the eddy current magnetic damping system (ii). Once the microscope stage is decoupled from the noise and vibrations of the outside world, the tip is transported close to the surface using piezo motors (not shown). Once atomically close, the piezo tube scanner (iii), raster scans the tip with sub-atomic precision. The sample is held inside a sample holder (not shown) upside down, and inside the sample stage (iv). If the sample needs to be cooled to perform low temperature scanning, the cooling block is lowered and locked in place (v). It is connected with copper braids to a liquid Helium or Nitrogen flow cryostat.

3.2.1 Ultra high vacuum (UHV)

Ultra high vacuum is achieved using a combination of (i) a roughing pump, (ii) a turbo molecular pump (TMP), (iii) an ion getter pump (IP), and lastly (iv) a titanium sublimation pump (TSP). Each pump optimally operates at different pressure ranges, using a range of techniques to pump different species with varying degrees of efficiency.

The chamber and load lock are initially pumped by a 210 \( \text{l s}^{-1} \) turbo-molecular pump, connected in series to a mechanical, rotary, two stage, oil sealed, sliding vane pump. This rotary pump, or roughing pump, is a positive displacement pump allowing
gases to flow into a cavity, before rotating and being expelled in a continuous manner. The pump is the most effective at high pressures, with a high backstream flow through its mechanical seals limiting its usefulness at higher vacuums. Consequently, it is the first pump used, producing a rough vacuum of approximately $5 \times 10^{-4}$ mbar, after which the TMP is switched on.

The TMP is a high speed, multiple rotor pump which imparts momentum to atoms and molecules effectively “kicking them out” of the chamber. The turbo reduces chamber pressure to approximately $1 \times 10^{-8}$ mbar, but is less robust than the roughing pump, handling pressure surges, or low vacuum with great difficulty. These two pumps can be disconnected from the chamber or the load lock, if desired, using a pneumatic gate valve or a manual gate valve respectively. This feature facilitates the safe transfer of tips and samples to and from the main chamber via the load lock, without breaking overall vacuum.

Upon reaching pressures in the low $10^{-8}$ mbar region, improving vacuum any further is severely inhibited by outgassing. Outgassing is the release of adsorbed gases and vapour, principally water vapour, from solid surfaces inside the chamber, and if the chamber outgases at a rate greater than the pumping rate, one needs to bake the UHV chamber. Baking temporarily increases this outgassing by increasing the chamber temperature. After baking, the outgassing rate falls far below the pumping rate, so once again, improvements in pressure are made. Despite this, ultra high vacuum would not be achieved without the use of ion getter and TSP pumps.

The ion pump is an entrapment pump, using strong electromagnetic fields to ionise and propel gases into a titanium cathode. The pump optimally operates after a bakeout, reducing system pressure to the low $10^{-10}$ mbar region. It cannot efficiently pump inert gasses such as argon.

The last pump we use to produce UHV is the TSP. A large current ($\approx 50$ A) is passed through a titanium coated tungsten filament, heating it, and subliming the coating of reactive titanium onto the chamber walls. The reactive species then traps gaseous molecules as they collide with the chamber walls, immobilising them, and thus reducing the chamber pressure. The effectiveness of this pump is reduced with time as the surface layer is fully reacted, so TSP’s are used at regular intervals of approximately four hours. It also inhibits outgassing from the chamber walls.
Figure 3-3 Electrochemically etched tungsten tips observed using an electron microscope. The tips are prepared by electrochemical etching at the meniscus metal interface. This leads to a directed thinning of the metal just above the liquid etchant level. The metal piece below the liquid etchant surface, then stretches the wire, thinning it, until it breaks. With careful control, this procedure leads to atomically sharp STM tips.

With careful handling of all UHV components, chamber pressures of $2 \times 10^{-11}$ mbar may be achieved following successful bake-outs and continuous pumping.

### 3.2.2 Samples and Tips

Once ultra high vacuum has been achieved, atomically clean samples such as silicon (111)-7x7 and copper (100) may then be successfully prepared in the preparation chamber using specific recipes for each surface or reconstruction, see Chapter 4. These are likely to include some form of heating and Argon ion sputtering.

STM tips are prepared using 0.38 mm diameter, 99.9% pure polycrystalline tungsten wire. Sections of wire ~ 5-8 mm long are cleaned by sonicating in HPLC grade acetone, isopropanol, and de-ionised water before being mounted on an Omicron UHV gold tripod tip holder. Using an Omicron W-Tek tip-etching tool, wires are electrochemically etched in a 5M aqueous solution of NaOH using the direct current drop-off method. Typical etching parameters are listed in Table 3-1.

Once lowered ~2 mm into the etching solution, tungsten begins to oxidise into a soluble WO$_2$ from which flows away from a meniscus at the air/electrolyte interface. This process of wire thinning ultimately leads to the weight of the lower piece stretching the wire into an extremely thin section, which eventually breaks to form an
Instrumentation

<table>
<thead>
<tr>
<th>Wire</th>
<th>Ø 38µm tungsten wire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching solution</td>
<td>5 Mol/l NaOH</td>
</tr>
<tr>
<td>Etching voltage</td>
<td>~ 6.5-6.9 V</td>
</tr>
<tr>
<td>Insertion depth</td>
<td>~ 1-1.5 mm</td>
</tr>
<tr>
<td>Threshold current</td>
<td>~ 3.0-4.5 mA</td>
</tr>
<tr>
<td>Initial current</td>
<td>~ 45-50 mA</td>
</tr>
<tr>
<td>Typical etch time</td>
<td>5-7 mins</td>
</tr>
</tbody>
</table>

Table 3-1 Typical STM tip etching parameters used in our experiments for preparing atomically sharp tungsten tips.

ultra sharp point. Following electrochemical etching, tips are re-cleaned by rinsing with de-ionised water and acetone to remove any electrolyte residues. Tip sharpness is then assessed using an Olympus microscope with up to 100 times magnification. If the tips are suitably sharp, they are transferred into UHV via a fast entry load-lock chamber.

Once in-situ, further tip preparation is often performed using a range of ad-hoc techniques. Tips may be sputtered using Argon ion gas or sharpened using field evaporation. Neither of these techniques are routinely used in our lab, though large voltage pulses are used to stimulate drastic tip changes, with soft indentations used for more subtle alterations.

Having prepared atomically clean surfaces and atomically sharp tips, we now address two key experimental challenges inhibiting STM operation; (i) the physical challenge of moving a tip with sub-angstrom precision, when the amplitudes of noise vibrations of most laboratories, equipment and hence tip holders is larger, and (ii), the electronics challenge of how Pico-ampere tunneling currents are retrieved and measured considering typical electrical noise ($I_{\text{rms}}$) values exceed $I_T$ magnitudes.

### 3.3 The physical challenge: Scanning

In typical SPM set-ups, probes are scanned in three dimensions using piezoelectric actuators to obtain topographic data. The experimental challenge is to approach a
Figure 3-4 Schematic illustrating the basic set-up of an STM. The tunnel current is used to control the tip-sample distance $z$ via a feedback circuit. The distance $z$ is recorded by a computer as a function of scanned coordinate $x$ and $y$. A high voltage amplifier is required to drive the piezoelectric scanner. Good vibration isolation of the microscope is a necessity for high-resolution imaging.

surface from millimetre distances, scan with sub-angstrom precision, whilst remaining decoupled from the outside world's potentially fatal (for the tip) vibrations. A control
unit guides the interacting probe to maintain a constant preset value, e.g. \( l_r, z, F, \Delta f \). The probes z-movements are then recorded as a function of the (x-y) location, and in this manner, a topographic image is created. With probe-surface distance often, only a fraction of an angstrom, high mechanical stability is an absolute requirement. This necessitates a rigid construction with multiple vibration isolation techniques. Figure 3-4 introduces the important elements of a scanning probe microscope.

3.3.1 Precise positioning of tips

Precise positioning in z over two orders of magnitude requires two independent positioning solutions. Large microscopic probe approaches are performed using stick-slip shear piezo-motors. An application of a high voltage (HV) sawtooth potential causes the piezos to shear, inducing several Newtons of force, easily sufficient to move the stage. The withdrawal of the probe is fast and so the Piezo may slip, leaving the stage in its new position, and thus moved. This mechanism is widely used for both microscopic z and x-y positioning, see Figure 3-5 (a).

The probes also need to be positioned with an accuracy of 1 pm if atomic resolution is required. In our set-up as is usual, this feat is performed using a highly sensitive piezoelectric tube set-up. Piezoelectric materials change their shape in response to an applied voltage, and a typical extension value for (PZT-5H) is 0.262nm/V [143]. In this set-up, vertical movement of the tube is achieved through the elongation of a tube of piezoelectric material, whilst bending of the tube results in horizontal displacements, Figure 3-5 (b).

3.3.2 Vibration Isolation

Vibration isolation in probe microscopy is an essential prerequisite to avoid tip crash and poor resolution due to vibrations. This is essentially a two-pronged approach. The first tenet is the construction of an extremely rigid and robust design, which ensures that the vibrational eigenfrequency of the instrument is high, and that there is a common mode rejection of vibration frequencies in the tip-sample gap. This means any movement, i.e. collective movement, does not affect the tip-sample gap, since they move in unison, and hence effectively do not contribute to noise. The second tenet involves frequency filters.
Figure 3-5 The two components responsible for transporting the tip over micron ranges with pico-meter precision. (a) Coarse approach piezo motors. Upon application of a high voltage (circa ± 200 V), the tip may be transported in (x,y) over micron distance ranges. The same stick-slip mechanism used is also responsible for the tip coarse z approach, though additional precautions now need to be taken to ensure linearity and consistency with both motion against and with gravity. (b) The piezo tube scanner is used during imaging to move the tip with sub-atomic precision. The piezo electric material extends upon application of a suitable voltage. However, caution needs to be exercised, since this is non-linear, and temperature dependent.

![Figure 3-5](image1)

Figure 3-6 Typical power spectrum of vibrational noise for a typical STM tip-sample gap. This data was acquired at RT by focussing the optical fibre interferometer normally used for AFM cantilever deflections, onto a dummy sample. The power spectrum then corresponds to the analysis of this interference pattern in a frequency spectrum analyser. Integrating over 2.5 kHz, gave 70 pm rms.

![Figure 3-6](image2)
The first frequency filter used in our system was a spring-suspension system. Since the spring-suspension system only dampens vibrations over a selected frequency range, i.e. it has a transfer function describing the frequency-dependent response of the system to external noise. A second vibration isolation set-up is used in conjunction with the springs. The combined frequency filters, have resonance frequencies well below building and acoustical frequencies and are strongly damped. For STM the most important frequency range that needs to be filtered is the 0.5 Hz - 1 kHz range. One experimental method employable to measure the amplitude of vibrations, is to use an optical beam, or interferometer normally employed for an AFM, and direct it onto a sample. A power spectrum of vibrational noise for a typical tip-sample gap is shown in Figure 3-6.

3.4 The electronics challenge: Signal recovery

Overcoming the physical challenges associated with atomic resolution probe microscopy, i.e. securing the ability to scan a sharp metal tip fractions of an angstrom distance from a sample surface, whilst simultaneously ensuring mechanical noise vibration amplitudes are in the femtometer range, are the first key experimental milestones.

With this achieved, the second key challenge is to record the tunnel current as function of tip position \((x,y)\). Tunnel current magnitudes in typical STM experiments are in the picoamperes range. Electrical noise sources of relevance include Johnson noise and ground loop noise (50 Hz noise), and noise from stray electromagnetic fields. In this section, we examine the steps taken to reduce the electronic noise, the amplification of the tunnel current signal, and how this is used to regulate the tip height, and hence image the samples surface.

3.4.1 Processing the tunnel current signal

The extremely small tunnel currents occurring in STM, typically 0.01 to 50 nA, require amplification, and conversion to a voltage. The tunnel current is typically measured with a current-to-voltage (I-V) converter with a simple form shown in Figure 3-7. It consists of an operational amplifier (op-amp) with low noise, low input current and a
Figure 3-7 A simple current-voltage converter for an STM. It consists of an operational amplifier (op-amp) with high speed, low noise, and low input bias current, as well as a feedback resistor (typical impedance $R = 10^6 \, \Omega$) that has low parasitic capacitance $C_R$. With careful design $C_R$ should be less than 0.5 pF. There is also an inevitable parasitic input capacitance $C_{in}$. The parasitic capacitance, the thermal noise of the feedback resistor, and the characteristics of the op-amp are the limiting factors of the $I$-$V$ converter.

feedback resistor with a typical impedance of $R = 100 \, \text{M}\Omega$. Small parasitic capacitances are inevitable, $C_R$ and $C_{in}$. To a very good approximation, the output voltage should provide a feedback current through the feedback resistance $R$, to compensate for the input current such that the net current entering inverting input of the op-amp is zero. The non-inverting input is grounded, and the voltage at the inverting input should be equal to ground. This implies that:

$$V_{out} = -R I_{T(in)}$$

Equation 3-1

where $V_{out}$ is the output (recorded) voltage, $R$ is the feedback resistor $^{[175]}$.

Since tunnel current change exponentially with tip-sample distance, a logarithmic amplifier is typically used to linearise the $I_T$ signal $^{[143]}$. For a 100 M\Omega resistor, a 1 nA input tunnel current results in an output voltage of 100 mV. With careful design, $C_R$ should be less than 0.5 pF. There is also an inevitable parasitic input capacitance $C_{in}$. The parasitic capacitance, the thermal noise of the feedback resistor, and the
characteristics of the op-amp are the limiting factors of the \( I-V \) converter \[175\]. To reduce noise the amplifiers are typically, kept close to the tunneling tip, and hence inside the UHV chamber.

For more challenging environments, such as recording very small inelastic tunnel currents, lock-in amplifiers may also be employed. Here, a small dither voltage sits on top of the normal voltage, at a specific frequency, which is then recovered using lock-in-detection.

### 3.4.2 Electrical noise

The noise in the imaging (the tunnel current in STM, force in AFM), needs to be small enough that the corresponding vertical noise is considerably smaller than the atomic corrugation of the sample. Having already satisfied ourselves in section 3.3.2, that mechanical noise may be sufficiently suppressed using the combination of a spring suspension system, eddy current damping, and a rigid, (common-mode rejecting) construction, we now consider electrical noise in STM.

The electrical noise that typically causes problems in STM is Johnson noise, Shot noise, ground loop noise or 50 Hz noise, noise from the mains lines, stray electromagnetic radiation, and cross talk between instruments and data channels. This electrical noise translates to an inherent vertical noise in an STM.

Johnson noise, or thermal noise, is a thermally generated noise source inside all conducting circuits which occurs regardless of the voltage applied. It is a white noise, meaning the power spectral density is nearly equal across the frequency spectrum, and the amplitude of the signal correspondingly has a nearly Gaussian distribution. For a given bandwidth, set by the STM electronics, the root mean square (RMS) voltage,

\[
V_n^{\text{rms}} = \sqrt{4k_B T \Delta f}
\]

**Equation 3-2**

where \( \Delta f \) is the bandwidth in hertz over which the noise is measured, \( k_B \) is Boltzmann’s constant in joules per Kelvin, \( T \) is the absolute temperature in degrees Kelvin, \( R \) is the resistor value. In typical STMs the tunneling current is of the order of \( I_T \approx 100 \) pA and is measured with an acquisition bandwidth of \( B \approx 1 \) kHz, where B is roughly
Figure 3-8 Tunnel current as a function of a distance on the copper (100) surface and the relationship between current noise $\delta I_T$ and the vertical noise $\delta z$. In typical STMs the tunneling current is of the order of $I_T = 100 \, \text{pA}$ and is measured with an acquisition bandwidth of $B = 1 \, \text{kHz}$, where $B$ is roughly determined by the spatial frequency of features that are to be scanned times the scanning speed. Thus, for a spatial frequency of 4 atoms/nm and a scanning speed of 250 nm/s, a bandwidth of $B = 1 \, \text{kHz}$ is sufficient to map each atom as a single sinusoidal wave. With a gain of $V/l = R = 100 \, \text{M\Omega}$ and $T = 300 \, \text{K}$, the rms voltage noise is $v_{\text{rms}} = \sqrt{4k_BT \lambda f} = 40 \, \mu\text{V}$ at RT, corresponding to a noise of $\delta I_T = 0.4 \, \text{pA}$. If the tunnel current is given by $I_T(z) = I_0 e^{-2k_T z}$, where $I_0$ is a function of the applied voltage and the density of states in both tip and sample, and $k_T = \frac{\sqrt{2m\phi}}{\hbar}$, the vertical noise may be given by $\delta z_T = \frac{\sqrt{4k_BT B}}{2k_T |I_T|}$, which amounts to a $z$ noise of 0.2 pm. Thus in STM the main electrical noise in the tunneling current is not critical, because it is much smaller than the required resolution.

determined by the spatial frequency of features that are to be scanned times the scanning speed. Thus, for a spatial frequency of 4 atoms/nm and a scanning speed of 250 nm/s, a bandwidth of $B = 1 \, \text{kHz}$ is sufficient to map each atom as a single sinusoidal wave. With a gain of $V/l = R = 100 \, \text{M\Omega}$ and $T = 300 \, \text{K}$, the rms voltage noise
Instrumentation

is \( v_{\text{rms}} = \sqrt{4k_B T R A f} \) 40 \( \mu V \) at RT, corresponding to a noise of \( \delta I_T = 0.4 \) pA. If the tunnel current is given by \( I_T(z) = I_0 e^{-2\kappa_T z} \), where \( I_0 \) is a function of the applied voltage and the density of states in both tip and sample, and \( \kappa_T = \frac{\sqrt{2m\phi}}{h} \), the vertical noise may be given by:

\[
\delta z_{\text{v}} \approx \frac{\sqrt{4k_B T B / R}}{2\kappa_T|I_T|}
\]

This amounts to a \( z \) noise of about 0.2 pm. Thus, in STM the main electrical noise in the tunneling current is not critical, because it is much smaller than the required resolution.

Grounding of 50 Hz noise is one of the classical experimental issues affecting all STMs and AFMs. This arises from different electronic devices do not have exactly the same ground. Extremely small difference in the ground levels, from one socket to another, is sufficient to cause significant noise destroying STM images. Careful wiring, universal grounding racks, voltage regulators and stabilizers, and filters are all used to combat 50 Hz noise.

Stray electromagnetic radiation is also a considerable problem considering the extremely small signal currents, that the chamber is effectively a large antenna, and, that the STM to electronics wiring is so long. To combat this noise source, coaxial cables, twisted pair wiring, and a floating microscope are used.

Wiring is also a problem in UHV STMs since only special insulating materials may be used, finite space limitations, and the extremely small current (Picoamps) and extremely large voltages (for motors, and piezos) means cross talk invariably occurs. Careful experimental set-up ensures this problem is kept to a minimum. Electrical noise is quantified by feeding the tunnel current line directly into a frequency analyser and recording a spectrum over a given bandwidth. Care must be taken to ensure that the measuring instrument does not itself introduce more noise than the STM itself.

3.4.3 Imaging: feedback loop

In the constant current imaging mode tunnel currents are kept constant by altering the tip-sample distance \( z_0 \) using a proportional-integral (P-I) feedback control system.
Instrumentation

Currents are initially amplified using a logarithmic amplifier and then using the $P-I$ control, an error signal is calculated. This is the difference between the tunnel current set-point and the measured current. This difference, or error signal, is then multiplied by the proportional gain ($P$-part) and integrated ($I$-part) with a characteristic time constant. $P$ and $I$ parts are then added together. The output from the feedback circuit is then amplified and fed directly to the $z$-piezos to alter their height. In this manner, recorded changes in $z$ as a function of $(z,y)$ give a direct image of the sample surfaces density of states at $E_F$.

3.4.4 Low temperature set-up

Scanning at low temperatures (LT) offers many experimental advantages. Tunnelling stability increases due to reduced sample drift, and thermal related effects such as reduced surface atom diffusion are advantageous. Atoms and molecules are too mobile at room temperature can be physisorbed and studied at low temperatures. Spectroscopy measurements are greatly improved due to reduced thermal drift, and reduced spectral broadening.

In our system, a liquid helium flow cryostat is used to cool the sample to 25 K. Thermal coupling to the sample is achieved with a clamping block mechanism connected to copper braids in contact with the cooling agent. Temperature measurements are performed with a Si diode thermocouple situated on the coupling stage whose accuracy is approximately $\pm 1$ K below 100 K. The flow cryostat can be used in conjunction with the heating unit to operate at any temperature between 25 K and room temperature. The temperature controller uses a Lakeshore $PID$ controller to adjust power output to the heater to facilitate reaching intermediate temperatures.

3.4.5 Variable temperature imaging and manipulation

At temperatures above room temperature, scanning is far more difficult to perform, with problems increasing with temperature. High temperature imaging generally leads to drifts from thermal expansion of the sample causing z-gap to change, as well as laterally shifting the scan area. Both are disastrous for manipulation experiments where it is essential to be able to see the same area before and after the manipulation event. At elevated temperatures surface contamination also increases,
with surface atoms becoming mobile and disruptive for the STM tip. Despite this, there is plenty of interest in working at higher temperatures where thermally driven physical and chemical processes are observed at an atomic scale. The VT-SPM has two heating options, a direct heating method and a resistive heating method, both of which were used in our experiments.

Direct heating requires high resistivity samples like semiconductors and achieves peak temperatures of typically 1400 K, depending on the sample material, dimensions and clamping contact. Resistive heating is possible for all sample types and achieves peak temperatures of 750 K.

The direct heating method passes current through the sample to generate thermal energy due to resistivity. This leads to a voltage drop across the sample. Therefore, the local true gap voltage depends on the geometric position of the tip with respect to the sample. The maximum heating voltage is 90 V. A rigid electronics design prevents its failure but a compensation voltage $V_{\text{comp}}$ is still necessary to adjust the gap voltage to less than a few volts.

$$V_{\text{gap}}^{\text{eff}} = V_{\text{gap}} + V_h \cdot \frac{I}{I_{\text{sample}}} + V_{\text{comp}}$$

Equation 3-4

Therefore, a reference output of the heating power supply is connected to the floating preamplifier to ensure compensated measurements. No further numerical correction has to be made. The gap voltage is still arbitrarily selected to be between ±10 V to the tip regardless of what voltage $V_h$ drop occurs across the sample due to heating. The time period for image stabilisation is realistically 4 hours despite the manual's guide time of 1 hour. After this, achieving atomic resolution imaging, requires using drift control techniques which applies a voltage to the x-y piezos. As the drift rate changes, the correction voltage also needs to be continuously changed, nevertheless it still helps with imaging.

For resistive heating, a solid state $PBN$ heating element is integrated into the resistive heating plate. The power to the heating element is supplied by contact bars using the sample contact brushes of the sample stage as is used for the direct-
heating option. Power is supplied using a low noise current regulated power supply (HC600)

3.5 Room Temperature AFM/STM

The AFM-STM is a modified Omicron RT-SPM, which can simultaneously acquire tunnel current, force gradient, energy dissipation and barrier height data. The AFM system is housed in a small vacuum chamber operating exclusively at RT. Its pumps and facilities are identical to the STM system, so a detailed description is not repeated here.

The key difference between the two instruments is of course, the sensor. The AFM uses a cantilever to “feel” or detect a force or force related parameter. This force on the tip apex is translated into a deflection of a cantilever beam. To detect this deflection we employ an interferometer-deflection detection system. Improved functionality over typical commercial optical beam system is achieved by employing a Fabry-Perot type interferometer deflection detection system, in conjunction with extremely stiff and conducting tungsten cantilevers. This replaces an original optical beam deflection set-up, which was removed entirely.

The interferometer is extremely sensitive to lever displacements, facilitating operation in challenging signal-to-noise regimes such as sub-angstrom cantilever oscillations. A single-frequency laser diode coupled to a single mode optical-fibre provides the optical signal. Laser light travels along the fibre passing through a 2 x 2 3 dB coupler. One output terminates at a reference photodiode to monitor laser power fluctuations with the second output passing light to the back of the cantilever. **Figure 3-9**, is a schematic of the optical fibre interferometer set-up. On reaching the end of the optical fibre, light beam is both transmitted onto the back of the cantilever, and reflected back up the fibre. The transmitted portion undergoes multiple reflections in
Figure 3-9 Schematic of all-fibre Fabry-Perot interferometer deflection-detection system. (a) The optical signal is provided by a single-frequency laser diode coupled to a single mode optical-fibre. Laser light (IR) travels along the fibre passing through a 2 x 2 3 dB coupler with one output terminating at a reference photodiode to monitor laser power fluctuations and the second output passing light to the back of the cantilever. The resulting interference signal is filtered and processed to detect dynamic changes of the lever reflecting changing tip-surface interactions. (b) Schematic illustrating the homemade Fabry-Perot cavity. (i) The cantilever backside, one of the mirror elements, consists of a “sticky” chromium base layer with the more reflective gold layer atop. The chromium layer prolongs the gold layer’s lifetime whose tendency to peel is otherwise detrimental. (ii) The second mirror element, the fibre end: consists of a transmissive silicon layer and a reflective gold layer.
Figure 3-10 In-situ recording of optical fibre reflectivity as a function of material deposition. The gold layer was found to enhance reflectivity, though this came at a cost of transmittance. Using a silicon base layer, both the transmittance and reflectivity can be improved.

the cavity between the mirrored lever and fibre ends, before being transmitted back up the fibre. The reflected beam becomes the reference signal. Power fluctuations at a photodiode record different interference signals due to varying path length differences, in response to displacements shifts.

3.6 Preparing the optical fibre

Optical fibre preparation for UHV involves three key steps: (i) making the fibre UHV compatible and bake-safe, (ii) mounting it onto a UHV flange and (iii) improving performance by coating its end. Optical fibres are prepared for UHV by removing a metre of the Teflon sheath along with a surrounding wire wool case. The Teflon coating is removed by soaking the UHV end in ethanol for up to 2 hours and then cutting with a specialised stripper. This is cleaned using acetone and isopropanol before a final cleaning with optical fibre wipes. The fibre end, which is to remain outside vacuum, but within the bakeout panel, is then prepared to withstand bakeout temperatures. A silicon tube of sufficient length to carry the fibre out of the panel is placed over a section of bare fibre. This protective jacket is held in place using a small piece of removed sheath, and some heat shrink tubing. Once thermally set, this
Instrumentation offers protection during bake out temperatures up to 140 °C. The UHV end of the prepared fibres is then placed concentrically into a mini UHV flange, with a 0.2 mm diameter hole at the centre of the flange. Using Torr-seal to provide a vacuum seal and support the fibre, only the fully stripped section of the fibre is fixed in place. This sets after roughly 5 hours at room temperature. Since cavity performance determines the signal quality, improving reflectivity of both the cantilever back, and the end of the optical fibre is crucial. Standard reflectivity from a cleaved fibre is ~ 4%, so this needs enhancing. Previous work by Özer [11] established that improved reflectivity could be achieved by using a bi-layer coating. The author established that higher reflectivity was achieved through gold deposition. This is accompanied, however, by a corresponding loss in transmittance. If a double layer of silicon and gold was used instead, the problem is overcome. Our optical fibres are coated in an Edwards evaporator in high vacuum with ~ 50 nm of both silicon and gold. Figure 3-10

Figure 3-10 is a plot of reflectivity recorded during the coating of an optical fibre, as a function of silicon and gold deposition. A layer of about 25-35 nm of silicon is evaporated which is transparent in the infrared. This is deposited until a maximum is observed in reflectivity, followed soon afterwards by a dip, at which point coating was stopped. Gold is then evaporated to increase reflectivity taking far less material to exceed earlier maximums in reflectivity.

The cantilever backside, which forms the second mirror face of the Fabry-Perot cavity is also coated with gold. This however had a tendency to fall off, so a base layer of chromium is used to improve its sticking power. In addition to increasing the amplitude of the reference signal, the gold layer forms the Fabry-Perot cavity with the back of the cantilever. This amplifies the signal beam considerably as a result of multiple reflections. Using this method we can achieve reflectivity of ≈ 60%.

The end of the optical fibre is accurately positioned using an inertial fibre slider system, which can precisely position the fibre with any angle desired. With occasional lever misalignments, and/or inhomogeneities in lever reflectivity, fibre-positioning systems are essential for achieving high S/N ratios.
Figure 3-11 Scanning electron microscope (SEM) image of a homemade tungsten cantilever. The levers are made from tungsten wire, which is flattened, machined, and polished. The lever is then imaged for its dimensions, so calculations regarding spring constant can be made. Further preparation may also be performed, by Focused Ion beam (FIB) milling. Once a sharp tip is achieved, the spring constant of the cantilever is then directly measured using a nano-indentor.

3.6.1 AFM-STM Cantilevers

Highly conductive, and very stiff homemade tungsten cantilevers are used in our experiments to decrease potentially detrimental thermal oscillation amplitudes, avoid snap into contact, and facilitate direct comparison of simultaneously acquired tunnel current data with STM literature. Tungsten cantilevers are made from 50 μm diameter 99.9% purity polycrystalline tungsten, flattened between two polished tungsten carbide pieces and then bent to produce a flat L-shaped piece. These pieces are electrochemically polished by applying a dc-voltage between the wire and a graphite anode, while both are immersed in a beaker of Ilford multigrade photo-developer.

After polishing, the wires are rinsed in HPLC grade acetone, isopropanol, and finally in deionised water. To produce atomically sharp tip-apex the bent section of the L-piece is electrochemically etched using an Omicron W-Tek tip etching tool in a manner similar to STM tip production. Once etched, cleaned and checked using an
optical microscope, such a lever is mounted on stainless steel carriers from Omicron, which are shortened to suit the configuration of our microscope. Cantilevers are then set in place via oven curing of a UHV compatible conducting epoxy H20E or H21D which is supplied by Epo-Tek UK. Following mounting, levers are transferred to an Edwards vacuum evaporator and coated with ~30 nm layer of chromium followed by a ~120 nm thick layer of gold. This process optimises reflectivity on the back sides of the levers and focussed ion beam milling is occasionally used to further define the levers shape and sharpness.

To obtain quantitative information from our data it is necessary to know the stiffness of the cantilever. A combination of direct and indirect methods are used in our experiments to calculate the cantilever stiffness. One method of calculating the stiffness of the lever is to relate the geometry and Young's modulus to the stiffness using the formula:

$$k = \frac{E}{4} \frac{w}{t} \frac{t^3}{l^3}$$

Equation 3-4

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 \(^{[43]}\). The lever dimensions are measured using an electron microscope.

Another method of spring constant calculation uses thermal oscillations of the cantilever. Using a spectrum analyser a vibrational spectrum of the cantilever due to thermal oscillation is recorded. Fitting a curve to the thermal resonance curve gives a value for the thermal energy of the oscillation which can be related to the mechanical energy by:

$$\frac{1}{2} k \langle z \rangle^2 = \frac{1}{2} k_B T$$

Equation 3-5

Where $\langle z \rangle$ is the rms amplitude, $k_B$ is the Boltzmann constant and $T$ is the temperature in Kelvin. Whist the vibrational spectra of the cantilever are readily
available once on the microscope, stiffness values are occasionally skewed by the presence of a secondary peak close to the cantilever resonance frequency. This can lead to an over estimation of the rms amplitude of the thermal vibrations.

3.7 Halogen dosing cells

Solid-state electrochemistry is regularly used to produce extremely clean sources of highly reactive halogens in ultra high vacuum\cite{177-184}. For example, fluorine gas is poisonous, corrosive and potentially explosive so a controllable mechanism for safe production of small volumes of halogens with minimal corrosion to UHV hardware is required. Solid-state cells for in-situ generation and dosing can successfully perform this task, whilst sources may be collimated, brought very close to sample surfaces, and have their output controlled and quantified in a manner impossible using alternative production methods\cite{185}. The halogen cells used in this work are based on a design by Spencer et al.\cite{186} using heat sources and/or dopants to increase electrochemical cell activity. The halide cells routinely operate at pressures below $1 \times 10^{-10}$ mbar making them ideal sources for in-situ UHV use.

3.7.1 Bromine electrochemical dosing cell

The operational basis of the halogen source is a solid-state electrochemical cell $\text{Ag/AgBr/Pt, Br}_2$ in which silver bromide is electrolysed to form silver and bromine. The electrolysis results from an electric field (voltage) induced motion of silver ions through defects in the AgBr lattice whilst bromine is simultaneously released. Increased ion mobility, which increases bromine production, is achieved via thermal heating. Introduction of a halide dopant such as cadmium bromide increases defect concentration. This in turn increases cell activity at a given temperature. In our design, introducing cadmium bromide is not found to be necessary, though cells are heated to increase electrolysis.

The halide pellet is traditionally pre-melted to form a compact mould, but in our arrangement, Figure 3-12, the pellet is formed with a pellet press. This pellet is placed in a Pyrex tube 20 mm in length and 10 mm in diameter with a platinum gauze electrode placed at one end and a silver wire electrode pressed against the other,
Figure 3-12  (a) Photograph and (b) schematic of homebuilt electrochemical bromine dosing cell. The cell is supported on top of two copper wires, and fixed in place via two copper beryllium barrel connectors. The clamping / heating foil at the top and bottom, labelled (i) wraps around the Pyrex ® tubing (ii), with a tapped hole at either end. The tapped holes, which align once wrapped, have the barrel connectors screw piercing either hole, and is then tightened in place to ensure good electrical contact, and a thoroughly rigid and robust design. Spot welded to this is the thinner wire which, winds round the tubing until it reaches the bottom electrode, where it is then spot welded also. This thinner wire was necessary to achieve higher heating temperatures faster. The ceramic tubes surrounding the copper uprights is to offer mechanical support, and, reduce outgassing effects. The solid-state pellet is inside the Pyrex ® tubing and has two electrodes (1) a platinum gauze at the top, and (2) a silver wire spiral at the bottom and into the pellet. These electrodes, are connected with silver wire to two different copper uprights via spot welding (v). The entire apparatus is supported on UHV electrical feed-through.

Figure 3-12-a. A K-type thermocouple is sandwiched between the pellet, and the Pyrex ® tube recording the pellet temperature during use, Figure 3-12 (ii)-b.

To heat the bromine pellet, a surrounding Pyrex® tube is converted into a resistive heating unit, using Tantalum foil and wire. Tightly wound Tantalum wire is spot-welded at both ends to a Ta foil fixed in place using barrel connectors Figure 3-12 (ii)-c. During cell operation, electric currents through the wire and foil resistively heat themselves and the electrochemical cell to an operational temperature of ~ 450 K. This modification to Spencer’s design drastically speeds up the heating process.
Figure 3-13 Representative "stills" from a time resolved mass spectrum sequence taken (i) before, (ii) during and (iii) after halogen cell use indicating the production of atomic bromine. Residual bromine was often found for extended periods of time after bromine dosing. In some occasions, though very rare, molecular bromine was also detected, Figure 4-19.

To mount the cell on a UHV flange, the tantalum foil is rigidly secured to Copper-Beryllium barrel connectors using screws through tapped holes in the foil. The whole unit is then mounted on top of stainless steel support rods, each connected at their other ends to a UHV flange, Figure 3-12 (ii)-d. In addition to offering physical support, rods are also used as electrical Feed-throughs, so, to reduce outgassing and
the risk of a short circuit through contact, these rods are isolated using insulating Macor® tubing, Figure 3-12 (ii)-e.

The non-supporting electrical feed-through rods are connected to the thermocouple and electrodes using spot welded silver wires, Figure 3-12 (ii)-f. Cell resistances of 2 MΩ are typical, which falls as the cell is heated. Extremely low resistances are usually a warning sign of dendrite growth, which is found to limit the cell lifetime. Power spikes may be used to break dendrites returning the cell to normal operation.

The lab-side of the cell set-up is connected to two power supplies and a thermometer. One power source provides an adequate heating power, ~ 12 W, to achieve operational temperatures after approximately 20 minutes. During cell operation, cell currents oscillate wildly, and for this reason a current controlling device is occasionally used. Successful operation of the bromine cell is confirmed by a number of facts.

First, a pressure change and cell current are observed exclusively, when both the cell reaches a suitable operation temperature, and a voltage has been applied to the electrochemical cell. Second, using a well-characterised surface like silicon (111)-7x7, bright protrusions associated with bromine, which display characteristic voltage dependent behaviour, scaled with dose. Coverage versus dosage data indicates that bromine production is a function of cell current multiplied by time, μAs.

Finally, mass spectrum analysis, before, during, and after cell operation in Figure 3-13 shows the emergence of a peak at 80 a.m.u. This is consistent with atomic bromine production, and chlorine has been found to be produced in an identical manner \[^{187}\].

### 3.7.2 Fluorine Electrochemical dosing cell

Flourine is also produced using a solid-state electrolytic mechanism with a cell set-up based on the design by Nakayama et al. \[^{186}\]. At high temperatures, large electric fields drive a migrationary ionic current to a gold anode where it is thermally desorbed. Cell resistances and operational voltages are much higher, 80-150 V, so there is greater emphasis on thermally reducing the cell resistance.
Instrumentation

In our set-up, an optical grade calcium fluoride, CaF₂ crystal is clamped between a fixed upper gold electrode and a spring supported gold disc. The upper electrode has a tapped hole allowing fluorine to escape. A Pyrex® tube houses the electrochemical cell, which is heated in a manner similar to the Br cell design. With far greater heating required, experimental heating techniques involving a silicon wafer were tested. Initial investigations suggest the design can reach sufficiently high temperatures very quickly to produce F₂, though its highly reactive nature appeared to cause such serious damage to our samples, that tests were discontinued.
4 CRITERIA FOR MANIPULATING ATOMS AT RT

4.1 Introducing the energy criteria for RT manipulation of atoms

Using STMs at low temperature (4-80 K) to manipulate single atoms and molecules has already shown considerable promise, section 1.4. With low thermal energy, physisorbed species are weakly bound (≈ 10-100 meV) or "frozen" to a sample surface, so an STM tip can readily manipulate a wide array of species over a range of metal and semiconductor surfaces.

At higher temperatures however, phonon-coupled thermal fluctuations increase the species' energy at the rate of $\frac{3}{2}k_B T$, nearing 75 meV at RT. Estimating a typical diffusion rate for a physisorbed species, at RT, using the Arrhenius equation:

$$v_D = v_0 \exp \left[ -\frac{E_B}{k_B T} \right]$$

Equation 4-1

where $v_D$ is the hop frequency, $v_0$ is the attempt frequency (≈ $10^{12}$-$10^{13}$ Hz), $E_B$ is the bond energy (≈ 100 meV), $k_B$ is Boltzmann’s constant, and $T$ is the temperature in Kelvin; gives a hop frequency in the $10^{12}$ Hz range. With a typical STM scan taking 180 seconds in our set-up, physisorbed species are clearly too mobile to be imaged at RT. Worse still, you can’t manipulate what you can’t see!

Immobilising adsorbates for manipulation at RT then requires an adsorbate to be chemisorbed to the sample surface. That is, unlike its physisorbed counterpart where the electronic structure is only barely perturbed upon adsorption; strong ionic or covalent type chemical bonds involving considerable charge transfer, typically of the order of 0.5-5 eV binding energy per atom or molecule, is required. Breaking bonds of this magnitude however, is a significant challenge for STM tips.

As a result of this, RT manipulation of atoms and molecules requires the careful consideration of a number of factors largely inconsequential when manipulating at 4K.
These factors, a set of energy ranges, must overlap for reliable STM manipulation is performed. The following is a list of energy considerations for RT Manipulation using SPM's:

(i) The corrugation energy or adsorbate-substrate bond strength \( E_B \) must be large enough to immobilise the adsorbate at RT, i.e. \( E_B \gg k_B T \)

(ii) The species must be manipulable, i.e. the adsorbate-surface bonds must be weak enough that a tip coupled energy \( E_{\text{tip}} \) is enough to break them, \( E_{\text{tip}} > E_B \)

(iii) The tip must be able to deliver such a quantity of energy, i.e. the tip-energy-coupling mechanism times the energy-coupling efficiency \( \chi \), must be greater than (i), i.e. \( E_{\text{tip}, \chi} > E_B \), or alternatively put, the rate of energy dissipation must be high, and finally,

(iv) The tip-apex reconfiguration energy needs to be very high, \( E_{\text{reconfig}} > E_{\text{tip}} \)

When these criteria are met, an overlap of energies occurs, i.e. an energy window opens, and successful manipulations can be performed. Then,

\[
E_{\text{reconfig}} > E_{\text{tip}, \chi} > E_B \gg k_B T
\]

Equation 4-2

We begin this chapter by examining two well-studied, technologically relevant surfaces; copper (100), and silicon (111)-7x7, which are utilised as atomic-scale "building sites". The importance of well-understood substrates for manipulation centres on the influential role the physical and electronic structure of a surface has on the bond type an adsorbate makes with the surface. Since our desire is to break this bond, a deep understanding of the physical and electronic properties including; the bonding energetics, vibrational lifetimes, corrugation energy, desorption energy, phonon frequencies, and diffusion mechanisms, are all relevant for devising a destabilisation strategy.

To investigate criteria (iii), namely, that a sufficient quantity of energy is deliverable
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from the STM tip; simultaneous non-contact atomic force microscopy/scanning tunneling microscopy (nc-AFM/STM) is performed to determine typical force gradients between a tungsten tip and the surface, $E_{T/\rho}$.

With this value in mind, a comprehensive literature review is then presented, focusing on the dynamics of various adsorbates on the same sample surfaces. This review, provides three promising adsorbate-substrate candidate systems, whose energetics are investigated for room temperature manipulation suitability, $E_{T/\rho} \chi > E_B >>> k_B T$. One system is found that satisfies all our energy considerations.

4.2 Copper

Copper is a $3d$ transition metal whose technological relevance has consistently evolved in tandem with advances in scientific sophistication. Today, as over 3000 years ago, copper is at the forefront of modern technology, and is currently evolving as an interconnect material for microelectronics circuitry. Earlier technological uses monopolised on copper’s ductility, malleability and stability; though its thermal and electrical conductivity are its current championed properties.

Copper is an interconnect material primarily because of its superior resistivity compared to the previous industry standard, aluminium. Using low resistivity materials decreases $RC$ delay times, in turn increasing integrated circuit (IC) speed. With an $RC$ time constant directly proportional to resistivity, and copper and aluminium’s resistivity at 1.7 $\mu\Omega$cm and 3 $\mu\Omega$cm respectively, copper fuels a 40% improvement in IC speed [199]. Additional advantages of copper circuitry include, improved thermal conductivity, twice aluminium’s; its resistance to electromigration, $= 100$ times better than aluminium’s; and its lower power consumption, $= 30\%$ better than aluminium’s [190, 191].

Despite these advantages, switching to copper is not without its difficulties. The failure of reactive ion etching to pattern copper surfaces fuelled many investigations into alternative methods of pattern formation, including halogen etching [179, 192-199]. An IBM invented Damascene [200] process eventually solved the problem.

With Moore’s law [201] driving this technology towards a 65 nm limit, the importance of surface properties on interconnect behaviour, continues to grow. In addition to plain
curiosity, this provides a strong technological motivation to investigate the physical and chemical behaviour of copper surfaces at the atomic-scale.

4.3 Copper (100) surface

4.3.1 Physical properties

Physically cleaving copper along a single axis of its face-centred cubic cell by “cutting” cohesive interatomic bonds, forms two identical (100) surfaces with rows of four-fold coordinated Cu atoms. Low energy electron diffraction (LEED) reveals that copper atoms remain in registry with the bulk lattice, producing a 1x1 pattern with an interatomic spacing of 2.68 Å. Figure 4-1. This symmetric simplicity, and small variation of bonding sites, makes the surface ideal for quantitative SPM manipulation experiments. In reality however, the copper (100) surface is awash with additional structural defects that complicate this simplicity.

There are two boning sites: (i) the four-fold hollow sites, and (ii) the on-top sites. See Figure 4-3.
4.3.1.1 Defects

In the late 1920's, Kossel and Stranski introduced a terrace-ledge-kink model (TLK-model) for intrinsic defect formation on crystal surfaces. The authors suggested that a wide range of imperfections are thermodynamically preferred, and hence always present on newly cleaved surfaces. Such defects act as centres of reactivity and are hugely important in mass transport mechanisms and catalysis. As such, imperfections often dominate surface properties and reactivity, so their quantities are engineered as a property control tool. Kossel distinguished terraces, steps, vacancies, adatoms, kinks, islands and vacancy islands, classified by dimensions and/or by the addition (adatom) or removal of surface atoms (vacancy). Some defects of relevance to this body of work are shown in Figure 4-2.

The presence of a low concentration of defects is energetically favourable as defects initially reduce the free enthalpy of the surface. The TLK model is based on the idea that the energy of an atom's position on a crystal surface is simply determined by the bonding to neighbouring atoms, and that transitions only involve the counting of broken and formed bonds. As a consequence, the creation of surface defects on a perfect crystal involves the investment of a certain amount of energy, for example, a vacancy formation energy. Though a greatly simplified model, it qualitatively explains why adatoms are less bound on terraces than adatoms at step edges, with coordination numbers of one and two respectively. The model can be taken further to extract the formation energy of an adatoms by subtracting, the adatom energy from the kink atom energy, to find $\Delta G$. One can then determine the concentration of point defects at thermal equilibrium, with the process extendable to other defect types through substitution of $\Delta G_{adatom}$:

$$\frac{n_{adatom}}{n_{atoms}} = \exp \frac{\Delta G_{adatom}}{k_B T}$$

Equation 4-3

where $n$ is the concentration. Using effective medium theory, adatom vacancy formation energy on copper (100) was calculated by Stolzte et al. to be equal to 0.984 eV, with a step energy formation of 0.125 eV. Adatoms on the (100) surface of...
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Figure 4-2 Three STM topographs of the copper (100) surface illustrating the different defect types: (a) surface vacancy, (b) adatom, and (c) a step edge. Defects alter the surface potential energy corrugation in its immediate vicinity, causing defect sites to act as pinning centres, growth centres, and to generally alter the surface chemistry. The lower left of each image names the mass transport mechanism taking place in each image.

copper are produced at steps and/or kink sites each with formation energies of 0.676eV and 0.507eV \[205\]. Stolzle's results indicate that islands are more stable than individual atoms, in addition to quantifying island dissociation values as a function of size, with 9 atom vacancies, a surprisingly low, 0.29 eV. A key reason for the importance of these reactivity centres, i.e. the defects, is their mobility and hence importance in mass transport mechanisms.

4.3.1.2 Mass transport

Diffusion of adatoms and vacancies and on metal surfaces is of vital importance for many technologically important processes, such as: adsorption, desorption, surface reactivity, catalysis, and crystal growth. Diffusion is a thermally activated process and in order to get from one energy minimum to a neighbouring minima, the adatom or vacancy species must overcome an energy barrier for diffusion \(E_D\). The hopping rate of adatom diffusion is expected to follow the Arrhenius relation, already shown, \(E_{q}\). The hop direction is left to chance. Adatom diffusion may proceed by hopping and/or an adatom exchange mechanism on copper (100) and energy barriers calculated via action-derived molecular dynamics equal 0.477 and 0.708 eV respectively \[206\]. Calculations indicate that the energy barrier for adatom self diffusion via a hopping mechanism from one four-fold hollow site to an equivalent adjacent site...
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Figure 4-3 (a) Tunneling topograph taken in the constant current mode of the copper (100) surface, indicating the 1 x 1 atom periodicity. This symmetric simplicity of the surface, and the low number of different bonding sites; i.e. two: (i) four-fold hollow and (ii) on-top sites make this surface ideal for quantitative atomic manipulation studies. (b) Current-distance spectroscopic curve taken at a single atomic site using the scanning tunneling microscope at room temperature. Plotted in blue is the current on a linear scale. Plotted in black is the current on a logarithmic scale. The red curve is a linear fit to the logarithmic data. From this curve, a barrier height 4.37 eV is calculated. This compares to the work function values mentioned in the main text, which ranged from 4.5-4.95 eV.

via a two fold bridge ranges from 0.39 - 0.53 eV on copper (100). Understandably, adatom exchange processes involving greater numbers of broken bonds, have higher barrier values ranging from 0.72 - 1.03 eV. The rate of the diffusion processes outlined above can be altered using a local stimulus, such as an SPM tip, with two main approaches (i) the diffusion barrier may be lowered, thus increasing the hop rate, or (ii), extra energy may be coupled into the system.

4.3.2 Electronic structure

By disrupting the lattice periodicity, the new surface imprisons usually free valence electrons, and a work function, which is closely related to several measurable properties; including the photoelectric threshold, thermionic emission, and the tunnel barrier height, is calculated at 4.5 - 4.95 eV. Figure 4-3 shows a current-distance \( I_V(z) \) spectroscopic curve of the copper (100) surface, from which a barrier
height of 4.37 eV is extracted. It should be noted that considerably conflicting experimental conclusions regarding the behavior of the tunnel barrier as a function of gap distance have been reported in the past. In most studies, it is concluded that the barrier decreases for $z \leq 6 \text{ Å}$ \cite{217-218}. On the other hand, Dürrig \cite{220} and Besenbacher \cite{221} independently found that the barrier is constant all the way to point contact. Nevertheless, this value, along with many surface phenomena, are strongly affected by a redistribution of electronic charge leading to the formation of an intrinsic double layer at the newly formed surface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-4.png}
\caption{\textbf{(A)} Redistribution of electron clouds \hspace{1cm} \textbf{(B)} Resulting interlayer movements}
\end{figure}

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{figure4-4.png}
\caption{\textbf{(a)} In response to significant alteration of the electron density in the outermost layers, atoms re-arrange their atomic positions in responses to forces generated by the redistribution. This ability of surface atoms to relax their atomic positions plays a crucial role in many, if not all, STM measurements on Cu (100) surface. The forces present due to the presence of an STM tip, can induce similar surface relaxations \cite{222}, which may influence the measurement of the atomic corrugation \cite{165}; the barrier height \cite{223}, electronic structure and the barriers to manipulation \cite{224}. \textbf{(b)} LEED studies show that the second and third layers also change the separations as a result of such relaxation.}
\end{figure*}
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Figure 4-5 Current-voltage spectroscopy curve of the copper (100) surface taken at RT with our commercial Omicron STM. The experimental data, a near straight line (red) reflects the near uniform band structure around $E_F$. No energetically localised states are apparent, and spatially resolved $dl/dz$ maps reveal no detectable difference in the localised density of states LDOS across the surface.

The electron fluid at the surface edge does not end sharply at the boundary. Rather it spills out, beyond the surface edge of the positive charge, and an outer layer of negative charge is formed. An inner positive layer results from the corresponding electron depletion. The existence and thickness of this double layer is determined through a balance of the kinetic and potential energy. The kinetic energy favours an electron distribution spreading away from the surface, thus avoiding sharp curvatures of the $\psi$ associated with high kinetic energy. On the other hand, the potential energy, favours an abrupt end to the distribution, since this keeps the electrons as close as possible to the attractive electropositive material $^{[226]}$. The double layer and an image correlation-exchange contribution $-e^2/4x$, combine to give a total potential energy gradient along a line through the surface and into vacuum. The form of this potential energy curve is influenced by the distribution of electron density, and hence the $\psi$ amplitude. Using DFT methods to find an electron density which minimises the energy to the interacting electron gas, it is found, that in addition to the gas spreading into the vacuum, the electron gas exhibits Friedel oscillations with a wavelength of $a \approx 0.42 \, \text{Å}^{[226]}$ upon reaching the surface.
Improved work function calculations can be obtained by taking into account the atomic structure. In place of the jellium models hitherto assumed, the surface is then dimpled with an outer layer of the positively charged ionic spheres whose positive charge distribution traverses the surface in a manner similar to electron distribution. Better matching of this positive and negative charge distributions weakens the double layer, thus reducing its contribution to the work function. Incidentally, it is this atomic variation of positive charge on the surface which is utilised in STM to observe the atomic structure of the (100) copper surface.

The local density of states (LDOS) of copper is spatially delocalised, and energetically symmetric around $E_F$. This means, STM images of copper surfaces should reflect an almost flat LDOS structure, and hence show no corrugation. Figure 4-5 is a current-voltage ($I$-$V$) curve on copper (100). The $I$-$V$ curve confirms that there is a continuous band structure of empty and filled states. This suggests an absence of
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spatially localised discrete states. Yet, an examination of Figure 4-3 shows a clear perturbation in the electron sea modulated at atomic sites.

STM images of close-packed metal surfaces usually reveal anomalously large corrugation amplitudes in direct conflict with the standard model for STM contrast formation, Figure 4-6 (a). Since the Tersoff and Hamann (T-H) \(^{[140]}\) model predicts that corrugations should reflect an almost flat LDOS, this dichotomy is typically explained by invoking tip induced effects.

Electronic effects such as tip induced localised states and resonant tunnelling have been suggested by Chen \(^{[227]}\), Ciraci \(^{[162]}\) and Doyen \(^{[228]}\), with Dürig \(^{[164]}\) and Clarke \(^{[164]}\), pointing out the influence of forces. During atomic resolution imaging of close packed metal surfaces, tunnelling tips approach so close to the sample surface they experience short range repulsive interactions \(^{[71]}\). On the other hand, adhesive forces, tip and surface relaxations may also make significant contribution to the large atomic corrugation \(^{[164]}\).

4.3.3 Relaxation and reconstruction

In response to significant alteration of the electron density in the outermost layers, Finnis and Heine \(^{[229]}\) point out; that atoms rearrange their atomic positions in response to forces generated by the redistribution, Figure 4-4 (a). With reduced coordination, and a redistribution of electrons, outermost atoms shift parallel and/or perpendicular to the surface, inducing surface reconstruction and/or relaxations.

It was previously mentioned that the two-dimensional symmetry of the (100) surface does not reconstruct. Despite this, the surface does relax perpendicular to the surface plane, and LEED analysis indicates that the topmost layers contract inwards with a range of -1.0 to 2.1% \(^{[230-231]}\). Smoluchowski \(^{[225]}\) pointed out that in response to cleaving a metal surface, the electron cloud at the surface smoothes out, flowing from the "hills" into the "valleys" formed by the surface atoms. Finnis and Heine \(^{[226]}\) went further, noting, that "Smoluchowski smoothing" actually induces an inward electrostatic force acting on the top layer nuclei causing an inward relaxation. Since this effect increases with surface roughness, the model confirms a general relationship between surface roughness and relaxation observed \(^{[230]}\). It could not however, correctly model all noble metal relaxations \(^{[236]}\).
Pettifor thus proposed that crystal geometry is determined by the balance of partial pressure of localised \( d \) bonds and the homogenous positive pressure of the \( sp \) electrons\(^{[237]}\) pulling in opposite directions. According to Heine and Marks\(^{[238]}\), a metal surface’s mobile \( sp \) electrons flow into the vacuum, while \( d \)-bonds between the first and second layers remain practically unchanged. Thus, \( d \)-electrons give rise to an inward force on the surface, which is proportional to the strength of the \( d \)-bonds. This model correctly predicts the outward relaxation of some noble metals, which other models failed to predict. Methfessel \textit{et al.}\(^{[239]}\) then combined the effects of \( sp \) smoothing, and localised \( d \) bonds, with their results show the basic parabolic character for top layer relaxation of 3-\( d \) transition metals. In addition to this top layer relaxation, relaxation of subsequent layers exhibits a damped oscillatory form.

With charge redistribution clearly able to influence the actual positions of atoms, it is a straightforward extrapolation to suggest that: (i) single atoms and/or lack thereof, or (ii), the presence of an STM/AFM tip, influences the local charge distribution and hence surface relaxation.

This ability of surface atoms to relax their atomic positions plays a crucial role in many, if not all, STM measurements on Cu (100) surface. The electrostatic and short range chemical forces resulting from the presence of an STM tip, induce surface relaxations\(^{[220]}\), which then influences the measurement of the atomic corrugation\(^{[166]}\), barrier height\(^{[223]}\), electronic structure, and hence the barrier to manipulation\(^{[215]}\).

In summary, the symmetric simplicity, and small variation of bonding sites appears to make copper (100) an ideal surface for SPM manipulation experiments. The measured corrugation amplitude of \( \approx 25 \) pm at standard, and supposedly, “non-perturbative” imaging conditions, conflicts with theoretical expectations and is in reality quite smaller. This is probably due to tip-induced outward surface relaxations. This alteration of corrugation amplitude as a function of tip proximity, serves as a warning when attempting to quantify the manipulation process.

The delocalised nature of the electron sea means that bonding with any proposed species is likely to be intermediate in strength between the physisorbed species (\( \approx 100 \) meV) and the highly ionic chemisorbed species (up to 2 eV), circa 0.5 eV. Based on this, the adsorbate surface bonds may turn out to be too weak to sufficiently stabilise adsorbates of interest. The absence of discreet states in \( I-V \) curves,
indicates that electronic excitation mechanisms are unlikely to play a significant role in manipulation process, with screening effects likely to negate the influence of the electric field as a destabilisation mechanism. The mechanism of manipulation is expected therefore, to be force based.

Defects, and the mass transfer route a manipulant species takes, will have a significant impact on manipulation threshold experienced. Specifically, manipulating along a step edge, or, inducing vacancy-mediated motion will have significantly higher manipulation barriers.

4.4 nc-AFM/ STM of copper (100): The tip-surface force gradient

To examine the energy ranges deliverable from a tungsten tip to an adsorbate we now examine some non-contact simultaneous atomic force microscopy/scanning tunneling microscopy (nc-AFM/STM). In this mode, we can simultaneously acquire force gradient, dissipation, barrier height, tunnel current and topographic data.

The set-up employs a homemade tungsten cantilever, whose preparation is described in section 3.6.1. These cantilevers have two main advantages over typical commercially available levers is that: (i) they are made of tungsten, so force gradients measured are directly comparable to a vast array of already published STM literature (not so for Si levers), and, (ii) their high stiffness values, typically 50-200 Nm\(^{-1}\) in conjunction with the off-resonance excitation and fibre-optic deflection detection, means that ultra small oscillation amplitudes are achievable. This provides a means to quantify the force gradient without the need for complicated de-convolution techniques.

Loppacher et al.\(^{[46]}\) pointed out, that the decay length of short range chemical force is twice as large as the decay length of the tunnelling current. Thus, it is expected that during imaging, considerable tip surface interactions occur. This rather simple premise is the basic tenet of atomic manipulation with STM.

**Figure 4-7** is a simultaneously acquired force gradient and tunnel current image of copper (100) acquired with a homebuilt non-contact atomic force microscope/scanning tunneling microscope (nc-AFM/STM).
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The tips distance from the surface is regulated using the tunnel current set-point and in this manner, force gradient data is directly comparable to forces experienced by a normal STM tip during manipulation. The technique is thus unique in being able to describe the forces typically occurring during normal STM operations.

The microscope employs a Fabry–Perot fiber interferometer for deflection detection with high sensitivity. The lever is oscillated with ultra-small amplitudes (0.25 Å peak-peak) at a frequency well below its resonance. Rastering across the surface at constant tunnel current, the changes in the oscillation amplitude due to force interaction are recorded using a lock-in amplifier. In the case of very small oscillation amplitudes applied at frequencies far below resonance the force gradient interaction between tip and sample can simply be expressed as:

\[
\frac{dF}{dz} = k_0 \left[ 1 - \frac{A_0}{A} \right] \tag{Equation 4-4}
\]
where $k_0$, $A_0$ and $A$, are the stiffness, free oscillation amplitude and measured amplitude of the cantilever, respectively. The amplitude changes are converted into the force gradient, for images and force spectroscopy. Compared to large-amplitude resonance enhancement techniques, the oscillation amplitude data directly give quantitative force gradient information without need of deconvolution. It is straightforward to calculate the force gradients at each pixel point of an image. Hence, not only the $F-d$ curves, but also the force gradient images, give quantitative information. Furthermore, the energy input to the interacting tip–sample system is very low, and the perturbation is minimal in probing the interactions. Home-made tungsten cantilevers with spring constants of 50–200 Nm$^{-1}$ were used in the experiments. The preparation and calibration of the cantilevers were discussed in section 3.6.1.

Figure 4-7, demonstrates the onset of atomic resolution in the force gradient channel before an equivalent onset in the tunnel current channel. Force gradient images showed atomic resolution whereas STM scans exhibited almost no contrast. Though the tunnel current is set to 9.1 nA, only 0.1 Å corrugation is detected in the image, corresponding to a flat tip trajectory during scans. This is quite reasonable in LDOS terms suggesting there is minimal tip perturbation.

Force gradient and tunnel current were also directly measured as a function of separation, to determine the operating conditions during STM imaging. Over a series of images, the tunneling current set-point was altered (4-16 nA) in order to study the dependence of the corrugations in both scans on the tip–sample separation. The tip bias voltage and free oscillation amplitude were kept constant for all of the experiments at 20 mV and 0.25 Å, respectively. The corrugation height in force gradient images was found to increase as the set tunneling current was increased, and correspondingly, the STM operation regime is found to lie between the minimum of the stiffness curve and the start of repulsive force. The change in corrugation is indicative of site specific outward relaxations of surface atoms from there mean position.
Akin to the pair of images shown in Figure 4-7, no STM images show an atomic contrast whereas the force gradient images revealed atomic resolution with corrugation heights increasing with the average tunneling current during imaging. Figure 4-8 shows the line profiles measured across the atomic positions on force gradient images at different tunneling current set points. The dependence of the force gradient corrugation on average tip–sample separation was found to be strong. An average tunneling current of 4.1 nA resulted in corrugation of about 5.5 Nm$^{-1}$ and the stiffness was always negative during the scan. When we increased the current to about 9 nA, the corrugation increased up to 15 Nm$^{-1}$, with the stiffness varying around zero. As we proceeded with imaging at even higher currents, the force gradient corrugation increased at a steep rate, and at 15.9 nA average current we measured about 60 N m$^{-1}$.

In addition to acquiring simultaneous nc-AFM/STM images, spectroscopy curves were also taken. During spectroscopy, the feedback loop is switched off, and the sample is approached towards the tip whilst simultaneously recording the oscillation amplitude of the cantilever and the tunnel current. Figure 4-9 shows the total interaction stiffness and the tunnel current as a function of the sample piezo displacement. The total interaction stiffness, which is a sum of long- and short-range components, was calculated from the measured oscillation amplitude data using
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Figure 4-9 Simultaneously acquired force gradient, tunnel current and force vs distance spectroscopy curve on copper (100) at room temperature. The data is acquired by turning the feedback off and approaching the surface using piezo scanners. The tunnel current signal shows its typical exponential type dependence with distance. The interaction stiffness (red) and force (blue) indicate both attractive and repulsive force are present. The turquoise arrows indicate the force regime STM typically operates within. The cantilever is a homemade tungsten oscillated at sub-angstrom amplitudes, making the $F-d$ data directly comparable to normal STM conditions.

In order to study the short-range behavior it is crucial to subtract the long-range contributions such as Van der Waals (vdW) forces. We found that a fourth order power law dependence fits well with our data, with the assumption of a truncated cone geometry for the tip. The vdW fit to the long-range part of the stiffness curve shown in Figure 4-9 yields a vdW radius of 25 Å. Once the vdW component is subtracted we end up with the interaction stiffness due to short-range interactions, which are known to be responsible for atomic-resolution nc-AFM imaging of various surfaces.
4.5 In search of manipulable species at RT: literature review

Despite early achievements [6, 19, 32, 43, 53-65, 64, 120, 121, 241-247], the development of room temperature control and construction of atomic structures has been limited by (i) an inability to find stable, yet manipulable species at RT, and (ii) the difficulty and time-consuming nature of atom-by-atom repositioning.

In principle, there are two main routes to finding suitable species for manipulation at RT; (i) adatoms and, (ii) molecules. Substantial research [124, 213, 249-308] has sought to determine and understand the dynamics of adsorbed particles on metal surfaces, partially because of their importance in ordering and in chemical reactions at surfaces [309]. Knowledge of diffusion coefficients and their temperature dependence is important for many surface mechanisms including; catalysis, friction, lubrication, corrosion and crystal growth, if only to determine whether or not diffusion is a rate limiting step [243]. But Feynmanesque reasons also exist for an interest in surface dynamics. Building RT nanostructures atom by atom necessitates not only seeing, but also moving individual particles.

One class of species for STM manipulation experiments is the use of large molecules [27, 310, 311]. Gimzewski for example pushed buckyballs on Copper surfaces [58], and by and large, the manipulation field has widely chosen this route in its search for useful nano building blocks. Yet, problems of electronic coupling to surface states hamper the usefulness [312] of these molecules for widespread use. More importantly, for this body of work is that their motion is often complicated, typically electronically induced, and usually troublesome for STM tips to remain intact. Because of these difficulties, quantifying any manipulation process is perilous.

Finding atoms, which are stationary, yet manipulable on the other hand, is also rather difficult. Physisorbed hydrogen and noble gases are very weakly bound to metal surfaces [243, 246, 313-315]. Consequently, tunnelling and low diffusion barriers (typically < 200 meV), result in high adatom mobility at RT. Alkali-metal diffusion barriers range from ≈ 50 to 100 meV meaning sufficient thermal energy is also available at RT to ensure, that they too, are stationary for less than 10 ps on copper (100) [275, 276, 290, 298, 306].

Diffusion of transition metal adatoms is hugely important for magnetic thin film growth and presents an entirely different proposition. Cr [316], V [296], Fe [295], Mn [253, 317], Ag [296], Cd [304], Sn [316], Ni [258], Au [293] and Pb [294, 295] are all mobile on Cu (100) at RT.
Nevertheless, since some transition metals have comparable electronic structures and radii to copper atoms, they can alloy and/or embed themselves in surface layers. Though alloying does not necessarily occur with the first atomic layer, atomic movements that are in this layer, undergo very different transport mechanisms, and hence diffusion coefficients, than their chemisorbed counterparts. Sm \([255]\), Pd \([124]\), In \([256]\), Ir \([272, 273]\), Co \([256]\), all for example, become embedded in the surface layer of Cu \((100)\). In, Ir and Co, are both stable and moveable, with an STM tip at RT. However, the usefulness of these species in forming stable structures is limited due to their natural tendency for interlayer diffusion.

Monovalent halogens on the other hand, which have very large electronegativities and are not surface embedded, (and are hugely important owing to their widespread utilisation in surface etching), offer some hope. In fact, Fishlock et al. \([32]\) suggested that not only are they stable, but have even reported manipulating them at RT. Altman and others on the other hand, have suggested independently, that halogen atoms, including bromine, are already mobile at RT \([179, 192, 193, 195, 197, 198, 270, 292, 319-321]\).

With these conflicting reports in mind, we now cautiously study our first candidate adsorbate-substrate system; Copper \((100)\):Br for suitability as an RT manipulation system. Critically, the aim is to determine if \(E_{\text{reconfig}} > E_{\text{Tip}} \chi > E_B >> k_B T\).

### 4.6 Adsorbate-substrate system (i): Copper \((100)\): Br

In a pioneering paper in June 2000, Fishlock et al. \([32]\), reported for the first time, an adsorbate substrate combination that had sufficiently stable atoms at RT to be imaged for extended periods of time, but, if perturbed by a threshold tunnel current density, could be manipulated with atomic precision.

#### 4.6.1 Preparation

To recreate, and further develop the manipulation methods proposed by Fishlock et al. \([32]\), a copper \((100)\) sample was prepared by repeated cycles of Ar ion bombardment at 0.6 keV, followed by annealing at \(-600^\circ\text{C}\). Following approximately 50 cleaning cycles, STM scans reveal a clean copper \((100)\) surface dominated by flat
terraces typically in excess of 50 nm, with the (1x1) periodicity expected for the bare surface, Figure 4-10 (a). The structure is verified with characteristic interatomic-distance data, Figure 4-6 (a), and, independently verified with LEED [231] and AFM results [71, 240]. The transition metal surface is then dosed with bromine, as indicated in Figure 4-10 (b), showing a bromine-dosed copper (100) surface.

4.6.2 Room Temperature STM

Molecular Br$_2$ is widely believed to dissociatively chemisorb upon adsorption from previous TPD$^{[197]}$, angle resolved photoemission$^{[22, 323]}$, x-ray photoelectron spectroscopy $^{[323]}$, and LEED $^{[197]}$ results. In agreement with Altman $^{[170, 192-197, 198]}$, Fishlock $^{[32, 170, 183, 184, 324, 325]}$ and previous studies, I also found that the highly dosed surface once fully saturated, reconstructs to a characteristic c-(2x2) periodicity, shown in Figure 4-10 (b). The reconstruction induces a change in interatomic spacing from $\sim 2.6$ Å to 3.9 Å, resulting
from bromine atoms, like chlorine, occupying every second four-fold hollow site, as illustrated in Figure 4-10 (a) and (b).

The main bonding contribution comes from the interaction between the Cu 4s and $3d^2$ bands, and the bromine 4p$_z$ orbital and, because of bromines highly electronegative nature, strong ionic bonds are formed. With sufficient coverage, a halide layer forms which, upon annealing, sublimes. Because this halide contains copper atoms, the copper surface is then etched. This ability to etch copper has led to a wide range of studies aiming to elucidate the etching mechanisms of metal surfaces. Altman et al. suggested a two-step process for halogen etching of copper (100), the two steps proceeding with (i) halogenation to form a bulk halide followed by (ii) sublimation of the copper halide. This ability to etch indicates the existence of a strong, electronegative bond, though exactly how this bond affects the lateral mobility of the atoms on the copper (100) remains unclear. In this respect, Fishlock and Altman's experimental data conflicts considerably with each other.

Figure 4-11 illustrates the main findings from Fishlock and co-workers. For bromine atoms adsorbed on the Cu (100) surface, the atoms remain stable when imaged with low tunnel current set-points ($I_T$ set-point), (typically <1 nA), Figure 4-11 (b). If however, the $I_T$ set-point is increased beyond a particular $I_T$ threshold value, the atoms are manipulated and slid across the surface with atomic precision. The individual bromine atoms were reported to be imaged by STM as either, sombreros, or as hollows.

In direct contrast, Altman’s LEED data indicated that the formation of a c-(2x2) pattern immediately upon the dissociative desorption of bromine, they argued that thermal fluctuations in the adsorbed layer prevents the structure from being observed with STM until coverages of approximately 80% are reached. The discrepancy between LEED and STM data was explained by the authors as fluctuations in the adsorbed layer, which are quick with respect to STM scan rates, but slow compared to electron-ion interaction time for diffraction.

To determine the characteristics and properties of isolated bromine atoms on a copper (100) surface, we dosed a copper (100) surface in a fashion similar to the above authors, with increasing quantities of Br$_2$ up to monolayer saturation. This data series was then recorded as a set of STM images vs dosage.
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Figure 4-11 (a) Manipulation of bromine atoms on copper (100) at RT, as reported by Fishlock, Oral, Egdell, and Pethica. The authors report that the manipulation mechanism responsible for the atom movement was a tunnel current density mechanism causing localised heating. In figure (a) location (i), the $I_{set-point}$ is temporarily changed to 3 nA, the tunnel current threshold identified in this system for inducing the onset of adatom motion. Once sweeping occurs, the authors, could then “drop the atoms off” at will, location (ii). (b) The key criteria in energy terms for performing these experiments were that $E_{TIP} \chi > E_B >> k_B T$. i.e the authors unveiled a manipulation system that was stable yet manipulable. The key problem with the result however, is that considerable experimental evidence suggests the species moved are not bromine atoms.

Key questions of interest to this body of work include: what exactly is bromines appearance on copper (100), how and where does it bond to the copper (100) surface, how does it reconstruct, and importantly, is it mobile at RT?

Figure 4-12 shows a set of STM topographs of the copper (100) surface, exposed to ever-increasing bromine dosages. The first image in the series, Figure 4-12 (a), shows an undosed surface, displaying a characteristic 1x1 reconstruction associated with a clean copper (100) surface. Line scans of this image, taken along the [110] direction, reveal an interatomic spacing of 2.69 Å, as expected. The copper surface is then dosed using a homebuilt electrochemical cell, (explained in detail in section 3.7.1, with an 800 μAs dose.

Figure 4-12-(b) is an STM topograph taken immediately after this bromine dose, showing, little or no, discernable difference to image 4-9 (a). Line scans again taken in the [110] direction, again reveal an interatomic spacing of 2.69 Å. This indicates that the bromine atoms on the copper surface cannot be imaged with an STM at room temperature.
Figure 4-12 A sequence of STM topographs of copper (100) showing areas of equal size 5 x 5 nm. (a-d), illustrating the effects, exposing the surface to increasingly large dosages of bromine atoms has. Image (a) shows the atomically clean surface prior to dose. The surface has, as expected, a 1x1 structure, with an interatomic lattice spacing of 2.96 Å. The surface is then dosed with bromine atoms, using a homebuilt halogen cell described in section 3.7.1, image (b). No new adatoms are seen on the surface. Rather the 1 x 1 copper lattice structure is retained and the interatomic spacing remains intact at 2.96 Å. The surface is then dosed with more bromine, this time with a 2000 μAmpsec dose, image (c). Again however, the surface retains its 1 x1 structure and interatomic spacing. The final dose, 6000 μAmpsec, is found to alter the surface. The surface now reconstructs to a c-(2x2) periodicity, indicating a bromine reconstruction. The absence of any images showing isolated bromine atoms, prior to full monolayer saturation is highly indicative that the atoms are mobile at RT. This is in direct conflict with Fishlock and co-workers’ results [32], but is supported by Altman’s findings [30].
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Figure 4-13 Line profiles of the increasingly bromine dosed copper (100) surface. The interatomic line profiles, taken along the [110] direction, for 10 consecutive atoms, indicate if an atomic rearrangement has occurred. (a) The interatomic spacing for the clean substrate copper atoms is 2.96 Å as expected. (b) and (c) Do not change as the surface is dosed with sub-monolayer coverages of bromine atoms. (d) Only when near monolayer coverages are achieved, does the surface reconstruct to form the c-(2X2) Cu:Br phase.

Upon further dosing of the copper surface with bromine atoms, this time with a 2000 μAsec dose, Figure 4-12 (c) again shows obvious or identifiable change. An associated line scan shown in Figure 4-13, again indicates that the interatomic spacing between ten consecutive atoms remains identical to the clean copper surface. So where, are the bromine atoms?

The bromine dose has either been (a) unsuccessful or, (b) the bromine atoms are present, but cannot be imaged with STM at RT. One point to note is the apparent increase in "noise" once the surface has been dosed. This "noise", observed as bright speckles in Figure 4-12 (b), may be Br atoms interacting with the tip apex during scanning. This indicates that bromine atoms could in principal, be seen with STM.

Imaging the surface after even higher bromine dosages, 6000 μAsec, Figure 4-12 (d) results in a c-(2x2) pattern being observed. This pattern is the bromine reconstruction. This experimental finding which was reproduced many times over with both this and different bromine dosing cells. This, along with mass spectrum data, and STM studies of bromine dosed silicon (111) 7x7 surfaces, indicates that bromine
atoms are definitely produced with the electrochemical cells. Why then, are bromine atoms not visible on copper (100) at low coverages, with STM at RT?

A density functional theory (DFT) study by Kenny et al. investigated the mobility of bromine on the (100) face of copper. They calculated that the barrier for bromine hopping between adjacent hollow sites along the [011] directions via the twofold saddle points is estimated to be 0.23 eV, and that the barrier for hopping along the [010] directions via on top sites is only 0.37 eV. These low barriers to motion between hollow sites indicate that imaging low coverages of Br on copper (100) at room temperature is not possible, thus supporting Altman’s findings. Recognising that their results contrasted greatly with Fishlock’s experimental results, Kenny et al. went on to suggest that features previously attributed to Br atoms in the four-fold hollow sites as seen in Figure 4-11, were in fact, bromine atoms bound inside surface vacancy sites. This, it was thought, could reduce mobility enough to account for the experimental and theoretical discrepancy. The explanation put forward by Kenny and co-workers fails to account for why neither Altman, nor our work, finds similar species, i.e. hollows and sombreros, after bromine dosing. To investigate the appearance and mobility of bromine a little further, we performed low temperature STM imaging.

4.7 Low Temperature STM

From a simple Arrhenius type picture of adatom diffusion, it is expected that bromine mobility on the copper (100) surface ought to be reduced logarithmically with respect to $k_BT$. Thus, it is expected that reducing the temperature to approximately 50 K will result in the bromine species hitherto, unseen as isolated atoms, should become sufficiently immobilised to be imaged with STM. Figure 4-15, a through d, shows a sequence of images whereby an initially clean copper surface is imaged, then dosed and imaged at RT, then cooled to circa 75 K and imaged, and then allowed to reach RT where once again, it is imaged. Figure 4-15 (a) is a clean copper surface with its characteristic reconstruction displaying no particular anomalies. After dosing the surface with 2500 μAsec of Br₂, Figure 4-14 (b) mirrors previous findings by showing no vivid signs of reconstruction or dosing. Without any additional treatment or dosing, the sample is then cooled to 75 K where again, the bromine dosed surface is imaged.
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with STM. Now however, single white (false colour scale where white indicates high tunnel current) protrusions are observed, indicating that the mobility of bromine has been quenched as a result of a reduction in thermal energy, Figure 4-15 (c). At low coverage and low temperature, STM images confirm that molecular Br$_2$ does in fact dissociatively chemisorb on the (100) surface of copper. There is no sign of the hollows or sombrero structures seen by Fishlock and co-workers [32], with only bright protrusions measuring only 0.56 ± 0.015 nm wide and 0.051 ± 0.011 nm high with respect to the underlying lattice. This is considerably less than the measured values for either of the aforementioned structures.

![Figure 4-15](image)

Figure 4-15 Bromine mobility as a function of temperature.

At these temperatures and coverages, atomic resolution of the copper lattice was not achieved. Thus, a direct observation in real space preferred binding site is not achieved. A significant increase in adatom density at step edges and defects is observed, with the randomly dispersed bromine atoms showing no signs of atom coagulation, or nanostructuring, Figure 4-15 (c).
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Figure 4-16. The influence of substrate temperature on the diffusion of atomic bromine on the copper (100) surface.

Figure 4-16 (a) shows three STM topographs of diffusing bromine atoms at 75 K, ≈ 90 K and at RT. Even at the lower temperatures, adatom mobility is still not completely quenched. As the temperature is increased to 90 K, bromine atoms are still seen during STM scans, though now, the bromine atoms appear as trails, Figure 4-16 (b). When the dosed surface is finally returned to room temperature without any additional treatment, the bromine species are again invisible to STM, Figure 4-16 (c).

4.7.1 Conclusion

It is evident that the ability to see bromine atoms with STM is, as expected, temperature dependent. Based on the experimental data shown, it is projected, that the thermal threshold for stable bromine imaging with STM is approximately 50 K. At these temperatures the thermal energy is 0.0043 eV, giving stability lifetimes in the $10^{10}$ second regimes. At these timescales, atoms will easily be stationary in comparison to scan times of circa 180 seconds.

At room temperature the thermal energy rises to 0.026 eV, inducing a hop frequency of approximately 68,000 hops/sec. Considering the scan takes 180 seconds, and that the bromine lifetime in one site is now reduced to approximately 15 μsecs, this shows, that bromine is in fact too mobile to be imaged with STM at RT.

The sombrero and hollow in Fishlock’s nature publication attributed to stationary bromine atoms is therefore believed to be incorrect. Low temperature STM
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topographs indicate that single protrusions, which scale with dose, and appear only after bromine dosing (corroborated later with Silicon data, and detected with a mass spectrum analyser) is in fact how bromine appears on copper (100) to an STM. The sombreros and hollow the authors imaged, are, it will be shown later, in fact thermally produced, and believed to have no relationship whatsoever with bromine.

The key query of this set of experiments, i.e. to determine if the adsorbate substrate system could be used as a RT manipulation system has been answered. In direct conflict with the results of Fishlock and co-workers \cite{Fishlock}, it is found that the energy condition \( E_{T \beta} < E_B > k_B T \), is not met, specifically \( E_B \gg k_B T \) does not hold, and as such, the bromine-copper (100) system is not suitable as a RT manipulation system.

4.8 Adsorbate-substrate system (ii): Silicon (111)-7x7: Br

The failure of the first adsorbate-substrate system (Copper (100):Br) to meet the energy requirement, \( E_B \gg k_B T \); coupled with the lack of a single suitable alternative identified in literature, section 4.5, led to the consideration of more reactive substrates. Silicon (111)-7x7 is a well-characterised substrate, readily prepared for ultra high vacuum (UHV), which has highly directional and energetically discrete bonds around \( E_F \). Furthermore, it is widely reported that many adsorbates are stationary at RT on the substrate \cite{Silicon1, Silicon2, Silicon3}, but importantly for this body of work, some have reportedly been manipulated using STM \cite{Silicon1, Silicon2}.

4.8.1 Preparation

Silicon (111) spontaneously reconstructs into a 7x7 superstructure, with terraces in excess of 100 nm routinely prepared using standard thermal annealing procedures. To degas both the sample and holder, samples are initially heated in UHV overnight to approximately 600 K. Following outgassing, the silicon sample is then flash annealed to 1100 K removing an atomically precise, and protecting, oxide layer. The oxide layer is grown in ultra clean environments on the clean silicon surface ensuring that any potential contamination is confined to residing on top of this layer. By removing this layer, unwanted contamination is simultaneously removed and pumped from the chamber. The preparation continues with a slow reduction in sample temperature to room temperature (RT), encouraging high adatom mobility, and
ensuring that terrace growth proceeds at an optimum pace. Over or under flashing can lead to melting or a failure to remove the oxide layer, respectively. Careful attention to dopant levels should be exercised since these values affect the flash and annealing temperatures from one sample batch to another. Under UHV conditions, the samples remain clean for approximately two days, after which time they are reflashed, or replaced.

Figure 4-17 (a) Top view of the dimer-adatom stacking DAS model for the 7x7 reconstruction of the Silicon (111) surface. The unit cell consists of (i) twelve adatoms (large black circles) (ii) six rest atoms (small black circles), (iii) one corner hole, and (iv) nine dimers per unit cell (marked by the shaded circle). (b) Side profile highlighting the physical height difference of the surface atoms with special attention drawn to the depth of the cornerholes. (c) STM topograph taken in constant current mode showing the 7x7 unit-cell. The image is of the unoccupied orbital's. (d) Line-profile taken along the longitudinal direction of the unit-cell as indicated by the red line in (a) and (c). There is a small, difference in the recorded heights of these adatoms. The rest atoms are also detected (ii)

4.9 Silicon (111)-7x7 surface

4.9.1 Physical properties

The silicon (111)-7x7 surface is perhaps the most complex and widely studied substrate in all of surface science. It is now generally accepted that the geometry of the 7x7 surface is well described by a dimer-adatom-stacking fault (DAS) model, as
originally proposed by Takayanagi. The DAS model for silicon (111)-7x7 surface shown in Figure 4-17; consists of 12 adatoms (large black circles) Figure 4-17 (a)-(i); six rest atoms laying one layer below the surface (smaller black circles) Figure 4-17 (a)-(ii); and a single corner-hole in each unit cell, marked with the shaded circle Figure 4-17 (a)-(iii). Together, these nineteen atoms account for the nineteen unbonded electrons on the reconstructed surface. Hollow circles mark the remaining atoms of the first bilayer below the surface. Nine dimer pairs surround each triangle of the first bilayer Figure 4-17 (a)-(iv). The stacking sequence in the right half of the unit cell is the same as in the bulk, while the stacking sequence in the left half, is faulted. The deep corner hole with its dangling bond is one full bilayer below adatom surface.

Cleavage of the surface results in the 2x1 phase, which is annealed to achieve the 7x7 structure. Theoretical calculations by Brommer et al. indicate that the 7x7 structure is 60 meV more favourable than the naturally cleaved 2x1 structure. The same author also found, that the first surface layer relaxed outwards, while the second layer was compressed. For a review of the exact rearrangements of each atom, the reader is referred to excellent independent works by Brommer and McEllistrem.

4.9.2 Electronic structure

STM has been used to probe the electronic structure is real space. Examining the unoccupied half of the unit cell one observes the 12 adatoms of each unit cell surrounded by four deep cornerholes, Figure 4-18 (b). The adatoms on the faulted and unfaulted halves appear to have equal heights, resulting in a flat ring of six adatoms surrounding each cornerhole. For topographs of the occupied electronic states however, one also observes the same twelve adatoms per unit cell surrounded by four corner holes, but with several additional features present, Figure 4-18 (a). Rest atoms are now visible as light regions between adatoms, particularly on the unfaulted half of the unit cell. Adatoms on the faulted half appear brighter than their counterparts on the unfaulted half. This effect is particularly noticeable when looking at the adatoms surrounding each cornerhole. Corner adatoms Figure 4-18 (a)(i) appear higher than centre adatoms Figure 4-18 (a)(ii) within the same triangular cell. The faulted and unfaulted halves have a height difference of \( \approx 0.04 \) Å. This height...
difference, is a function of voltage; falling with decreasing voltage. This phenomenon, and the surface in general, is better understood by taking a closer look more at the electronic structure of the surface.

Figure 4-18 Two STM topographs of the same surface area taken at different bias voltages. The different voltages allow for the examination of both the filled and empty surface states. (a) Faulted (F) and unfaulted (UF) halves of the unit cell are clearly visible. Rest atoms (RA) are also visible as light regions between adatoms, particularly on the unfaulted half of the unit cell. Adatoms on the faulted half appear brighter than their counterparts on the unfaulted half. (b) Same region of space, showing the 12 adatom dangling bonds.

4.9.3 Electronic structure and reactivity

As previously mentioned, breaking bonds with an STM tip requires an understanding of the bonds around $E_F$. Chemisorption of adatoms on Si (111)-7x7 depends on variety of factors especially electronic effects, which typically dictate the existence and magnitude of activation barriers, steric constraints, and surface diffusion. It is well known that the valence electrons of surface atoms not involved in covalent bonding, referred to as dangling bonds, constitute active sites for surface reactions. Dangling bonds thus largely determine the chemical properties of the surface. STM can provide information about a range of states beginning or ending at the $E_F$. Hence, it is possible to subtract two images to find information about particular surface states.
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Hamers, Tromp and Demuth\textsuperscript{[332, 333]} first performed this on Si (111)-7x7 and identified three surface states; an adatom state at -0.35 eV, a rest atom state at -0.8 eV and a backbond state at -1.7 eV.

In an elegant STM study of NH\textsubscript{3} decomposition on the Si (111)-7x7, Wolkow and Avouris\textsuperscript{[334]} have shown that among all the silicon atoms with dangling bonds, the Si rest atoms are more reactive than Si adatoms and the centre adatoms are more reactive than the corner adatoms. STS spectra obtained by the same authors indicated that the rest atoms are more reactive because they transfer extra charge to the neighbouring adatoms and thus react with NH\textsubscript{3}. The dangling bond of the adatoms appears to be more delocalized with a low DOS at the adatoms site leading to lower reactivity.

Theoretical results from Brommer and Joannopoulos\textsuperscript{[336]} confirm these findings. These authors calculated the charge capacity for the different atoms on the Si (111)-7x7 surface, finding, that the charge capacity order of the surfaces is as follows:

<table>
<thead>
<tr>
<th>Surface donor capacity:</th>
<th>corner hole &gt; rest atom &gt; adatom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface acceptor capacity:</td>
<td>adatom &gt; corner&gt; rest atom</td>
</tr>
</tbody>
</table>

**Table 4-1** Relative charge capacity for the different surface atoms on the Silicon (111)-7x7 calculated by Brommer \textit{et al.}\textsuperscript{[336]}

<table>
<thead>
<tr>
<th>As a donor</th>
<th>Faulted rest atom&gt; unfaulted rest atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>As an acceptor</td>
<td>Faulted centre adatom&gt; unfaulted centre adatom</td>
</tr>
</tbody>
</table>

**Table 4-2** Comparison of the faulted and unfaulted halves of the unit cells

Based on these calculations, the authors then determine reactivity as a function of adsorption site and incoming species. They found that electrophillic attacking groups interact in favour of corner hole > rest atom > adatom. The corner hole and rest atom reactivities are strong while the adatom reactivity is relatively weak. Nucleophillic
groups on the other hand, interact mainly through the adatoms; to a lesser extent with the corner holes, and most weakly with the rest adatoms. Among the seven different dangling bond sites, the corner hole is unique in exhibiting a strongly for electrophillic reactants as well as exhibiting some reactivity for nucleophillic reactants. Adatoms are more selective towards nucleophillic, while the rest atoms are strongly reactive towards the nucleophillic species the rest atoms are weakly reactive towards the electrophillic species.

Considering the effects the stacking fault has on the reactivity of the Si (111)-7x7 with respect to donor capacity, there is a clear distinction between reactivity at the faulted and unfaulted halves. Electrophiles should prefer to bond with the faulted half of the surface, and in particular, the rest atoms. With respect to acceptor capacity, no strong selectivity between the faulted and unfaulted halves is found.

To classify the reactants as donor or acceptors, the electronegativity between the surface and the reactant is determined, and if negative, the reactant is the acceptor and the surface is the donor. If the difference is positive, these roles are reversed. The surface electronegativity is the work function 4.8 eV.

4.10 Silicon (111)-7x7: bromine

Bromine is deposited at low coverages using an in-situ electrochemical doser, and because of the corrosive action of halogens on ultra high vacuum components, a homebuilt solid state electrochemical source for the generation and dosing of submonolayer dosages of bromine was constructed, section 3.7.1. The cell is based on a design by Spencer et al. [198] and its successful operation is verified with real time mass spectrum data taken during cell operation, Figure 4-19. The cell’s output was calibrated during experiments on Silicon (111) 7x7, by counting individual atoms per dose, and is found to be proportional to the electrochemical cell current multiplied by the dose time, Figure 4-20.
Energetics of a room temperature manipulation system

Figure 4-19 Time dependent mass spectrum graphs illustrating the production both atomic and molecular bromine at 80 and 160 atomic mass units (a.m.u) respectively. (a) Taken just prior to the "dosing", indicating the UHV chamber is devoid of any bromine. (b) Mass spectrum taken during cell operation of the halogen cell, indicating the abundant production of Br$^2$ molecules. (c) Just following the bromine dosing, the most prevalent species then appears to be atomic bromine.

Figure 4-20 Plot of monolayer coverage as a function of bromine dose. The coverage is calculated as the number of adatoms sites which have reacted with bromine adatoms as determined by the number of bright protrusions. An exponential fit line has been used to fit the data.
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Figure 4-21 Two 20 nm x 20 nm STM topographs of the unoccupied states of Silicon (111)-7x7 taken in the constant current mode. Typical tunnelling parameters of 2 V and 0.03 nA are used. (a) STM topograph of the surface just prior to bromine dosing. The 7x7 structure is visible, and the presence of some vacancies are noted. There are no bright protrusions (indicating increased tunnel currents) which we associate with bromine atoms. (b) The surface following an 400 μAmps dose of bromine. The surface is now dotted with many bright features, which we assign to bromine. The bright features appear as single species and pairs. The neighbouring pairs appear to be separate from each other, indicating that the incoming bromine dissociatively chemisorbs upon reaction with the surface.

4.10.1 Room temperature STM:
Like hydrogen, atomic bromine only requires one electron to form a closed shell configuration, so it readily terminates surface dangling bonds. Figure 4-21 (b) shows an unoccupied state STM image following exposure to 400 μAsecs of bromine. The image is speckled with bright features which we associate with the adsorption of bromine atoms at adatom sites. The 7x7 reconstruction remains intact up to saturation, and the number of bright features is observed to scale with bromine dose. Analysis of the bright features indicates that both single atoms (i) and pairs (ii) of bromine atoms appear on the surface. It is believed the pairs are unbonded bromine atoms due to their interatomic separation and apparent cloud density separation which is indicative of a dissociative chemisorption process. The single-to-pair ratio is found to be 65:35. Analysing site specificity and I-V spectroscopy we now investigate how bromine bonds to the silicon (111)-7x7 surface.
Kummel and co-workers [236] have related adsorption site preferences to chemisorption and reactivity. They surmised that abstractive chemisorption producing a single chemisorbed halide atom always prefers centre adatom adsorption, indicating that the site with the lowest electron density is more reactive. Similarly, dissociative chemisorption producing a pair of chemisorbed halide atoms also showed extreme preference for the closest neighbouring pair of centre adatoms.

To the contrary however, experimental evidence by Boland [236], Weaver [237] and Mochiji [183, 338-340] fails to support Kummel’s results. These authors independently show that adatom occupancy is random. Statistical analysis of bromine distribution in our STM images indicates an almost equal occupancy of both corner and centre adatoms at, 54%:46%. How the impinging bromine’s form (molecular or atomic) affects the result at present remains unclear. Kummel’s source was molecular bromine, whilst halogen cell use is expected to be primarily atomic bromine. Analysis of our mass spectrum data shows we usually observe atomic bromine, though as seen in Figure 4-19, molecular bromine is also occasionally observed. No preference for vacancy or atomic steps is observed suggesting that thermal diffusion of bromine is insufficient to allow sampling sites of higher reactivity.

At low coverages, Boland [236], and Mochiji [183, 338-340] expect adatom sites to be the exclusive adsorption site, with STM [183, 338-340], and photoelectron studies [341] indicating that rest atom sites do not serve as adsorption sites for molecular chlorine. Despite this, our experimental data suggests that bromine bonds at more than one dangling bond site on silicon (111) 7x7.

Simultaneously acquired STM images taken at 2 and 3 volts above $E_F$ respectively produce significantly different images as seen in Figure 4-22. Using this voltage dependent imaging technique, we identify three different voltage dependencies, indicating that three different adsorption sites or, that three different species exist. All three features scale with dosage, indicating they are bromine related.

The three voltage dependent effects are summarised as features whose appearance with respect to increasing voltage is: (i) dark (2V) to bright (3V), (ii) dark (2V) to regular (3V) and (iii) regular (2V) to bright (3V). Effect (ii) is the most common feature observed, and the ratio of effect (i) to (iii), is 1:4. No site preference was noted for any of the bond types that were observed.
Simultaneously acquired STM topograph images at: (a) 2 V. and (b) 3 V. Both images show the unoccupied states with bromine dosed surface. The voltage dependent features which scale with bromine dose, are (i) depression-to-bright, (ii) depression-to-regular and, (iii) regular-to-bright This is indicative of multiple species, or multiple bonding sites of atomic bromine.

Effect (i) was previously observed by Weaver, Mochiji and Boland independently. Images of this bond type, dark to bright, indicate that the density of states (DOS) in the energy window 0-2 eV above $E_F$ has been reduced, whilst the DOS in the energy window 0-3 eV above $E_F$ has been increased with respect to the normal silicon adatom dangling bond site DOS. As discussed by Boland and Villarubia for chlorine interaction with Si (111)-7x7, the occupation of silicon dangling bond states, reduces the electron density near $E_F$, so the dangling bond adsorption site appears dark relative to unreacted sites when imaged at 2 V.

If the same area is then imaged at 3 V, the features become bright. Bonding states or anti-bonding states (negative/positive sample bias) formed by the interaction of the Br 4p orbital and the Si adatom dangling bond state can be accessed so the sites now appear bright. Boland stated for chlorine bonding on silicon (111)-7x7, that, tunneling at these biases is into the tail of the Br derived $\sigma^*$ bond which disperses in a band extending from 2.4 to about 6 eV above the Fermi level. This state may undergo additional broadening due to hybridization with the bulk states. $I$-$V$ spectra taken on a clean adatom site, shows a peak just above $E_F$ arising from the adatom dangling

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**Figure 4-22** Simultaneously acquired STM topograph images at: (a) 2 V. and (b) 3 V. Both images show the unoccupied states with bromine dosed surface. The voltage dependent features which scale with bromine dose, are (i) depression-to-bright, (ii) depression-to-regular and, (iii) regular-to-bright This is indicative of multiple species, or multiple bonding sites of atomic bromine.
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bond state. I-V spectra over corresponding reacted sites are almost completely absent.

**Figure 4-22** also shows the second voltage dependent process (labelled (ii), i.e. a dark site becoming a “regular” site. Weaver *et al.* suggested that such features may reflect adsorption at rest atom sites, which Wolkow and ourselves found to be more reactive than adatom sites. Bromine adsorption in this layer should reduce the electron density near the Fermi level affecting tunnelling conditions. Bright spots would not be seen at higher voltages because the tip cannot directly access the rest layer atoms. Bonding to rest atoms on silicon (111) 7x7 has also been suggested by Tanaka *et al.*

The last effect, i.e. effect (iii), a regular appearing site, that is, an unchanged DOS between 0-2 V, showing an increased DOS in the energy window between 0-3 V, has never been discussed in literature to my knowledge. In this effect, no perturbation of the STM image is observed at low biases, though, bright species are clearly visible at higher voltages. Such an effect may arise if the bromine atom is bonded to a state not significantly contributing to STM images under standard imaging conditions, i.e. 2 V. In this scenario, the bromine species would not be visible at 2 V, but would appear bright at 3 V once tunnelling into a higher energy state commenced. The precise nature of the bond however, remains unclear at present.

In addition to producing three different voltage dependent features with STM, simultaneously acquired force-gradient and tunnel-current images using a nc-AFM/STM show that some bromine species are invisible in STM constant current topographs but clearly visible in force gradient images. That species are invisible in STM is not uncommon, nevertheless, in conjunction with STM evidence that heretofore unaccounted for reaction products exist, a revision of thought on the interaction of atomic bromine with the silicon (111)-7x7 surface is surely required.

The implications of this rich array of bonding types is expected to be reflected in the success rates and destabilisation mechanisms employed during controllable bond-breaking, i.e. manipulation. One should not for example, expect an equal success probability for manipulating species embedded between the rest atom layer and the adatoms, as a species sitting on-top an adatom.

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11 Unpublished data by Özer, O'Brien, Norris, Pethica.
In summary, the interaction of bromine with the silicon (111)-7x7 surface has provided an atomic adsorbate which is stable at room temperature (RT). The species is dissociatively chemisorbed, but due to the density at step edges being equivalent to terrace sites, it is believed, that the adsorbate can not diffuse sufficiently at RT to sample higher reactivity sites. This is a significant result with respect to RT-SPM manipulation.

No sign of a serious selectivity for centre or adatom sites is observed, though bromine is believed to interact with multiple dangling bond sites, namely adatoms sites, rest atom sites, and possibly backbond sites. This, in combination with nc-AFM/STM data indicates a rethink of the bonding nature is required.

The nucleophillic bromine preferentially reacts with the rest atom sites (dark-to-regular), followed by a possible backbond incorporation (regular-to-bright), and finally with the adatom sites (dark-to-bright). These results are supported, wholly or in part, by the independent works of Avouris, Brommer, Tanaka, Weaver, though it conflicts with Boland’s summation that adatoms are the exclusive bonding site. The bond types, energies and orbital’s involved suggest the Si-Br bond is in excess of 4 eV. Whilst the energy condition \( E_B \gg k_B T \) has clearly been met, whether or not the second energy consideration, i.e. that the STM tip can deliver sufficient energy amounts to move the species, \( E_{\text{tip}} > E_B \), is now investigated.

4.11 RT-STM Manipulation of bromine on silicon (111)-7x7

In addition to demonstrating a promising new technique for device fabrication 1.4.1, atomic manipulation using STM, provides a unique means of probing the physical and electronic properties of surfaces. The silicon 7x7 unit cell, Figure 4-17, features a rich array of chemically-inequivalent adsorption sites, so by determining site-specific hopping rates, one may be able to determine spatially-inhomogeneous reactivity, binding energy, and the site-specific atomic chemistry.

In 1993 John Boland reported the successful manipulation of chlorine atoms on the Si(100)-(2x1) surface. Like the Si (111)-7x7:Br system, chlorine is strongly chemisorbed at dangling bond sites (\( \approx 4 \) eV), nevertheless, using an STM, Boland hopped chlorine atoms between adjacent adsorption sites.
The origin of this behavior is reported to be an interaction between the field of the probe tip, and the dipole moment of the silicon-chlorine bond. Chlorine atom migration is then facilitated by the presence of an energetically unfavorable, metastable chlorine bridge-bonded minimum, which lowers the barrier for atom migration between neighboring sites. The STM probe is used to excite chlorine atoms into this bridging configuration, resulting in a local population inversion. Selective application of voltage pulses between the probe tip and the surface, also rearranged the local bonding, and induced transformations between different types of chlorine sites. No directional control or total sweeping motion was observed.

Injection of tunneling electrons and holes from the probe tip of an STM was found to enhance the hopping motion of Cl atoms between neighboring dangling-bond sites of Si dimers on Si(1 0 0)-(2 x 1) surfaces by Maeda and co-workers. The rate of hopping was found to increase linearly on the injection current. The hopping rate formed peaks at sample biases of +1.25 and -0.85 V, which agree with the peaks in the LDOS spectrum measured by STS. The Cl hopping was enhanced at Cl-adsorbed sites even remote from the injection point. These findings were interpreted by the model, that the holes injected primarily into a surface band originated from the dangling bonds of Si dimers propagate quite anisotropically along the surface becoming localized at Cl sites which somehow destabilises the Si-Cl bonds, inducing hops of the Cl atoms. The electrons injected into a bulk band propagate in an isotropic manner and then get resonantly trapped at Si-Cl antibonding orbital's, resulting in bond destabilization and hopping of the Cl atoms. Control of the length and direction of the hop manipulations, was not achieved.

Weaver and co-workers reported the manipulation of bromine atoms. Tunneling electrons from the tip of an STM was used to induce adatom hopping on Br-terminated Si (100)-2x1 at low current and without voltage pulses. Contrary to Maeda's results, hopping did not occur in their case when electrons tunneled from the sample to the tip. The threshold energy is 0.8 V, and tunneling spectroscopy shows antibonding Si-Br states 0.8 eV above the Fermi level. Electron capture in these states is a necessary condition for hopping, but repulsive adsorbate interactions that lower the activation barrier were also required.
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Figure 4-23 Two STM topographs taken in the constant-current imaging mode, demonstrating RT manipulation of bromine atoms. For successful manipulation, the tunnel current set-point was increased from 0.2 nA to 7 nA thereby increasing the manipulation success rate. Increasing the voltage was not found to increase the success, indicating localised heating is not the responsible mechanism of manipulation. High voltages unsuccessfully employed in attempts to increase hop rate indicate an electric field based mechanism is not involved. Rather it is thought, a force gradient between the STM tip and the bromine atoms is responsible for bromine manipulation. (a) STM image before the manipulation attempts. (b) STM image taken during the manipulation events (i-v). Several atoms are manipulated. Controlled sliding is not observed. Atom specific sliding is not achieved.

Such interactions are strong near saturation for Br but are insufficient when the coverage is low, or when Br was replaced by Cl. The authors thus demonstrated that atomic manipulation could be accomplished through a combination of electron capture in long-lived resonance levels, and inherent adsorbate repulsive interactions. Control of the direction and the length of the diffusion events was not achieved.

We attempted to manipulate bromine atoms on the silicon (111)-7x7 surface using a range of different destabilizing strategies. The first control parameter utilized for manipulation was the tunnel current set-point ($I_{\text{set-point}}$). Increasing $I_{\text{set-point}}$ may increase the localised heating rate or increase the tip surface force gradients. Figure 4-23 shows the successful hopping of bromine atoms at room temperature. We now examine the mechanisms involved in this RT manipulation.
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4.11.1 Tunnel-current control of the manipulation rate

Figure 4-23 is a pair of constant current topographs demonstrating RT manipulation of bromine atoms on silicon (111)-7x7. The first image, Figure 4-23 (a), shows the silicon surface just prior to manipulation. Figure 4-23 (b) is an STM scan taken during RT manipulation in which bromine atom hopping is observed. The hops are detected as atoms in new binding sites, when compared to the previous scan, but are not observed “live”. This is indicative of an induced diffusion-type manipulation mechanism, in contrast to a well controlled and directed manipulation mechanism. Manipulation “trails” are not observed and atom specific hopping is not achieved. 100% movement of all species can not be induced, so consequently, no structures could be constructed. The STM probe typically breaks during this manipulation mode, especially so, if the $I_{set-point}$ is increased beyond 7 nA, Figure 4-24. Occasionally the tips broke before this set-point value. Manipulation was not even guaranteed to occur at this set-point value, and commonly the tip broke before any manipulation was achieved at all.

At higher $I_T$ set-points, say 15 nA in Figure 4-24 (b), manipulation of bromine atoms is now occasionally seen “live”, and identified as slice shots in the STM image, Figure 4-24. This is indicative of a move from a diffusion type hop mechanism of manipulation, to a force-type, push or pull manipulation mechanism. Again however,
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no positional control is achieved and rather quickly after beginning scanning at these

tunnel current set-points, the tips typically break, Figure 4-24 (c).

In summary, bromine atoms can be moved using tunnel current as the control

parameter. Unfortunately, such manipulation attempts are typically accompanied by
tip failure/rearrangement. When tips break, the manipulation work area is typically

lost, and can most often not be re-found. Furthermore, the low manipulation yield

exclusively at a small range of high tunnel current set-points (low tip-surface
distances, often accompanied by tip failures), means statistics quantifying

manipulation success as a function of tunnel current then can not be calculated. Thus

the usefulness of this technique, for device construction or fundamental physics

analysis, is limited at present.

If on the other hand, the threshold values for manipulation can be lowered to

facilitate increasing the range of values which induce manipulation; this might permit

the development of meaningful parameter-success relationships, and increase the

adsorbate-substrate systems usefulness as a manipulation system.

4.11.2 Anti-bonding destabilisation

To develop a better understanding of the manipulation process involved in moving

bromine atoms on the silicon (111)-7x 7 surface, voltage dependent tunneling was

performed. Specifically, the transformation in STM images scanned at 2 V, versus

images scanned within the 0-3 V energy window, from dark-to-bright, was of interest,
since the dark-to-bright transitions occur as a result of the opening of new tunnelling

channels within the 2-3 eV energy window with respect to \(E_F\). As independently

reported by Boland \cite{245} and Weaver \cite{247} such channels open because of the accession
to anti-bonding states lying within this energy region, section 4.10. As reported by

Weaver, tunneling into anti-bonding states, causing the capture of electrons in the

anti-bonding state results in a repulsive potential, which reduces the hopping barrier.

With Weaver' results in mind, we repeated the STM manipulation experiments

outlined above, at 3, 4 and 5V. Scans at various different \(I_T\) set-points were performed,
up to 20 nA \(I_T\) set-points, however, under no condition was a significant increase in

manipulation probability is observed, as a function of voltage.
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Figure 4-25 Three STM topographs taken at standard tunneling conditions (2 V, 0.02 nA). (a) X1 indicates the exact location where a current-voltage (I-V) pulse is applied between the tip and sample. (b) (i) Indicates the manipulation (possibly desorption) of one bromine atom. The absence of a bright spot was generally believed to infer the physical manipulation of bromine atoms, though it should be pointed out that bond manipulation was more commonly observed, i.e. the voltage dependency of the species changed from a dark-to-bright (with 2-3V imaging) to a species which changes in an alternative manner as outlined in section 4.10.1. This infers that the species may be forced from one bonding configuration to another. Again, no directional control is achievable, nor was it possible to reach high success rate (i.e. > 30%).

This a little surprising, since it conflicts with Weaver and Mochiji findings that tunneling into the anti-bonding states, destabilises the bromine atoms.

In summary, anti-bonding destabilisation is found in contrary to Weaver and Mochiji to have no net effect on the manipulation success rate.

4.11.3 Voltage-pulse manipulation

Application of voltage pulses between the probe tip and the surface, was found to rearrange the local bonding and induced transformations between different types of chlorine sites by Boland and co-workers. Magnitude and duration controlled voltage pulses were applied, in our set-up, by performing I-V spectroscopy as already, over bromine species on the silicon (111)-7x7 surface. This was performed by holding the tip above the bromine atom, controlling the distance with the tunnel current set-point; switching off the feedback; sweeping the voltage between a chosen range; after which; the feedback is turned back on; and the area is re-scanned to determine if the manipulation attempts have been successful, or not. Figure 4-25 is a set of three STM topographs taken in the constant current mode. The $I_T$ parameters are considered standard and non-perturbative, i.e. (2 V, 0.2 nA).
Figure 4-25 (a) indicates the exact location where a current-voltage (I-V) pulse is applied between the tip and sample, $X_1$. Figure 4-25 (b)-(i) is an STM topograph of the exact same region of space. Some atoms are seen in the same positions between the consecutive scans, so serve as markers or identifiers. Manipulation (possibly desorption) of one bromine atom has been successfully performed. The absence of a bright spot was believed to infer the physical manipulation of bromine atoms. It should be noted that bond manipulation was more commonly observed with this manipulation mechanism, in a fashion similar to that reported by Boland [50]. Again, however, no directional control is achievable, nor was it possible to reach high success rates (i.e. > 30%), and typically tips broke precluding the statistics gathering necessary to draw reliable conclusions regarding the manipulation process.

In summary, the failure of all manipulation modes to provide directionality or high success rates, coupled with the high probability of breaking tips in both the constant current, and voltage pulse techniques of manipulation strongly suggests that the energy condition, $E_{\text{tip}} > E_B$ has not, and can not, be attained. In effect, we have found a manipulation system, which is sufficiently bound at RT to enable us to see the species stationary for large enough periods of time, in which useful experiments can readily be performed. Despite this, the silicon-bromine bond between the 4s and 2p orbital’s, estimated to be 4 eV [50], is simply too large to facilitate quantitative, statistically sensible, manipulations, which leading to structure construction. As such, a new mechanism of coupling energy is required, or a new manipulation system needs to be investigated.

4.11.4 High Temperature STM Manipulation

The only moderate successes of the previous experiment’s ability to induce hopping motion of bromine atoms, coupled with the failure to manipulate atoms with multiple hops and directional control, led us to the concept of high temperature manipulation.

If insufficient quantities of energy cannot be reliably transferred from the STM tip to the bromine atoms, it seems that increasing the Si-Br energy by coupling thermal energy into the system may provide a mechanism, akin to Weaver’s use of repulsive inter Br interactions, of destabilisation in combination with the tip’s energy.
The final candidate, surface vacancies, is yet to be fully explored. It is widely reported that single vacancies are highly mobile on metal surfaces. But "stationary" larger vacancy clusters, are observed at RT and above. The principle problem with these structures however, is that whilst their centre of mass is stationary they constantly undergo periphery edge diffusion. In particular, Frenken and co-workers have reported impressive measurements of vacancy mobility, yet they too, have been unable to stabilise vacancies.

4.12 Adsorbate-substrate system (iii): Copper (100): ?

4.12.1 Introduction

Both adatoms and vacancies on copper (100) have been found to be unsuitable candidates for RT manipulation due to their high mobility. Despite this, Fishlock and co-workers’ Nature paper showed clear evidence that “something” was indeed manipulated on the copper (100) surface. So, what exactly did they manage to move?

The first idea involves one of the author’s own suggestion in a subsequent DFT paper acknowledging that the species manipulated were not solely bromine. The authors believed the species might be a complicated, complex mixture involving multiple species, possibly bromine inside a vacancy. Work on a similar type system, i.e. Indium inside a vacancy on the copper (100) surface by Frenken and co-workers, led to widespread acclaim because of the vacancy mobility data which was extracted. Their results provided experimental evidence that adatom and vacancy mobility could be altered when part of a complex. If this concept is applied to Fishlock’s data, then it must be presumed that only a single STM observable species exists, which scales with dose or vacancy concentration.

4.12.2 Fishlock’s results revisited

The Nature report by Tim Fishlock shows a single species being manipulated using STM. Figure 4-11. The authors did acknowledged however, that with different tips the bromine atoms could appear as either sombreros or hollows. Then, as was evident

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12 And reference therein
13 This review by Karina Morgenstern, offers considerable insight into the mobility of vacancy and adatom clusters on metal surfaces
from Figure 4-11 (a) and (b), the species would then be sufficiently stable and stationary at RT to remain still for prolonged periods of time, or, be deliberately moved with an STM tip. Taking a closer look at these results however, it is not clear to me that only one species exists.

Figure 4-26 is a pair of STM topographs taken in the constant current mode. The images both show some semblance of atomic resolution. From the images, it seems that species (i) i.e. the hollow, is smaller than species (ii) the sombrero. Furthermore, if they are indeed the same species, one may expect to occasionally see both in the same images, and witness flips from "conformation" type to the other.

Figure 4-26 Set of STM constant current topographs taken from Tim Fishlock's PhD thesis. They illustrate with high resolution a hollow (a) and a sombrero (b).
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Figure 4-27 (a) 50 nm x 50 nm STM constant current topographic image of copper (100) taken at RT. The three objects observed fail to form any recognisable reconstruction. With standard tunnelling parameters (0.03 V, 0.2 nA) the three objects remain stationary for prolonged periods of time making them potentially useful for device construction. (b-d) Adatoms, hollows, and sombreros respectively.

Despite this, no evidence of this was shown in Fishlock's PhD thesis. It was previously demonstrated the stationary species must be something other than bromine. Whilst trying to recreate the experiments of Fishlock and co-workers, and ensure the surface was as clean as possible before dosing with bromine, the sample surface was somewhat fortunately “over-prepared”. The results of this over-zealous preparation are shown in Figure 4-26 below. An explanation of exactly how the species are “prepared” is proposed in the following chapter, as are, their various different physical, electronic, and dynamic properties. But two clear results were found: (a) the species are stationary at RT, and (b) they could be manipulated, see chapter-6. As such it appears clear they are in fact the same species Fishlock had, and as such they meet our key energy requirement $E_{\text{tip}} > E_B \gg k_B T$. Thus we have succeeded in finding a stable yet moveable, manipulation system at RT.
4.13 Conclusions

Manipulating atoms at RT on semiconductor surfaces was found to be unsuitable for a statistics based analysis of the manipulation process. First, the highly directional covalent bonding typical for systems of interest to us, had rather large associated diffusion barriers (≈3-6 eV). Typically, this meant that electron stimulated-time limited destabilisation mechanisms such as electronic transition states, anti-bonding destabilisation, and/or vibrational excitations were employed in conjunction with a tip-apex related force or electric field gradient to controllably manipulate. Such complexity seriously inhibits reliable identification and/or quantification of the tip-species energy-coupling process. Second, whilst the chemistry and bond-types may have been manipulated with a variety of different mechanisms; the far simpler concept of atom displacement was difficult to achieve. Thus, hop success rates as a function of a parameter had small ranges from which little or no science could be extracted. Third, due to the high $E_b$ values already mentioned, STM tips usually broke during experiments. The failure of the adsorbate-substrates bond energy to lie within the key energy window, $E_{tip} > E_B > \gg k_b T$, proved a difficult hurdle to overcome even if extra stimulus, or energy source (e.g. thermal energy) was provided. As such, if ones desire is to quantify the manipulation process, using semiconductors may not be the best approach.

Attempts to recreate the experiments of Fishlock using bromine on copper (100) indicated that bromine was mobile at room temperature. Hence they key criteria, $E_B > k_b T$ can not be met. Furthermore, the species previously identified as sombreros and hollows by the same authors were in fact reproduced. Though the production was somewhat accidental their production was repeatable, and indicated the species in question have no connection with bromine at all.

Simultaneous nc-AFM/STM measurements indicate that circa 1 eV of energy can be reliably transferred into the adsorbate-substrate system. This it is expected is sufficient to reliably manipulate.
5 TUNEABLE AND MANIPULABLE NANO-LEGO

5.1 Introduction

Despite early achievements\(^6, 19, 32, 43, 53-55, 64, 120, 121, 241-247\), the construction and control of nanostructures on metal surfaces has been limited to either weakly bound atoms and molecules at low-temperatures or, to large molecules at high-temperatures. Molecules offer dynamic stability and occasionally, some functionality but organising them on surfaces is not so easy. Atoms on the other hand can be moved with relative ease ensuring that enough movements can be performed to develop structures, statistics and understandings regarding the mass transport and manipulation mechanism. On the downside, atoms are rarely tuneable or dynamically stable at RT. The development of a system which combines these advantages, i.e. has tuneable and functional properties, and is readily transported on metal surfaces yet is stable at RT is therefore of considerable technological interest.

The importance of Tim Fishlock’s\(^{125}\) RT manipulation results had little to do with the “bromine” atoms being slid. Rather, it was the manipulation mechanism and the temperature at which these experiments were performed at, that aroused so much interest. The temperature was relevant since it demonstrated that the world of atomic engineering was open for business for “real world” technology. Exactly what these species were was of secondary concern. This remained so until it was revealed later in our experimental findings that the species in question have interesting and controllable electronic properties, see section.

This chapter describes a method for reproducing stable, tuneable, yet manipulable “defects”\(^{14}\) at RT. Their physical, electronic, and dynamic properties are examined, and used as “evidence”, to develop a plausible picture of what the defects may be. A tentative model of the defects nature is discussed and a mechanism for their formation is proposed from analysis of this evidence.

\(^{14}\) The term defect is used from here on to identify the species whose identity is at this point unknown. Only if the species need to be distinguished from each other, shall I use Fishlock’s nomenclature, i.e. “sombrero” and “hollow”\(^32\). Fishlock, T.W., et al., Manipulation of atoms across a surface at room temperature. Nature, 2000. 404(6779): p. 743-745.
5.2 Defect preparation

Figure 5-1 is a 50 nm x 50 nm STM topograph of copper (100) taken at RT. Three different objects are observed; namely (i) adatoms, (ii) hollows and (iii) sombreros.

Figure 5-1 (a) 50 nm x 50 nm STM constant current topograph of copper (100) taken at RT. Three different defects are observed using standard tunnelling parameters (0.03 V, 0.2 nA). The defects remain stationary for prolonged periods of time, which is highly unusual on this surface at RT (i) Bright spots are interpreted as copper adatoms and are the most mobile of the three defects. (ii) et (iii) i.e. hollows and sombreros as seen by Fishlock. Here, they are seen concurrently, indicating that the defects appearance is not a tip related effect. This implies these are two different, distinct defects on the copper surface. They do not change from one form to another (i.e. sombrero \(\Rightarrow\) hollow), even after considerable excitation (see chapter-6).

These structures have been observed in at least two different UHV systems, with little physical or construction similarities, and/or, chemical history in common [32, 178, 324, 351]. The
defects are stationary for prolonged periods, and yet as we saw in the previous chapter, with increased tunnel current, they were manipulated. There appears to be at least two different defects, along with an adatom on the surface. The two defect types are inter-dispersed within the image indicating, in contrast to Fishlock's findings \[^{[2]}\], that their differing appearances is not a tip related artefact. Furthermore, the defects are not found to "flip"\[^{15}\] from one defect type to the other.

Revealing the defects source it was anticipated, could help reveal what exactly they are. Originally, the defects were reproduced in our lab somewhat serendipitously. With an accidental and over zealous cleaning, the defects were created, i.e. because of an over sputter or anneal. Stemming from this result, we now examine their production as a function of each preparation technique to elucidate which of these preparations is responsible for the production of the defects.

As described in 4.3, copper (100) samples are prepared for UHV by repeated cycles of sputtering and annealing. Typical UHV preparation of copper (100) begins by sputtering with non-reactive Ar\(^+\) ions, which etch top layers of unwanted contamination and copper, and thereby clean the surface. Unhelpfully, this sputtering procedure also induces considerable surface pitting damage, the efficacy of which depends on the sputtering parameters and the surface crystallography. Following the sputtering procedure, samples are thermally annealed. The anneal procedure increases adatom mobility which in turn, fuels terrace growth and repair. Like sputtering, annealing also causes surface damage by eliciting different contaminations from different sources, e.g. bulk migration, to the surface. Since each process fixed the others damage, each technique is used in conjunction with the other, until the control values of each process can be reduced to "non-damaging" conditions. Reaching this point typically requires 50 sputter and anneal cycles. In this manner, UHV clean metal samples are routinely prepared in our laboratory. It should be noted that some research groups deliberately divert from these "ideal" preparation conditions to develop specific defect types, or damage, for specific investigations. It is our belief that we may have unwittingly done the same thing.

\[^{15}\] By flip, it is meant that a "sombrero" defect never changes its appearance to look like a hollow, or vice versa, save for tip convolution effects. Even with tip convolution effects, it is still with extra careful attention, possible to distinguish that there are two different objects.
5.2.1 Influence of sputtering on the defect concentration

Standard sputtering of copper (100) proceeds with the introduction of high purity Argon gas into the UHV chamber via a pre-pumped gas line that is fed through a needle-valve device, Figure 3-1. The chamber vacuum is reduced from the $10^{11}$ mbar region $\rightarrow$ $10^6$ mbar region during this process, with the increase in pressure expected to arise solely from an Argon partial pressure increase. Typically, the argon gas is accelerated with 600 eV towards the copper (100) surface for approximately 30 minutes$^{16}$. Sputter target currents of $\approx$ 20 mA are routinely achieved, though it is acknowledged that these values change with sample positioning, angle, beam focus, and of course, applied bias potential.

Figure 5-2 Two constant current STM topographs of the copper (100) surface taken at RT taken with different sputtering conditions, but without annealing. The aim of the experiment is to identify if the sputtering process creates nano-pits. Typical UHV preparation of copper proceeds with sputtering to remove the top layers and thereby clean the surface. This can however, also induce considerable surface damage depending on chosen sputter parameters and the surface crystallography. (a) STM image taken just following a long (= 2 hours) sputter sequence. This induced considerable planar etching. (b) STM scan of the surface following a sputter with higher energy Ar$^+$ incident ions (= 2keV). This process resulted in a more violent multilayer pitting of the metal surface. In neither process, were any “sombreros, or hollows” seen.

$^{16}$ Recipes depends on sample condition (old or new, clean or dirty), what chemicals may have already been on the surface due to previous experiments, and between different scientists in different labs.
To identify if sputtering was creating the nano-sized defects as a result of some anomalous sputtering procedure, the beam's energy, incident angle, and exposure times were varied, after which, the surface was imaged using STM. No surface changes were noted as a result of altering the sputtering angle.

As the beam's energy and sputter duration were altered, changes in the surfaces appearance were observed. Figure 5-2 (a) shows the result of sputtering for 2 hours at a normal bias potential (600 eV). Due to increased surface level etching, the relatively low energy incident ions, and the surface crystallography; the copper (100) surface undergoes a 2-d planar etching process. This procedure does not increase the density of "sombreros" or "hollows" on the metal surface.

The energy of the incident-ions was then increased in a separate experiment, and afterwards the surface was again imaged using the STM. The related surface damage is illustrated in Figure 5-2 (b). In this case, multi-layer nano-pits are formed, though it should be noted, the shape and dimensions of these nano-pits, is inconsistent with the defects observed by Fishlock et al. or by ourselves.

In summary, the quantities of sombreros or hollows structures seen on the copper (100) surface, is not influenced by the sputtering process.

5.2.2 Influence of thermal anneal on defect density

The sputtering investigations identified that the defects are not produced because of sputtering damage, therefore, attention is now focussed on examining how the anneal procedure produces the defects on the metal surface.

In a fashion similar to the previous experiments, the anneal procedure is varied around the standard annealing conditions used for copper (100) preparation in UHV (600° C for 30 minutes), by adjusting both the anneal temperature and duration, one at a time. Following each different anneal, the surface was imaged with STM and analysed.

In stark contrast to the effect of sputtering, defect density is found to be related to both anneal time and temperature. Thermal production of the defects is non-linear above a critical temperature, $T_c$, that is $\approx 1000$ K. Production increases rapidly with increasing temperature above $T_c$, but below $T_c$, virtually no objects appear and atomically clean copper (100) samples are formed. Characterising the defect density...
as a function of temperature is only qualitatively possible at present, since the anneal temperature data is not directly available. The data available is the anneal power, but since the sample is fixed in position using a spring-leaf system, the contact resistance changes between every single experiment. Thus, our finding that the defects are temperature dependent reflects experience with producing the species and ignores to some extent, this contact resistance problem.

Despite this uncertainty, it appears that there is a sharp nothing-or-many threshold, at \( \approx 900 \) K. Exactly what temperature this is requires further investigation, which could easily be performed with a well-calibrated optical pyrometer. It is found that annealing at \( \approx 850 \) K and 950 K, produces defect densities which increases by \( \approx \) three orders of magnitude / 100 K. Using this data, and assuming that the sharp increase is because the defect production is exponentially dependent on temperature, a crude measure of the defect energy is determined. If:

\[
\frac{N_S}{N} = \exp\left(\frac{-W}{k_B T}\right) \tag{5-1}
\]

where, \( N_S \), number of defects, \( N \) is the number of lattice positions, \( W \) is the energy difference of defect versus no defect, \( k_B \) is Boltzmann’s constant (\( 8.6 \times 10^{-5} \) eV / K), and \( T \) is the temperature in Kelvin, then counting 4100 defects per 150 nm x 150 nm area after an \( \approx 1000 \) K anneal, compared to 10 or less defects typically found after a normal anneal at \( \approx 900 \) K, the formation energy of these defects is calculated to be circa 4.65 \( \pm 1 \) eV. The value seems plausible, though more statistics, temperature measurements, and more developed models are clearly needed for more reliable estimates of the formation energy. The defect density is also found to increase approximately linearly with time.
Vacancy cluster production vs Anneal duration

Figure 5-3 Defect concentration as a function of anneal time at a fixed temperature. Monolayer percentage coverage ranges from 15% - 45%.

5.2.3 Discussion

Of the two preparation techniques for copper (100), thermal annealing is found to induce a temperature and time dependent defect production function. From these results, a crude estimation of a formation energy is presented, and it is believed that a sharp cut-off/on temperature exists. This critical temperature, $T_c$, is though to be $\approx 900$ K.

Despite elucidating the role of thermal energy in the production of defects, exactly how the thermal energy causes this production remains unclear. For example, the stationary species observed in Figure 5-1 may plausibly be produced via any of the following thermal mechanisms:

1. Outgassing or evaporation from the sample manipulator stage,
2. Thermal driving of bulk contaminants to the surface, i.e. surface segregation \cite{352}
3. An induced chemical reaction with residual and airborne chamber gases.
An induced chemical reaction is deemed an implausible mechanism by consideration the following points: (i) The species density at higher temperatures implies significant contamination which ought to be detectable using mass spectrum analysis. However, this is not the case. (ii) The defects have also been seen in other systems, and identical contamination in entirely different chambers would be very unlucky, if not unlikely. (iii) If the defect species/contamination is airborne, it ought to be visible on the Silicon (111) 7x7 sample, which it is not. (iv) There appears to be two different defect types: sombreros and hollows. That two thermally activated process with extraordinarily similar, yet different, properties occurring at the same temperature is rather unlikely. Thus, we suggest that thermal induced chemical reaction is not how the defects on the surface are produced.

In an attempt to, (i) narrow the range of plausible production mechanisms, (ii) better understand where the species originate from, and (iii) elucidate what they are: a test to eliminate outgassing or evaporation from the above list of possible production mechanisms was devised.

An atomically clean silicon (111) 7x7 sample was placed on the manipulator and heated to temperatures far exceeding 1000 K. Simultaneously mass spectrum analysis was performed. At these temperatures and sufficient anneal durations, near monolayer coverages of the defects are produced on the copper (100) surface. Hence, if an evaporation or outgassing process from the manipulator is the source of the defects on copper (100), the evaporate ought to be observable in mass spectra, and subsequent STM images of the surface. Despite this, no new mass spectrum peaks emerge during this heating process, and no contamination atoms are observed in STM scans of Si (111) 7x7. Since silicon is highly reactive, one would typically expect to see some chemical footprint of such a large volume of contamination as indicated by the high coverages observed in the STM images of copper (100). These points, in combination with the above airborne test results, suggest that the species observed on copper (100) is inherent to the copper (100) crystal.

Migration of atoms from crystal bulks to sample surfaces is a well-known, thermally activated process, and contamination source. Segregation from the bulk crystal to the substrate surface rules out the possibility of the defects being molecules. Sulphur is one well known surface segregate [296], and carbon is another reputed contaminant [353].
The size and structure of these contaminants is however, inconsistent with the defects we observe in Figure 5-1.

In a final experiment designed to understand if the defects observed in STM scans are clusters of adatoms or vacancies, we attempted to thermally desorb, or "boil", the "atoms" from the copper surface. Again, mass spectra were acquired during the experiments, and immediately afterwards, the surface was imaged using STM. Despite beginning the experiment with a high defect concentration as determined with STM, no mass spectrum peaks were observed whilst heating to 1100 K.\textsuperscript{17} Rather, the density of surface species simply increased. This suggests that the species desorption energy could not be reached, even though quite high temperatures were employed, or, that the species in question are not atoms.

In summary, it would have been ideal to have performed collimated Auger electron spectroscopy on the defects to help with their identification. However, such facilities were unavailable in our experimental set-up. From the data set so far presented, it seems on dynamic grounds, that the species cannot be single atoms or vacancies. On thermal production (bulk segregation) grounds, they cannot be molecules. With the constant absence of any mass spectra signal during their production, considerable suspicion is therefore aroused that the defects observed are vacancy-cluster structures. We now examine the defect properties to help elucidate what the defects are.

5.3 Defect properties: STM investigations

STM alone is unable to chemically identify any unknown species. In fact, even separating physical and electronic contributions in constant current topographs is problematic for STM \cite{34-38}. For example, dark spots in a constant current STM images may correspond to an embedded atom with a low LDOS near $E_F$, or, to a physical hole in the metal surface. Thus, by examining Figure 5-1 one could reasonably conclude, that the features observed as hollows are either poorly conducting atoms/molecules, or surface vacancies. Therefore, in an effort to identify the observed structures, we examine the defects:

\footnote{This is an approximate value, relating temperature to power in a heating supply, based on a calibration chart provided by the chamber manufacturers.}
Figure 5-4 (a) 20 nm x 20 nm STM constant current topographic image of copper (100) taken at room temperature. With standard tunnelling parameters (0.03 V, 0.2 nA) the objects remain stationary for prolonged periods of time. (b) Identical hollows, and sombreros observed with a blunt tip, appear circular as a result of tip-deconvolution.

- physical structure,
- electronic / chemical structure, and
- dynamics,

using RT-STM, VT-STM, and various spectroscopic techniques. Piecing together data from the above experiments, a confident hypothesis and model on the nature of the observed structures is presented.

5.4 Physical properties of the defects

Figure 5-4 is an atomic resolution (AR) image of the copper (100) surface, which was
deliberately over-annealed to produce the defects observed. The sample was annealed at 950 K for 10 minutes, and prepared as "normal" in every other aspect. In Figure 5-4, both the defects, and the underlying copper lattice are seen with AR. The defects, i.e. hollows and sombreros, are the same as those in Figure 5-1, with the obvious difference, they now appear square. The defects appear as 3 x 3 atom structures orientated within the four-fold lattice. They are mostly single defects (i), though some pairs, and higher multiple combinations of defects also exist, (ii) and (v). When they form linear combinations such as those shown in (ii), their individual shapes or overall surface area is not altered. When they join pairs and higher multiples, whether in-plane (ii) or out-of plane with each other (iii), the new combined structures shape does not tend towards the energetically preferred square shaped structures, on the copper (100) surface. This indicates that the defects have an anomalously high stability energy associated with the individual 3 x 3 structure. We now examine each species individually.

![Figure 5-5](image)

**Figure 5-5 (a)** 3nm x 3nm atomic resolution STM image of an atomically resolved hollow measuring 0.82 nm ± 0.08 nm wide and 0.79 nm ± 0.06 nm in length. (b) The same hollow observed with a blunt tip appears circular as a result of tip-deconvolution, and measures 0.92 nm ± 0.143 nm, 0.89 nm ± 0.156 nm respectively, 1 Å larger in either direction. A blunter tip's increased surface area, effectively elongates the cross-section of the tips wavefunction causing them to appear larger. The asymmetry between length and width, or alternatively, the fast and slow scan direction probably occurs as a result of piezo creep.
5.4.1 Vacancy-cluster

Figure 5-5 is a high-resolution STM topographic image taken in the constant current mode of a defect structure known by Fishlock’s nomenclature \([32]\), as a hollow. The structure observed in Figure 5-5 is a 3 x 3 square structure, which statistical analysis of line profile data, equivalent to the one shown in Figure 5-7, indicates that the cluster is 0.82 nm ± 0.08 nm wide, and 0.79 nm ± 0.06 nm in length. The measured dimensions almost perfectly correspond to the interatomic spacing for three consecutive atoms on copper (100) - (3 X 2.69 Å) in both width and length. The structure is aligned 4-fold symmetrically within the substrate-lattice, with the dark region positioned directly above copper lattice sites. This, alongside evidence thus far presented, suggests the defects are clusters of vacancies. The main area of interest, i.e. the “black-hole” is now examined.

This dark region in the STM scans of the defect represents either a poorly conducting region, (maybe an adatom-island), or a region of equal chemistry but farther away, (maybe a vacancy-cluster structure). If the LDOS at \(E_F\) inside the defect is small in comparison to the LDOS of copper atoms due to their different chemical compositions, one would expect to observe different \(I-V\) spectra taken inside in comparison to the copper terrace atoms. If on the other hand it is a vacancy cluster, the \(I-V\) curves should be identical. It is hoped that scanning “inside” the clusters will reveal atomic resolution of copper atoms, if indeed they are vacancies. Distance corrected work-function measurements taken inside the cluster structure, and on the terrace, should also be identical if they are vacancies. With these experimental ideas in mind, we now examine the properties of the cluster structure with an aim to better understand what they are.

From line profiles taken along the [110] direction through the structure, a cluster depth of 0.16 Å is measured. This is significant, considering it is \(\approx\) equal to one atomic-step implying the cluster structure, is a monolayer deep. The line profile of the region inside the structure exhibits two clear peaks, 2.9 Å apart, Figure 5-7. This is relevant, since this matches the copper-copper interatomic distance. The peaks have a 50 pm peak-to-peak corrugation which is comparable to terrace-atom corrugations which measures 60 pm.
Figure 5-6 (a) 34 Å x 34 Å STM constant current topograph of a "vacancy cluster" on copper (100) at RT. The species is 3 x 3 atoms wide, 1 layer deep (b-c) Forward and backward images of the same cluster.

Figure 5-7 Atomically resolved line profile of a vacancy-cluster structure. The cluster depth measures 160 pm, almost exactly equal to a step height. Atoms can be 'seen' inside the vacancy. These are 2.9 Å apart, the typical interatomic distance of copper atoms. Furthermore, their atomic corrugation is comparable to terrace atom corrugations.
The position of the peaks lying at the trough-trough intersecting rows, implies that the peaks observed correspond to copper atoms lying inside the pits, so achieving atomic resolution inside the cluster, should be possible.

**Figure 5-6**, (b) and (c), are enhanced STM images of the defect cluster shown in **Figure 5-6** (a). The z-piezo range is altered via image processing software to enhance the area of interest, and “see” inside the cluster. Sharp atomic contrast is not observed but this may be expected since the finite size tips, ensure that some of the tip tunnels with atoms surrounding the cluster. This is an inherent problem with STM measurement.

In both images, **Figure 5-6** (b-c), two peaks predominantly protrude. These peaks in the centre marked yellow as opposed to the atoms marked red should be less confined and have a reduced coordination, so it is reasonable to believe that they undergo outward relaxation.

**Figure 5-8** Topographic line scan of an atom row along a clusters side-wall, dashed red line in. The image is to illustrate that the centre atom of the species appears raised in STM scans with both neighbours moderately lowered. Whether physical or electronic in origin, is unknown at this point.

### 5.4.1.1 Defect induced atom relaxations

Distortions of copper atom positions surrounding the defect clusters is observed. The central atom of each sidewall is raised \( \approx 20 \text{ pm} \) with respect to average-atom heights, **Figure 5-5** and **Figure 5-8**. In contrast however, each of its neighbouring atoms heights are reduced by \( \approx 10 \text{ pm} \), see **Figure 5-8 (a)**. In addition to vertical distortion, central side-wall atoms display a relaxation towards the defect centre.
Figure 5-5 (i). These undergo a mean shift from their regular positions of almost 0.3 Å. This represents a non-negligible 11%, but the aforementioned central atom relaxes outwards by 0.6 Å, or 22%. Such relaxation commonly occurs at surface interfaces, with the most obvious example the relaxation of first-atom layers at cleaved surfaces. As briefly described in chapter 4, outward relaxation is an energy minimising process with competing influences. These competing factors often lead to displacements of atoms from their normal position. In this respect, AR imaging of the clusters with simultaneous nc-AFM/STM, and/or, theoretical modelling will prove insightful.

5.4.2 Adatom-cluster pair

Atomically resolved STM images of the second defect structure, a sombrero reveal that it too, is a 3 x 3 monolayer deep pit, with a bright peak in its centre. At 0.83 nm ± 0.22 nm wide, its dimensions are comparable to vacancy-clusters; however it is noted that at 0.89 nm ± 0.11 nm in length, it is 1 Å wider than a vacancy-cluster. Unlike its hollow counterpart, the walls of this structure are not found to be protruding. This may explain the difference in their measured lengths. This is shown in Figure 5-9.

![Figure 5-9](a) Adatom-vacancy cluster structure with an "atom" stuck in its centre. Dimensions are comparable to the vacancy-cluster structure, and the location of the central atom is noted to be slightly off centre. (b) As imaged with a blunt tip.
Table 5-1 Statistical averaged physical dimensions of the adatom-vacancy cluster structure with (i) atomic resolution and (ii) a blunt tip

The depth of this structure is 90 pm shallower than its vacancy-cluster counterpart; however this observation may be imaging influenced. As mentioned, STM tip's finite shape means STM probing of high aspect-ratio spaces is inherent, and as such, our tip may be unable to accurately measure the depth of this well.

In a manner equivalent to the vacancy-clusters, the central atom of each cluster-wall is swollen in the z-plane, relative to its nearest neighbour. This implies that there is a localised heaping of electronic charge density, or, a physical relaxation of the "atom", due to its reduced coordination at these sites. The key difference from the vacancy-cluster structure however, is the central atom. The central atom positively projects out of the z-plane peaking 130 pm above its nearest copper atoms, as seen in Figure 5-9. The atom is slightly off centre inside the vacancy-cluster, lying at the cross-section of the hollow rows.

Figure 5-10 Superimposed line profiles elucidating and comparing the z-dimensions of each species. The depth of the adatom-vacancy is shallower than the vacancy cluster structure. The height of the adatom inside the vacancy almost exactly equals the height of a free adatom. It is clearly seen to protrude above the lattice plane.
Figure 5-11 (a) Sombrero cluster with a peak/atom stuck in its centre. During manipulation when we push this structure, the central peak retains position (b) When the sample is heated 310 K causing significant diffusion to occur, again the species remains in the centre. This remains the case for several hours.

Performing statistical analysis indicates that the peak distance to the left wall, (as you look at the cluster), A is approximately equidistant to its right wall, indicated C in Table 5-1. Counter-intuitively, the position of this atom never changes within the vacancy cluster. This remains so, even if the structure is completely and continuously manipulated, and/or if significant thermal energy is added to the system, Figure 5-11 During manipulation, diffusion, high voltage pulsing, and even when a vacancy-cluster and an adatom-vacancy are pushed together, the atom, virtually regardless of outside influences, retains this positioning.

The centre atom is in thermal equilibrium with the surface, and the thermal energy during high temperature experiments, \( T \), carried by each microscopic “degree of freedom” in the system is at maximum of the order of \( k_B T \) (i.e. 0.035 eV). These particles have been observed stationary for hours of consecutive scans, so in the least case scenario (i.e. 3 hours), this means the atom is stable for 10800 seconds, i.e. its stability lifetime (= to the inverse of its hop frequency) is 10800 seconds. This gives a hop frequency of \( \approx 9.2 \times 10^{-5} \) Hz. Assuming an attempt frequency in the region of \( 10^{13} \) Hz, and that at most 1 eV is coupled from the tip during manipulation experiments; we can estimate a stability-energy for this particle. Considering a simple
Arrhenius type equation:

\[ N = N_0 \exp \left( \frac{E_x - E_{\text{tunneling}}}{K_B T} \right) \]

where \( N \) is hop frequency and \( N_0 \) is the attempt frequency, \( E_{\text{tunneling}} \) is the amount of energy that could be coupled into the system via, force gradient, thermal energy or any of the mechanisms outline in chapter-1. The minimum energy required to destabilise this particle is then estimated at 2.4 eV or higher.

In our experiments, no amount of tunnel current was ever found to dislodge the atom from its central position. Similarly at higher temperatures, the species was never found to change its position. Despite this, there is one way the atom can be dislodged from its central position. To determine how it is dislodged and fully separated from the vacancy cluster, we now examine the behaviour of clusters en-masse, and how they interact with each other.

A set of STM topographs taken from a drift corrected, cross-correlated video sequence showing an artificially created cluster of defects, are shown in Figure 5-12. On the set of images are two circles. The blue circle is a “marker” to demonstrate that we are imaging the same cluster. The white circle represents the cluster of defects we are interested in. It is first noticeable that the constituent defects are far more mobile than the surrounding terrace defects. Taking a close look however we observe that the numbers of sombrero type defects changes during the sequence, and furthermore, that these seem to be “feeding to and from the terrace layer copper atoms. Image (a) and (b) have four sombreros. In image (c) however the cluster of defect has six sombreros species. One extra sombrero may have become a terrace sombrero as indicated with the red arrow in (b). Nevertheless, there is still, one sombrero extra, and it appears to be coming from the terrace copper sites (ii). In image (d) the cluster has five sombrero defects, though a new sombrero is observed on the terrace, marked with a red circle. In (e) we are back up to six, and though it appears we have regained the sombrero just lost to the terrace, it appears we lost a new sombrero. This still indicates on new sombrero, and again it appears it is been fed from the terrace (iii).
Figure 5-12 Set of STM topographs taken from a drift corrected, cross-correlated video sequence showing an artificially created cluster of defects. On the set of images are two circles. The blue circle is a "marker" to demonstrate that we are imaging the same cluster. The white circle represents the cluster of defects we are interested in. It is first noticeable that the constituent defects are far more mobile than the surrounding terrace defects. Taking a close look however we observe that the numbers of sombrero type defects changes during the sequence, and furthermore, that these seem to be "feeding to and from the terrace layer copper atoms. Image (a) and (b) have four sombreros. In image (c) however the cluster of defect has six sombreros species. One extra sombrero may have come a terrace sombrero as indicated with the red arrow in (b). Nevertheless, there is still, one sombrero extra, and it appears to be coming from the terrace copper sites (ii). In image (d) the cluster has five sombrero defects, though a new sombrero is observed on the terrace, marked with a red circle. In (e) we are back up to six, and though it appears we have regained the sombrero just lost to the terrace, it appears we lost a new sombrero. This still indicates on new sombrero, and again it appears it is been fed from the terrace (iii). There are six in (f), but in the following image (g), there are now only four sombreros. One, maybe two sombreros are lost to the terrace then in the final images.
There are six in (f), but in the following image (g), there are now only four sombreros. One, maybe two sombreros are lost to the terrace then in the final images. The diffusive behaviour observed in Figure 5-12 indicates that the two defects are vacancy clusters, whose centre atom is a copper terrace atom. The videos clearly demonstrate the central species and the "core" black part, the vacancy may be separated from each other, and are in fact separate entities. This may explain how two species are produced at one temperature.

The over anneal serves to produce the vacancy clusters, after which subsequent capture of terrace diffusing atoms converts them to sombrero type structures. Why they would be so stable, is not understood at present.

5.5 Electronic and chemical properties of defects

5.5.1 Spectroscopy

Figure 5-13 shows two $l_T$-$z$ spectroscopy curves, one measuring the copper terrace atoms (red) barrier-height ($\varphi_{BH}$), the second measuring the inside of a defect-cluster $\varphi_{BH}$ (black). The tunnel current-distance relationship inside the cluster is identical to its terrace-atom counterpart, except, the curve is shifted 160 pm in z. This indicates that the atoms inside the defect-cluster are electronically equivalent to the copper terrace atoms; accept that they're one atomic radius deeper.

Figure 5-14 is a pair of current-voltage spectroscopy curves also taken at equivalent surface locations. The curves taken on the copper (100) terrace, and inside the defect-cluster structure are both linear, with approximately equal slopes. Notable from the graphs is the absence of any dominant spectral features and the almost equal slopes. This indicates, that the LDOS of both the terrace copper atoms, and the inside of the defect-cluster structure, are chemically equivalent. This, along with the previous result for the barrier height, indicates that the centre of the cluster structure is chemically equivalent to the terrace atoms, i.e. it's copper. It is noted however, that when measuring inside the defect-cluster it is expected that some current leaks from the surrounding atoms distorting the tunnelling current measurements. Secondly, due to spectral broadening, finite resolution, and other errors inherent with RT spectroscopy measurement, this result is accepted cautiously.
Figure 5-13  I-Z Tunnelling spectroscopy curve of a copper terrace atoms (red) and the inside of a vacancy cluster (black). One would expect some leakage current to surrounding atoms when measuring inside the vacancy. This could account for the higher onset slope in the black curve. Interestingly however, tunnelling inside the cluster appears virtually identical, except the curve is shifted by 160 pm.

Figure 5-14  Current-voltage (I-V) spectroscopic curve on bare copper terrace, and inside the hollow defect structure. There are virtually no spectral features on either curve and their respective slopes are almost identical. This crudely suggests that the species inside the “black-hole” is copper.
**Figure 5-15.** Is a set of STM topographs taken in the constant current mode. Images (a-d) are taken at 3 V and 0.2 nA $I_T$ set-point. This was performed in an attempt to improve the poorly resolving tip. What was observed however, was a modification of the sombrero type structures. A simple tip-related anomalous imaging process is ruled out as a credible explanation for the observed features, since not all the sombrero species change contrast. Investigations show that entire areas, centre part of image (e), or individual species can be deliberately “switched on”. Once the species was “on”, they remained bright indefinitely. Their mobility is also found to change once excited. We thus have an control mechanism, which can tune the species dynamic properties through electronic excitation. Similar results have recently been published by Repp et al. If it is thus tentatively proposed, that the ≈ 3 eV electrons may cleave a copper-copper bond leaving it dangling, making it unsaturated, and thus accessible for tunneling at lower biases, image (e). This simultaneously reduces its bonding strength to the copper surface, thus making it more mobile. It is expected that this excited defect should have measurably different I-v, I-z, curves, which may confirm this. Such data will be acquired in future research.

![Figure 5-15](image_url)
5.5.2 Vacancy-cluster interactions

Having already illustrated some of the main physical properties of individual defects, we now examine the distribution of vacancy clusters at step edges, defect sites, and on the flat copper terrace, hoping to elucidate how the defects interact with each other, and the underlying surface lattice. Following this, we analyse their interactions with each other and how they coagulate to form multiple units, i.e. their growth patterns and processes, and discuss what these results imply about the clusters chemical properties. We discuss the equilibrium shapes these growing clusters have, and discuss what this infers with regard to the defect rest energy. Finally, some electronic properties are discussed, noting that these affects also influence the particles chemistry.

5.5.3 Vacancy-cluster distributions

5.5.3.1 Terrace distribution

Figure 5-1 is an STM topograph taken in the constant current mode. From a defect distribution perspective, it is immediately noticeable that no recognisable pattern or reconstruction on the flat terrace is observed. This remains to be the case for all coverages and anneal temperatures examined in this body of work.

Species do come close to each other, even joining together, but hop away just as readily, indicating there is little or no attractive interaction. Growth through electrostatic interactions or an evenly spaced distribution resulting from repulsive interactions may be expected, but no evidence of either is found. This is somewhat unusual indicating that little or no lateral interactions exist between the vacancy clusters and adatom-vacancy pairs, or that any interaction that is present, is insufficiently large to induce redistribution.

5.5.3.2 Distribution at energetically favourable sites

On experimental timescales (scan time = 3 min) the defect clusters display extraordinary dynamic stability, yet despite this, thermal fluctuations still induce multiple hopping events. This is especially so if the sample is heated above RT, and if enough thermal energy is added, allowing random-walk thermal diffusion to occur.
This facilitates a multiple site-sampling process. The process provides sufficient mobility for clusters to seek, and find, potential wells, high coordination sites and other surface anomalies which typically act as energy traps for adsorbates. Figure 5-16 indicates one typical type of energy trap encountered at non-regular sites, including step-edges, islands, vacancy-pits, or chemically different regions. Illustrated is the Erhlich-Shwoebel barrier, which serves to trap species in the potential well in the region marked (a).

**Figure 5-16 (a)** Schematic indicating the Erhlich-Shwoebel barrier that a particle encounters when traversing a step edge. The potential energy trough at the lower terrace is often sufficient in magnitude to trap thermally diffusing particles.

**Figure 5-17 (a)** 37.5nm x 37.5nm STM topograph of copper (100) surface including (a) step edges, (b) islands and (c) vacancy pits. The image is poor resolution, so the objects appear as black blobs. This is a tip related convolution of the image. Nevertheless, no preference was ever observed for step sites, or defect decoration.
Despite such low energy sites being present on the surface, no particular affinity for step edges and/or decoration of defect sites is observed, Figure 5-17. This indicates site-sampling rates may be low, or, the potential energy drop at step edges relative to the diffusion barrier is insufficient in magnitude to significantly influence mobility.

5.5.3.3 Relative defect concentration

Having just examined the physical distribution of each defect type on the flat terrace and step edge locations, we now examine the "chemical" distribution of defects, i.e. how many of each defect type exists. We also determine if this ratio static or dynamic. The relationship with the preparation conditions is discussed.

Statistical analysis of more than 3500 thermally produced species from 26 different data sets reveals an overall increase in defect concentration with respect to anneal temperature. The ratio of "sombreros" to "hollows" however also changes. From the entire data set the ratio is calculated at 2:1, however this ratio deviates highly between individual data sets, and is found to be strongly correlated with anneal temperature / defect density. Figure 5-18 is a plot of the ratio of sombrero to hollow defects as a function of overall defect density. This is a de-facto measurement against temperature since defect density scales with temperature. The ratio appears to be 1:1 until a critical defect density is reached after which the sombrero density continues to increase, more or less, linearly with overall density. The hollow defect density begins to decline at the same turning point. This process indicates that transformation from one defect type to another is occurring. This is a hugely significant result since if the defects are be converted from a hollow defect, into a sombrero defect, as a result of the addition of thermal energy, this would indicate that only one species may be initially produced, with the second species evolving due to forced adatom trapping at a later date. Such a process could explain the defect density shift at higher temperatures, and how one thermal process can produce two different "species", (iii) why no chemical signature is ever seen during production in the mass spectra, I-V curves, I-z curves, or when we attempted to "boil" atoms from the surface, no evaporate was detected.
**Figure 5-18** Ratio of sombrero to hollow defects as a function of overall defect density. This is a de-facto measurement against temperature since defect density scales with temperature. The ratio appears to be 1:1 until a critical defect density is reached after which the sombrero density continues to increase more or less linearly with overall density. The hollow defect density begins to decline at this turning point. This process may indicate the transformation of one defect type to another.

**Figure 5-19 (a-b)** STM constant current topographs of copper (100) illustrating the role of anneal temperature in overall species density. The ratio adatom-vacancy clusters to vacancy clusters also changes with increasing overall species density. In image two, the mean free path (mfp), $\sum \frac{z_n}{n} = z_{\text{mfp}}$, of the adatoms is smaller, resulting in more frequent collision with vacancy clusters, converting them to sombreros.
5.5.4 Discussion

This ratio shift at higher temperatures/densities may be explained. With adatoms having higher kinetic energies and a decrease in the mean free path before colliding with a vacancy cluster, the likelihood of a collision, and the probability it succeeds in converting a vacancy cluster into an adatom-vacancy pair, increases with temperature. Such an increase in collision events and their success rates simultaneously increases the number of adatom-cluster pairs, whilst decreasing the number of vacancy clusters. Hence, the shift in ratio of island growth and reconstruction may not occur, but they do form small units, i.e. pairs, triples, etc.

5.5.5 Defect chemistry: Interactions and growth processes

Chemical properties of almost all species are dominated by their bonding. Their bonding is determined by valency, electronegativity and energy minimisation processes which direct and control their interactions with other species. Many energy specific methods exist for characterising unknown species; including the various spectroscopic techniques, structure determination techniques, and reaction product statistics. Most of these techniques are not at our disposal since the defects we are interested in, are stuck to the copper (100) surface. As such, we examine how the defects interact with each other, i.e. group together; evolve with time, and bond, using STM images and videos. From these results it is hoped that we can decipher similar data which the aforementioned techniques may have been able to provide. Namely, what are the species, why do they react the way they do, and how do they interact?

Vacancy-clusters and adatom-vacancy pairs join together forming larger clusters which are integer unit times the size of the individual species. This occurs for all combinations of “building block” as shown in Figure 5-21 (a-c). A histogram indicating the most common species size is shown in Figure 5-20. From the bar chart, it is clear that the most prevalent combination size are pairs, and as such, we now examine the properties of these pairs, in an attempt to elucidate how the species “bond”.

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Figure 5-20 Histogram of defect sizes observed during STM scanning. Only multiples of the fundamental 3 x 3 building block are observed in this data set, i.e. there are no 1x1, 1x2, etc... The multiples that are seen become less numerous with size, possibly showing an exponential decline in probability with increase cluster size. This ratio or histogram shape does not change with time. This is indicative that there is no growth process, or decay process taking place.
Figure 5-21 Three STM topographs taken in constant current mode with standard tunnelling parameters and associated line scans through the main features of each image. The main features are defect pairs, seen with both sharp and blunt tips (see insets). The features are not a double tip artefact. These defects are said to be a pair in-plane with each other, meaning they are aligned along one axis. (a) A double hollow. (b) A sombrero-hollow mixed pair. (c) A sombrero-sombrero pair. The dimensions of each feature are shown directly to their respective rights. The key trends are (i) a decrease in the measured depths of each pair with the addition of each sombrero defect. (ii) the sombrero-hollow feature has a double bottom. The sombrero-sombrero has higher protruding centre atoms than its sombrero-hollow counterpart. (iii) the sombrero-sombrero length increases in comparison to the other two defect doubles. (iv) Most interestingly of all, is that the protruding centre atom in species (b) and (c) does not change in comparison to its singular counterpart. One may expect, especially in defect pair type (b), that the centre atom would adopt a more central role. In fact, it is never observed changing its location in these defect types.
Analysing the hollow-hollow pair by examining the line profiles in Figure 5-21 visually shows the hollow-hollow pair to be almost direct unit additions of two single clusters. Little or no alteration of the individual components is observed. No new shape or appearance is noted to the pairing. Their mobility increases.

The hollow-hollow pairs are 0.14 Å deep, akin to single species depth at 0.16 Å. This value is close to a mono-step height. Their measured lengths are 17 Å, which is ≈ 3 % larger than the length calculated by adding the average length of two single cluster structures, (2 x 8.3 Å). Their width is measured at 9.19 Å which compares to the 8.2 Å measured for the singular hollow counterpart. This outward relaxation in contrast to the singular case may reflect a build-up of stress as the structure attempts to change or reshape itself. Atomic resolution inside the cluster is not achieved, but line scans do reveal “nodes” lying inside the cluster pair. At present, it is unclear exactly what these nodes may represent. The centre atoms of each cluster-wall are swollen, similar to the singular species, with the affect becoming far more prominent when species add asymmetrically, as shown in Figure 5-22.

The second defect pair between identical building blocks, i.e. the sombrero-sombrero defect pair is now examined. Again, it is noted, that these defect pairs appear to be simple linear additions of two individual species with no visible morphological changes, or structural transformations. They appear to experience no interaction with each other when combined, i.e. they retain their individual shapes entirely. This species are 0.55 Å deep with respect to the terrace atoms, compared to 0.5 Å measured for its singular counterpart. Its central atoms protrude 0.70 Å above the copper lattice, considerably less than the single sombrero defect value of 1.3 Å. Furthermore, it is 21 Å in length which is ≈ 15% longer than the calculated length of two singles added together. And again, relaxation and / or charging effects at the surrounding walls are detected. A key point of course is the behaviour of the central atoms. The central atoms do not join together or move in any way in response to each others presence. This indicates the defects display a certain degree of inertness. Finally, what happens if the two different species are combined, as shown in the Sombrero-hollow pairs in Figure 5-20 (b). Interestingly they exhibit two different
Figure 5-22 A sequence of constant current topographs taken at room temperature of the defect cluster structures on copper (100) indicating some of the defects characteristic features. (i) When the defects add as multiples of single units they do not tend to square structures as expected for vacancy structures on copper (100). (ii) and (vi) When a sombrero and a hollow combine, the central atom does not adopt a new position which is central of the two. Rather it "stays put". (iii) When groups of sombrero type defects are combined, the mentioned raised central atom in its outer wall becomes even more prominent. This is especially noticed with a blunt tip, image (f). (vii) During motion the defect structures retain their shape and structure.

"floors" levels. The first, at the vacancy-cluster side is predictably, 0.15 Å deep (equalling a step height), whilst the second floor, at the hollow side, is 0.6 Å deep. Both are comparable with their respective singular partners and the entire structure is
17 Å long; almost exactly equalling the length of added single values (hollow L + sombrero L). Surprisingly however, the central atom/peak does not change its position no matter what type of combination is found. Figure 5-22 is a set of STM topographs taken in the constant current mode after a deliberate high temperature anneal to produce the defect cluster structures. The series displays a collection of some additional observations, which are now mentioned as indicators of the defects behaviour, and consequently identity. **Figure 5-22 (a)-(i)** shows a linear triple defect. No matter how many combine, they do not tend to an equilibrium square shape pattern expected for copper (100) surfaces. The “surface area” of the larger defect clusters, always remains an integer number times the surface area of the individual defects. When the defects move, they retain their 3 x 3 structure, and the central atom stays in the centre, even during motion, Figure 5-22 A (a)-(ii) and Figure 5-22 A (c)-(vi). The heaping up of the surrounding wall is especially noticeable when the species combine asymmetrically, Figure 5-22 (b)-(iii). This may occur due to confinement effects, or increasingly reduced coordination. If it is an electronic effect, it may prove useful as a new “nano-building block” for standing wave studies, and for engineered chemical pinning sites. This effect becomes even more pronounced when the tip is “blunt”, Figure 5-22 A (f)-(x). When they touch at a corner apex, a neck is formed between the two defects, Figure 5-22 (b)-(iv) and (v). This is similar to vacancy cluster growth processes. When they combine into multiples asymmetrically, occasionally jagged edges remain, i.e. single atoms protrude into the “black” area. This is quite unusual, and they are expected to be highly mobile, or unstable. When multiples including hollows and sombreros combine into triples, the sombreros centre atom does not find a new position, Figure 5-22 .(c)-(vi). The central atom is believed to be a copper atom which may be provided from mobile adatoms or surface layer atoms “leaping into the hollow structure, Figure 5-22 (e)-(ix). Statistical analysis shows the ratio of single to doubles, is 6.5 : 1. Furthermore, this ratio fails to increase over time, indicating that not only are they energetically less stable, but they are neither attracted to each other nor interested in coagulation or growth.
Figure 5-23 STM constant current topograph still taken from a diffusion video. A single group of defects are highlighted in this Figure. The defects can be seen to diffuse and collide with each other, however they do not tend to stick together.

5.6 Diffusion

The comprehensive literature review examining STM images of adatoms, vacancies and molecules on Cu (100) indicated that with the exception of CO, and O, no species reported looked similar in STM scans to the defects we observe in Figure 5-1. At RT however, CO and O are both mobile.

STM images are not simple snapshots of surfaces, i.e. each line scan takes a finite amount of time to scan. For example, a 20 x 20 nm image, with 400 x 400 lines at a speed of $\approx 60$ nms$^{-1}$, means each feature circa 1 nm in size, observed in Figure 5-1, takes $\approx 13$ seconds to image. Since the species observed in Figure 5-1 remain stationary between consecutive images, this indicates their stability life times are at least 20 minutes. Correspondingly, their diffusion barriers easily exceeding 1 eV.

From this, it is thus concluded that single atoms or vacancies are unlikely to have diffusion barriers on copper (100) of this magnitude, and as such, are not likely to be the defects observed in Figure 5-1.

For a recent review of diffusion processes on metal surfaces the reader is referred to a comprehensive review by Morgenstern et al. Diffusion plays a critical role in many surface properties and is well characterised as a thermally activated process. With diffusing species in thermal equilibrium with an accommodating surface, thermal energy is coupled from the underlying phonon bath inducing a variety of different mass motion mechanisms. Figure 4-2 is a set of STM topographs illustrating some different diffusion mechanisms encountered in this body of work. Figure 4-2 (i) shows a vacancy diffusing via an adatom exchange process, with Figure 4-2 (ii), an example of simple adatom surface diffusion. For cluster diffusion however, it is thought that at least two different diffusion processes compete for dominance. These processes include a peripheral diffusion mechanism and a hop of the entire cluster. The former mechanism is more common when the clusters are large, and the second mechanism is more dominant for small clusters. When clusters grow there is a decline in the second mechanism and the former begins to dominate.
Figure 5-23 is a set of constant current topographs taken in sequence every three minutes. The images are acquired in standard, non-perturbing imaging conditions (0.02 V, 02 nA). The images are cross-correlated to overlap equal regions in space and simultaneously correct for thermal drift processes. Once the images are aligned, sub sections are cut, like the ones shown, and a video of the diffusing process can be constructed. The image sequence illustrates how the species diffuse, and what happens when they collide.

Diffusion events can occur anytime during the 3 minute interval between scans, and are therefore rarely found to occur as the tip is overhead. Diffusion is detected typically by the species being in a different location in subsequent scans, as indicated by the red circles in Figure 5-23 (a-b). Occasionally however, “hops” are caught “live” and from this we can directly observe how the species diffuse, blue circle, Figure 5-23 (f), and Figure 5-24. From these images it is apparent that the both the “dark
Figure 5-24 Set of STM topographs illustrating how the defects diffuse on the copper (100) surface. Images (a) and (b) show both sombrero defects and hollow defects moving in both crystallographic directions. The species seem to move as a unit, i.e. it retains its shape. It appears to be a sort of “all-or-nothing” type movement. It is therefore believed, that a new avalanche type diffusion takes place, whereby a single atom hops into the vacancy void. When this occurs, the structure quickly attempts to re-find the super-stable 3 x 3, so all the other atoms follow suit. The distance of the centre atom from the walls of the vacancy cluster is retained even during zig-zag sliding (d)-(iv), multiple hops (c)-(iii), and single hops (a-b)-(i-ii).
area" shape (likely a vacancy), and the centre atom-dark area walls distance, remain intact during movement.

This indicates that a new, avalanche-type diffusion takes place, whereby a single terrace atom hops into the vacancy void. When this occurs, the structure quickly attempts to re-find the super-stable 3 x 3, so all the other atoms become less stable and precede with an adatom-vacancy avalanche exchange until the 3 x 3 conformation is retained. The distance of the centre atom from the walls of the vacancy cluster is retained even during zig-zag sliding (d)-(iv), multiple hops (c)-(iii), and single hops (a-b)-(i-ii). This process may explain the particle's unusual dynamic stability, since the defects are effectively lying in between the optimum range for two diffusion mechanisms.

In addition to determining the hop mechanism, we are interested in what happens when the particles collide since that tells us a great deal about their energetics and growth processes. The video sequence stills shown in Figure 5-23, are utilised for this study by highlighting a group of 8 defects, marked on every image by a white dashed circle. We begin the analysis by noting in image (a) that there are 8 defects, 7 sombrero type structures, and 1 hollow type defect. There is a single sombrero-sombrero pair which is joined asymmetrically by another sombrero, a union which remains intact until image (e). Also formed in the intervening period is a symmetric sombrero-hollow combination without any input of energy. This indicates that there is a minute, or no barrier to formation for such sombrero-hollow pairs. In the following image this becomes an asymmetric pairing of a hollow and sombrero, indicating that there is little or no energy advantage of being aligned in-plane or out-of-plane with each other. The same pair then become symmetric, rotate and finally split apart in the subsequent images (f), (g) and (h) respectively. These results illustrate, that there is little energetic benefit for the defects to pair, and that there is little or no attraction, since they readily break apart. It also appears there is little repulsion from each other since they readily collide in the first place. So it appears they experience limited or no interaction with each other. It is almost as if the other species do not influence them at all. This is rather unusual chemical behaviour, and will require some further investigations at a later time, for clarification.
Such processes continue, throughout the sequence, but perhaps most significantly, though larger clusters do haphazardly form, they appear if anything to be energetically unfavourable, since their lifetime is short, typically minutes. This implies the defects do not, and will not grow into bigger clusters, in turn suggesting they have a very weak chemical footprint, and, that they are very stable and energetically favourable as single species.

In Figure 5-20, an Arrhenius Plot of diffusion of adatom vacancy clusters on Copper (100) is calculated. To construct this plot, diffusion events are measured by making simultaneous video sequences, and then cross correlating videos using WSxM software. This overlaps stationary species on top of each other, but moving species are revealed as trails. In this manner, we can determine the path start, end, and the course taken to reach there. We do this for every species and calculate a sum total of hops. This value is then divided by the total number of species, and the time taken to image the scan to derive a hop frequency i.e. number of hops/species/second. From Figure 5-20, the derive a lateral barrier to diffusion of the sombrero defects is calculated at 1.3 eV.

![Arrhenius Plot of](image)

**Figure 5-25** Arrhenius plot of elucidating the sombrero defect diffusion barrier on copper (100). Each data point is calculated from the hop frequency at a given temperature under standard "non-perturbing" STM conditions (0.02 nA, 0.02V). Hop frequencies are calculated as the hop/species/time(scan time).
A measure of the hop frequency of each defect type: sombrero and hollows as a function of imaging tunnel current set-point. It is clear there is a factor of at least two in their respective diffusion rates at RT indicating that the two species are different not just in appearance but also in their measurable properties.

5.7 Discussion

Having unexpectedly found both sombrero and hollow species on our sample surface, we endeavoured to determine exactly what they were. The reason for our keen interest, was twofold;

(i) They were stable on a metal surface at RT, and
(ii) We could manipulate them.

Low-resolution STM images revealed two different structures, sombreros, and hollows, but with this information alone, we were unable to definitively say anything regarding their physical or chemical nature. With high-resolution tips on the other hand, the underlying copper lattice was visible. Now, the structures appeared square, though they still had the same general features as for blunt tips, i.e. sombrero in both cases had a bright spot inside a dark "pit". This improvement imaging capability, enabled us to conduct a literature review for comparison.
Despite this, we failed to find any reports of similar species having been observed with STM. The stability of the species, strongly implied they were not atomic, and again, a literature review of both atomic species, and vacancies, confirmed that this is likely to be the case. The two remaining options the species could be, were then clusters or molecules.

Identifying that the species are thermally produced, through surface segregation ruled out any possibility, that the species observed were molecules. In any event, how could a single thermal process produce two different species at exactly the same temperature? With this in mind I tentatively propose, that the two structures have the same core unit, a vacancy cluster.

Analysing thousands of sequential STM scans, it is noted that a sombrero never flips contrast to become a hollow, or vice versa, furthermore, they have an interdispersed distribution on the metal surface ruling out tip-related contrast. It was also shown that each species had a different diffusion barrier, separated by an order of magnitude. This indicates that sombreros and hollows are somehow each “anchored” differently to the metal surface. Different coordination or bonding is a routine explanation for molecules, appearing and behaving, differently on surfaces. But we have already shown the sombreros and hollows are not molecules. It is also true that atoms/molecules form different bonding states, and/or, bind at different sites, but if this is the case, atomic manipulation would easily flip them between these different electronic states, or adsorption sites. Despite this, no amount of physical or electronic manipulation was ever able to convert sombreros to hollows, persuasively indicating, that the species are in fact distinct. Again, how are two very similar, yet different, species produced at the same temperature?

Suppose for a second only one species, a vacancy cluster, is thermally produced. This cluster then combines with an adatom to form a second structure, the sombrero. This would explain a single thermal process resulting in two different species, and why we were unable to flip between two nonexistent bonding and binding sites. It also explains why no chemical signatures are observed in mass spectrum analysis, and why silicon samples remained undosed during the “outgassing/evaporation” experiments.
The structural line profile data indicated they had depths equivalent to a step height. Spectroscopy, data, indicated that the electronic structure of the central species was identical to copper, i.e. it is copper. Observing the video sequence just prior to the discussion, indicates that the central species can be dislodged, and is indistinguishable from the copper lattice. Hence, it seems difficult to conceive what else the species could be. On the other hand, extensive literature searches, suggest that vacancy clusters of this size should be highly mobile on copper (100)\cite{304}. Furthermore, by examining Figure 7-5 a little closer, it is noted that the total number of species i.e. both vacancy clusters and adatom-clusters is 69. If the species are indeed vacancy clusters, this represents $\approx 600$ vacancies present in the 20 nm$^2$ area. The equilibrium concentration of vacancies is exponentially dependent with temperature and given below as;

$$N_V = N \exp \left(\frac{-Q_V}{k_B T}\right)$$  \hspace{1cm} \text{Equation 7-1}$$

Here, $-Q_V$ is the vacancy formation energy, 517 meV\cite{349}, $k_B$ is Boltzmann’s constant 8.62 x $10^{-5}$ eV/atom-K, and $T$ is the absolute temperature in Kelvin. At 1000K, with 4600/20nm$^2$ potential defect sites, only 15 vacancy defects are predicted to be present per 20nm$^2$ image. The same calculation at the melting temperature, 1339 K, gives $\approx 50$ vacancies per 20nm$^2$, so in effect we have a 4000% discrepancy with our experiment.

Adatom islands and vacancy islands are two dimensional crystals. At sufficiently high temperature, they adopt their equilibrium shape, which is determined by the variation of the step free energy with angle. The step free energy is the energy that is required to form a crystal step, and it is proportional to the chemical potential of the step as stated by the Gibbs-Thomson relation. This equilibrium shape, is maintained in most our experiments, but not during coalescence. The equilibrium shape for vacancy islands on Cu (100) is square, with the step edges orientated along the close pack directions. At elevated temperatures island shape is not static but continuously

\cite{165} And references therein
fluctuates due to stochastic mass flux along the islands perimeter. We however, do not observe shape fluctuations.

Motions of islands across the surface inevitably lead to encounters with each other. When two islands with an equilibrium shape meet, they form a new island, with a non-equilibrium shape, pairs in most our experiments. In theory, these vacancy islands should reshape themselves, relaxing into their equilibrium form. Again we don’t observe this.

What’s more, like single adatoms and vacancies, vacancy clusters ought to be extremely mobile at RT. The case for collaborative hopping of small vacancy groups is slightly more complex than atoms, but for simplicity, it’s easily understandable, that the more atoms moving in tandem, the less mobile the cluster. As such, one may expect small vacancy groups to be stationary, but hop probabilities even for eight vacancy clusters reported by Salo et al. show that these too, are completely mobile at room temperature. The probability for larger clusters >50 atoms collaboratively hopping drops off sharply, so at RT these are observable with STM.

Observable they may be, but stationary they certainly are not. The onset of a second diffusion mechanism, edge or periphery diffusion means that whilst the centre of mass is pseudo “stationary” the cluster continuously changes shape. I tentatively argue, that the anomalous structural integrity, indifference to coagulation and extremely high stability, results from the structures lying in between to two different diffusion mechanisms. Being a magic size, periphery diffusion is stifled, and thus unable to provide sufficient mobility for reshaping islands. Similarly, concerted sliding is prohibitive since at one is trying to move 9 vacancies at a time. I thus believe, that a new avalanche type diffusion takes place, where one atom is destabilised, unsettling the entire structure, which then attempts to quickly restabilise, and hence hops can occur.

To summarise, experimental evidence thus far presented emphatically suggests the species are vacancy clusters. On the other hand, considerable theoretical and experimental data imply they’re not. Experimental findings, especially their dynamic stability at room temperature and thermal production, puts real limitations on what the species may be and yet the vacancy cluster hypothesis appears obvious, but vacancy
production rates and mobility, even for clusters, appears to be at odds with conventional wisdom.
6 ROLE OF THERMAL ENERGY IN THE STM MANIPULATION PROCESS

6.1 Introduction

Having realised a workable "adsorbate"-substrate system, which is stable, tuneable and energetically suitable for STM manipulation, we now set about achieving some of the tasks and challenges outlined in Chapter-1. In an attempt to further develop and better understand the technique and mechanisms of moving atoms, the role of thermal energy as a control parameter during STM manipulation is investigated. From these investigations a new technique for quantifying the manipulation process is developed. The tasks and challenges are summarised as following:

- Perform STM manipulation at room temperature (RT),
- Develop procedures for better assessment of the processes and mechanisms of manipulation,
- Build rudimentary nano-scale structures,
- Investigate the role of thermal energy as a control parameter,
- Quantify of the manipulation process,
- Investigate and quantify the potential energy landscapes "dynamicism" as a function of tip-sample distance,
- Directly measure the tip-manipulant interaction forces, and dissipation, with an nc-AFM/STM, and compare these results to STM based techniques

Manipulating at RT is a relevant and necessary advancement since it expands the application of this fabrication technique both scientifically and technologically. Technologically, working at RT is simpler, cost effective and practical. Additionally, devices capable at working at temperatures above RT urgently need to be developed. Power dissipation in nano-scale devices is already an industry wide concern, and from this perspective, there is little point in building structures or constructing nano-
devices, which are only stable at LT. If a "nano-scale building block\textsuperscript{19}" is functional, positionable, and eventually employed for technological gain; high electron current densities will typically heat the structure causing its constituent parts to diffuse, and ultimately result in device failure. Highly bound species, which are stable, yet moveable at RT, inherently offer greater potential to avoid such calamities.

Scientifically speaking, building at RT will help elucidate thermal energies role in atomic scale dynamics and mechanics. In particular, the influence of temperature on bond making and breaking is investigated. By performing experiments at different temperatures, thermodynamic relationships are utilised and developed with a view to quantifying the energy transfer process from an STM tip to the surface bound defect.

As Fishlock \textit{et al.}\textsuperscript{32} pointed out, problems exist when attempting to manipulate atoms laterally at RT, since atoms which are sufficiently well bound to the surface to avoid thermal activation require stronger tip interactions to be moved. This usually results in uncontrolled, and randomly directed, electronic excitations and/or ruptured tips. To overcome these limitations, high temperature (HT) STM manipulation offers great promise.

Instead of battling with strongly bound species or continuing to freeze-stick species which ultimately cannot build devices, is it possible to move strongly bound species more easily, by supplying external energy in conjunction with the localised tip-provided energy, through heating?

Manipulation above RT could provide sufficient thermal mobility to perform otherwise difficult manipulations, and once a desired structure or device is constructed; it can be left to "set\textsuperscript{20}" in position. Such a technique would open the field of manipulation to a previously "off-limits" range of materials whose $E_B$ values are significantly larger than $E_{\text{tip}}$. In this new method, $(E_{\text{Ext}} + E_{\text{tip}}) > E_B$, but, $E_B \gg 3/2 k_B T$. Hence, a species could be moved with an STM tip, but would remain unaffected by thermal fluctuations. In this manner, we could "cheat" nature's imposed limitations on the class of materials useable for atomic, molecular and cluster manipulation. These techniques and more, are presented in this chapter.

\textsuperscript{19} Nano-scale building blocks include atoms molecules, and now the vacancy cluster complexes outlined in the previous chapter. They need to alter the LDOS and/or have some functionality e.g. rectification etc., and be moveable. Having properties, which are tuneable, is advantageous.

\textsuperscript{20} By "set" it is meant, to remain in a final, stable, and stationary state.
6.2 They’re moving!

Figure 6-1 is a 20 nm x 20 nm STM topograph of copper (100) featuring the two vacancy structures described in chapter-5: i.e. (a) the adatom-vacancy clusters (or sombreros), and, (b), the vacancy-cluster structures (or hollows)

Figure 6-1 is for analysis purposes divided into four different zones. In zones (i) and (iii), the tunnel current set-point ($I_T$ set-point) is set at a standard and non-perturbative value of 0.26 nA. In this regime, each structure appears point-like and as discussed in the previous chapter, the structures remain stationary for prolonged periods until perturbed by thermal fluctuations. When this occurs, the surface layer induces a random-walk diffusion process by coupling thermal energy from the underlying phonon bath. At RT, this coupling results in a hop rate in the region of $10^{-3}$-$10^{-4}$ hops/s, inferring a stability lifetime of $\approx 1000$ seconds. In zones (ii) and (iv) however, the presence of an STM tip causes the defects to move, and the clusters are then manipulated. Scanning the surface with 22 nA of tunnel current, $I_T$, in zones (ii), and (iv), the sombrero type structures are mobilised and controllably slid across the copper (100) surface.

The structures in these zones are identifiable as “half moons” during manipulation. Where multiple hops occur in sequence, the structures appear as a trail of half moons, as shown in Figure 6-1 (c). As the STM tip images the central atom in each sombrero structure with high $I_T$’s, the tip-surface interaction becomes greater between the tip and sombrero. Eventually as the interaction cross-section increases, the interaction becomes critical, and the sombrero hops away from the tip. When this occurs, the “second half” of the atom cannot then be imaged and the sombreros appear as half moons. In this image as with most of our manipulation experiments, atomic resolution of the underlying copper lattice is not achieved and the structures appear circular because the tips being used are blunt. Like Parschau [594], our experimental experience indicates that whilst blunt tips are undesirable from a resolution perspective, they are far more reliable, stable and are ultimately a requirement for STM manipulations. Other requirements, processes and procedures, critical for higher temperature manipulation success, are now briefly outlined.

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21 Since it is a little easier to use Fishlock’s nomenclature, i.e. sombreros and hollows, we will do so from this point forward keeping in mind they are vacancy clusters complex structures.
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Figure 6-1 20 nm x 20 nm STM topograph demonstrating controllable RT manipulation. Using 22 nA of \( I_T \), the sombreros are deliberately slid across the surface. The hollows remained stationary in this experiment (d), but these are moveable, they just require higher \( I_T \) values to induce motion. By toggling the \( I_T \) between high (22 nA) and low (0.02 nA) \( I_T \) set-points, defect motion is controlled. With this degree of control, rudimentary structures can be created, as shown in region *.

![STM topograph](image)

Figure 6-2 STM line profile from the tunnel current image from the bottom (left) to the top of image (right), indicating the change in magnitude required to induce manipulation of the clusters at RT.

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6.3 Experimental criteria for high-temperature manipulation

6.3.1 Tip criteria

In chapter-4, energy requirements specific to high temperature manipulation were outlined. One key criterion relevant for manipulation at all temperatures but increasingly problematic when bonds approaching 1 eV are being broken, is $E_{Tip}$, the interaction energy a tip can withstand before failing. This energy criterion is unique, since it is the only value which is experimentally controllable.

Sharp tips are ideal for high-resolution imaging, but for spectroscopy and atom manipulation, blunt tips are more suitable. Higher $I_T$ set-points are required for blunt tip manipulation (typically 4 nA for sharp tip, as compared to 12 nA for a blunt tip), but on the other hand, blunt tips are stable, reliable and ultimately a necessity for quantitative manipulation experiments.

If a tip fails during a $I_T$ set-point vs success rate experiment (i.e. changes configuration), the partial data set is usually useless. As such, tip stability is a key concern. Tip structures are controlled by inking, indentation, focussed ion beam (FIB) milling, and chemical functionalisation. In our experiments, tips giving resolution as seen in Figure 6-1 were the most suitable for manipulation.

This tip type is acquired by indenting the surface with an STM tip during controlled $l$-$z$ spectroscopy. If a sharp and atomically resolving tip is instead used, rupturing during manipulation typically occurred. If, on the other hand blunt tips, which resolved the vacancy clusters as "black blobs", were used, manipulation was difficult to achieve, requiring up to 30 nA $I_T$ to induce defect motion. This in turn induces tip failures. Exactly what type of tip our functionalisation procedure produces our favoured tip, can not precisely be known. Nevertheless, the production procedure was consistent.

To ensure that any minor tip alterations occurring during manipulation are detected; the tips integrity was constantly monitored. Monitoring is performed by analysing the resolution type and calculating the diffusion rate of the vacancy cluster structures. Since it is widely thought that STM tips influence diffusion rates, careful monitoring of hop rates under equal tunneling conditions provides a derivative means to measure the tips integrity.
6.3.2 "Seeing" manipulation"

To create images akin to Figure 6-1, tips are raster scanned forward and backwards along the same line before moving upwards and repeating the process. As topographic data is acquired in the "constant" current mode, 3-d images of both $I_T$ and topographic ($z$) data for all $x$-$y$ points are recorded.

Taking bottom-to-top line sections of the $I_T$ images of Figure 6-1, Figure 6-3, we can compare the $I_T$ signal during imaging and manipulation, Figure 6-2 and Figure 6-4. The deliberate and stepwise increase in the $I_T$ necessary for inducing manipulation is clearly visible. Also clearly visible, but unintentional is the increase in noise in the $I_T$ channel. Since the constant-current feedback circuit is unable to keep this channel constant, the corresponding ($z$) channels also become noisier with the increasing $I_T$, Figure 6-3 and 6-4 (b). Hence, during manipulation events which require high perturbation energies, and in our case high $I_T$, it becomes impossible to observe manipulation events "live", Figure 6-3, section (iv). This results in a loss of the most important manipulation data.

To overcome this limitation a dual scan imaging/manipulation-mode is developed. Here, we scan at different $I_T$ set-points in the forward and backward scans, manipulating in one, whilst non-perturbatively "seeing" in the other. Thus, we can both move and see structures in real time during STM manipulation experiments. This technique is later shown to be critical for quantifying the manipulation process.

6.3.3 Drift control

Another experimental challenge, instrumental for seeing and quantifying the manipulation process is drift control. We need stable tips for cross relating data, but we also need to see atom movements to understand hop dynamics. If the area we are looking at constantly changes however, we have neither of the above. This challenge may be solved by suitable drift control.

For high temperature manipulation, there are four tenets to this problem. One, using or developing an accurate drift control circuit. Two constant and tedious manual corrections of the automatic drift correction rates. Three, ensuring about four hours have passed between temperature changes. Anything less, made it to dangerous for the tips integrity. A fourth issue is $z$-drift of the sample into the tip. This final problem...
was a somewhat unanticipated problem, and overcoming this issue is critical. The sample tip gap decrease in z once heated begins, and if the tunnel current signal is not constantly monitored the tip will crash.

6.3.4 Thermal supply and temperature measurement

When performing room temperature, high temperature, and variable temperature manipulation experiments using STM, typical experimental issues such as noise and grounding issues are particularly troublesome. How for example, does one heat the sample without influencing the tunnel current line? Sample heating is performed by direct current heating, and/or coupling thermal energy through a “hot” finger type technique in our experiments, depending on the sample choice.

In this case, such as for Silicon 111 (7x7), thermal energy is supplied by a direct current resistive heating technique. Here, current is passed through the sample whilst tunneling. This in turn requires a potential drop across the sample, and as such, the potential between the tip and the heated surface is a function of tip $(x,z)$ position relative to sample. This affects the integrity of the bias voltage, and can induce noise.

Heating metals on the other hand, was performed using a poly-boron nitride (PbN) plate sandwiched underneath the copper sample and the base plate. This heats through electrical resistive heating, which in turn thermocouples heat to the sample surface. In this heating set-up, electrical noise was a key problem, which is likely to occur because of a 50 Hz ground loop.

Temperature measurement is performed using thermocouples placed on the microscope approximately 2 cm form the sample. This is typical in STM set-up’s and as such, the precise temperature is often difficult to ascertain. In our experiments, this problem is overcome using a technique requiring the precise temperature gradient rather than the temperature itself, so any offset in measurement is typically unimportant.
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Figure 6-3 20 nm x 20 nm STM topographs of the same area, acquired simultaneously, in the forward and backward direction illustrating z-instabilities during manipulation experiments on Cu (100) as a function of increasing tunnel current. (a) The backward scan is fine because the tunnel current is 0.26 nA. (b) The image deteriorates progressively as the tunnel current increases from 0.2, to 1, 3, and finally 6 nA until the species are eventually unidentifiable. Thus, in order to analyse manipulation events precisely, one has to perform dual imaging with different parameters in the forward and backwards scans.

Figure 6-4 Tunnel current noise as a function of $I_T$ set-point during manipulation. (a) With each incremental step in the tunnel current the noise also increases. This can result as because of increased tip atom instabilities in the tip gap region.
6.4 Room temperature manipulation of atoms

6.4.1 Results

Figure 6-5 (1-24) is a set of STM topographs demonstrating controllable and repeatable manipulation at room temperature on a metal surface. The manipulations are predominantly induced using high tunnel currents, though low voltages also induced motion\(^\text{22}\). The elapsed time, numbers of atoms moved, and manipulation currents are all displayed were relevant, in each respective image.

The sequence shown took \(\approx 5\) hours of continuous STM manipulation to create, in which time; almost a hundred scans were taken. These included before, during, and after manipulation scans, which facilitates the precise measurement of the manipulation pathways, hop directions, enabling us to determine the defects hop dynamics. In this period, almost 200 clusters were deliberately slid across the surface, which is achieved using tunnel currents up to 22 nA. Despite this, the STM tip never broke during the sequence indicating the manipulation process is highly reliable.

Up to 100% manipulation success is achievable (i.e. all species move all the time) and combined with the above mentioned tip stability, this enables the construction of rudimentary structures including single defect lines, as shown in Figure 6-5.

One part of every scan is always left un-perturbed. This is a deliberate technique we developed, which serves three different purposes. First, the defect diffusion rate in the un-manipulated part is calculated and compared with previous scans. If the diffusion rate changes, it can be determined that a tip change has occurred, even if minor, and the data set is discarded. Second, defects in the un-perturbed part act as a set of reference points so it is easily “proved” that manipulation takes place. Finally, and importantly, using the stationary species as 2-d markers, exactly how far the defects have been moved in both the x and y directions can be precisely determined. This is an extremely difficult process without these markers as seen in section.

During defect manipulation, atomic resolution of the underlying copper lattice is achieved in almost all manipulations in this sequence. This implies some form of “contact-mode” manipulation but it is noted that this effect does occur in all data sets.

\(^{22}\) We analyse the manipulation control parameters and mechanism in more detail in section 6.4.26.4.3
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Figure caption on page 37
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Figure 6-5 Sequence of STM topograph images taken from an STM video illustrating the construction of rudimentary defect lines at room temperature on copper (100). The defects are manipulated by increasing the tunnel current set-point beyond a threshold value. Manipulation is also achieved using lower tunnel current set-points by decreasing the bias voltage. The defects are “dropped-off” at any desired location by returning the \( I_{\text{set-point}} \) to a non-perturbative 0.02 nA. During manipulation, atomic resolution of the underlying lattice is observed. This indicates that a contact-type mode of manipulation occurs, but this phenomenon is not observed in all data sets. 100% manipulation is achievable (4), though this is not always achieved (6). This is a function of the tunnelling parameters, as seen in section 6.4.2. Collisions between manipulated defects and stationary defects result in the “picking-up” of the stationary defects (image (8) defect (ii)), and “dropping-off” of moving defects (image (8) defect (i)). Motion of the defects is almost perpendicular to the tip trajectory, indicating that a “slice-type snooker shot” takes place between the tip and defect. A key operational/experimental point, is that in order to observe the effects of manipulation, or build albeit very simple structures, in a 5 hour period, at RT, the STM drift rate needs constant correction using both a feedback circuit and manual adjustment. At higher temperatures, continuous adjustment of the z-range is also required to avoid tip crash. \( I-V \) and \( I-z \) spectroscopy is continuously performed to insure that any tip changes are detected.

Collisions between manipulated defects and stationary defects resulted in the “picking-up” of the stationary defects (image (8) defect (ii)), and “dropping-off” of moving defects (image (8) defect (i)). Motion of the defects is almost perpendicular to the tip trajectory, indicating that a “slice-type snooker shot” takes place between the tip and defect. This is indicative of the manipulation mechanism, and the precise hop motions are examined in more detail in section 6.6.

To develop statistics, manipulation is performed at a range of different tunneling conditions, with each value repeated to ensure that each the data point, i.e. \( (I_{T}, V, \text{hops}^{-1}) \), has at least 100 individual experiments (manipulations attempted). Scan speed nor scan angle dramatically increased manipulation success.

Collisions between manipulated defects and stationary defects resulted in the “picking-up” of the stationary defects (image (8) defect (ii)), and “dropping-off” of moving defects (image (8) defect (i)). Motion of the defects is almost perpendicular to the tip trajectory, indicating that a “slice-type snooker shot” takes place between the tip and defect. This is indicative of the manipulation mechanism, and the precise hop motions are examined in more detail in section 6.6.

To develop statistics, manipulations are performed at a range of different tunneling conditions, with each value repeated to ensure that each the data point, i.e. \( (I_{T}, V, \text{hops}^{-1}) \), has at least 100 individual experiments (manipulations attempted). These results are compiled for each defect type. The diffusion rate of the un-perturbed region is calculated, and represents one error component involving the hop statistics. Hop direction data was also recorded for every single defect, as was the hop path length. This value however, it should be noted is a function of the “traffic” i.e. defects in the way, in a given image. This is another error component which is difficult to
overcome. A final, and serious threat to statistics involving this type of sliding manipulation involves where the manipulation starts and ends. This partially determines the number of hops each species undergoes, but does not reflect any change in interaction. Some of these problems are addressed later, along with new methods of obtaining statistical data from STM images. We now take a closer look at the parameters controlling the manipulation process.

### 6.4.2 Manipulation control parameter (i): Tunnel current

Tunnel current is found to induce defect manipulation at room temperature (RT) on copper (100), as shown in Figure 6-6. The $I_T$ threshold for inducing manipulation is approximately 12 nA, though considerably more $I_T$ is required to induce 100% manipulation (i.e. all species move all the time). Considerable spreads in threshold values are observed for different tip-types, 10 nA - 20 nA, but for a single tip-type, as identified by the resolution type and diffusion rates; threshold values were remarkably consistent, ±20%. The inconsistency of threshold values with different tip-types represents an experimental difficulty which complicates the cross-correlation of data sets. This complication is side-stepped by only considering data from similar tip-types.

A tunnel current vs manipulation success rate graph is presented in Figure 6-7 as a log-log plot of hop frequency versus $I_T$. Hop frequencies are calculated as the total number of hops/atom in the time taken to acquire the image. The values are obtained by examining three different images; the before and after images, and the image in which the hops occur. To perform this task as precisely as possible, the three images are converted into video file using the WSxM image analysis package. The images are then cross-correlated, to position stationary defects at same points and counteract drift.

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23 How this is calculated was discussed in section 6.3.1. It is calculated in the un-perturbed part of the image.
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**Figure 6-6** STM topograph taken in the constant-current imaging mode, demonstrating the use of tunnel current as a control parameter for precise manipulation of defects at room temperature (RT) on copper (100). The defects are positioned deliberately into a defect line array.

**Figure 6-7** Log-log plot of hop frequency (hops/species/sec) vs tunnel current (nA). The data is acquired by making videos of before, after, and during manipulation images, so we can count the number of "hops" taken by each defects. Also calculated is the total number of species. The sum of the number of hops and divided by total number of species and the time taken to acquire an image (= 300 s) gives the hop frequency. The graph shows an upward progression after an initial decline in hop frequency. The error is the diffusion rate, measured in the un-manipulated part of images.
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Unmoved defects remain stationary in the video sequence. Defects moved reveal the start and end-points of the manipulation path and because of the dual imaging-manipulation technique employed by us, we can record the exact pathway, number of hops, and directions every defect takes.

Figure 6-7 displays an overall upward progression but an initial dip in the hop rate with increasing tunnel current is noted. After this dip a sharp increase in manipulation is observed. This dip in hop frequency is found to result from diffusion events which complicate the statistical analysis. This complication is resolved in Figure 6-8 and the solution and implications are discussed in detail in section

![Figure 6-8 Linear plot of tunnel current versus manipulation success rate. Success rate is defined as the number of hops per species per second (s⁻¹). An exponential-type variance is indicative of a short-range repulsive interaction though multiple interactions may concurrently occur. Tip-induced localised heating, potential barrier alteration, vibrational excitation, and/or electric field induced movements, may play a role in transferring energy from the STM tip to the defect as a result of a change in \( I_j \).](image_url)

**Figure 6-8**, is a corrected linear-plot of manipulation rate versus tunnel current for the system studied. Success rate is defined as the number of hops per species per
second ($s^{-1}$). All RT manipulation graphs obtained in this body of work, display similar characteristic shapes and can all be divided in two different regions.

Region-(i) in Figure 6-8 has a moderate slope of 0.04 hop/s/nA indicating a relatively weak interaction type. Species in this region correspond to manipulations shown in Figure 6-14 (A). Region-(ii) is typified by the onset of a more marked slope of 0.125 hop/s/nA. An exponential-type variance is indicative of a short-range repulsive interaction, though one may expect multiple interactions to be in effect. In addition to short-range chemical forces [19], tip-induced localised heating [16], $I_T$ density [20], electric-

![Figure 6-9](image-url)  
Figure 6-9  Plot of tunnel current and manipulation success rate as a function of tip displacement towards the surface. The tip displacement values are obtained from a measure of the distance travelled by the tip recorded by the Scala software. This not an absolute measurement of the tip-sample gap, and some caution is advised when interpreting the data. Nevertheless, qualitatively, it is a reasonable measure. The tunnel current set-point vs measured displacement (black curve) shows a typical exponential dependence. The onset of significant manipulation occurs after significant increases in $I_T$ are observed. This indicates a dominance of short-range repulsive interactions as a driver for manipulation.
field \[^{[51]}\], or vibrational excitations \[^{[19]}\] may all increase with increasing tunnel current. Additionally, the potential energy landscape may be locally deformed at an increasing rate with decreasing tip-sample gap (caused by an increase in $I_T$). As such, all mechanisms may be wholly, or partially, influential in manipulating the defect clusters.

**Figure 6-9** is a plot of tunnel current and manipulation success rate vs tip distance. The tip displacement values are obtained using Scala software. This not an absolute measurement of the tip-sample gap, and some caution is advised when interpreting the data. Despite this, qualitatively it is a reasonable indicator of the interaction-manipulation relationship. The tunnel current set-point vs measured displacement (black curve) shows a typical exponential-type dependence. The onset of significant manipulation occurs 0.5 Å after a significant increase in $I_T$ occurs. This
indicates a dominance of short-range repulsive interactions as the driver for manipulating defect clusters.

If the manipulation process is electronic in nature, examining log-log plots of tunnel current vs manipulation yield, can provide indications of the excitation mechanism. In particular, when manipulations involving molecules and/or adsorbates on semiconductor surfaces occur, activation-plots are employed to elucidate reaction pathways of electron-stimulated processes. The slope value is then used as an indicator of the bond type excited, to induce transfers, rotations, hops, or dissociations. This is in part possible because of the localised nature of the electronic states in molecular and semiconductor systems. But for metal-on-metal systems such localisation is typically not present.

Tip-induced localised heating effects resulting from high $I_T$ densities in the tip-gap region may also, or exclusively, occur. In the course of a tunnelling event, a certain amount of energy is lost by electrons via the adsorbate. This energy is released on the energy degrees of freedom. For Eigler's famous Xe switch experiments, temperature rises were calculated by Joachim et al. who found the temperature changes in the region of 1 K /100 nA.

Joachim et al. showed that power dissipation in nanoscale contacts maybe modelled with a simple Joule-like $P=RI^2$ relationship. Hence, increasing applied voltages are expected to give rise to increased manipulation rates if thermally activated. Such an increase in electromigration, or thermal heating of defects, was originally presented by Ralls et al. On the other hand, increasing the voltage also decreases the tip-sample distance, and thus, the short-range force components of the interaction energy. Furthermore, by increasing the tip-sample distance (by increasing the voltage) a secondary effect is to reduce the tunnel current density in the tip-sample region. This in turn lowers delocalises said heating effects. To examine the influence of bias voltage, and thus, tunnel current density, we performed variable voltage manipulation experiments.

6.4.3 Manipulation control parameter (i): Voltage

To investigate the manipulation process in greater detail, manipulation success as a function of voltage was investigated. This is specifically designed to determine if
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electric field mechanisms, electronic excitations, resonance states, or heating are dominant influences during the manipulation process. Most of these processes are “still on the cards” since the $I_T$ vs success data, is insufficient alone to distinguish conclusively between these competing processes. To our initial surprise, increasing voltage over two orders of magnitude, from 0.03 V up to 5 V did not increase the manipulation success rate in an incremental fashion. As mentioned in section , the sombrero species are electronically excited at 3 V, which in turn increased the diffusion rate, and decreased the manipulation threshold. This suggests an excitation process of a particular bond, which in turn decreases the binding energy to the surface. A lack of data however, precludes us from making a more definitive assessment of this excitation and manipulation mechanism.

![Figure 6-11](image)

**Figure 6-11** Plot of manipulation success rate versus applied bias potential. Decreasing the voltage increased the manipulation success rate. This is repeated at different $I_T$ set-points, and threshold voltage values required to induce manipulation correspondingly shifting upwards (increase in tunnel current set-point), or down with tunnel current. Thus, it is apparent that the tunnel gap resistance is the control parameter for inducing motion.

Decreasing the voltage as low as possible without causing a tip crash, i.e. to 0.0003 V, increased the manipulation success rate, **Figure 6-11**. This experiment was
repeated at different $I_T$ set-points, and the corresponding threshold voltage values required to induce manipulation shifted towards higher voltages with increased $I_T$ set-points. Thus, it is clear, that the tunnel gap resistance is the key control parameter for inducing motion, and not tunnel current per-se. This implies that distance, and thus forces, plays a decisive role during manipulation in this system. That significant heating effects or other mechanisms should still play partial roles in the manipulation of defect clusters, is reasonable to assume.

The results presented so far, strongly indicate that alterations in manipulation success rates are achieved by controlling the tip-sample distance. With this in mind, it is prudent and necessary to examine both the force-distance-manipulation relationship, and, line profiles along the manipulation path. Using line profiles to elucidate different manipulation modes was been pioneered, and extensively used, by Karl Heinz Rieder's group. Through their use of line profile data acquired during manipulations, they identified pushing and pulling, as repulsive or attractive interactions, respectively.

We investigate line profiles and additional data at our disposal, specifically the hop dynamics, to further distinguish which interaction mechanism and the hop mode is occurring.

### 6.5 Manipulation mode

The influence of tunnel current on defect motion was quantified in Figures 2-(7-10). Here, it was shown that increasing the $I_T$ set-point, increased the manipulation success rate, possibly due to short-range forces. As a result of the developed dual image-manipulation mode, the manipulation process may additionally be graphically analysed. From this data, shown in Figure 6-12, it is immediately clear that the mode of manipulation induced at different $I_T$ set-points is not uniform. To refine, and improve, our understanding of the interaction inducing motion, we now examine the hop dynamics of the manipulated defects.

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24 And citations thereafter
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Figure 6-12 Three STM topographs illustrating diversity, directionality and controllable on-off manipulation. Different manipulation types, directions and hop lengths illustrate the improving finesse and precision currently achievable in difficult operating regimes. Tailoring tip surface interactions, the potential landscape, and localised temperatures are some of the techniques used to achieve these aims. Conversely, by analysing these dynamic events in turn helps with the elucidation of bond breaking mechanics and thermodynamic processes.
Figure 6-12 (a) is a 12.5 nm x 5 nm STM topograph acquired with 15 nA of tunnel current. With 62.7% of sombrero species moved, only partial manipulation is achieved. No hollow defects are manipulated. The sombrero manipulation rate is 1 hop/species, but the average jump length is higher at 1.6 hops per manipulated species. There is poor control of directionality with only 54.8% of species moving in the [110] direction, see inlay of Figure 6-12 (a). Very few collisions occur because the hop length is less than the nearest neighbour distance. Hops in this interaction regime are characterised as short, weakly directed, individual hops, which are somewhat decoupled from their neighbours. A particular point of note is that 31% of species move in a direction opposite to the scan direction. This indicates the presence of an attractive, relatively mild, destabilising but poorly directing force.

In Figure 6-12 (b) the $I_T$ set-point is increased to 24 nA. Here, all sombreros and 24% hollows are manipulated. The manipulation success rate and average jump length are now equal. Both measure 4.07 hops/species. There is a higher degree of directionality, with 85% of species now moving in a direction opposite to the scanning tip, Figure 6-12 (b). Here, plenty of collisions occur, causing sombrero species to change direction, and/or be "dropped off" during collisions. Hops in this interaction regime are identified as, medium length, directed trails, whose paths are strongly influenced through collisions. These collisions complicate statistical analysis.

In Figure 6-12 (c) the manipulation current is yet again increased and the $I_T$ set-point is now 28 nA. Here, all sombreros are moved and the manipulation jump length is 13.4 hops/species. This is rather arbitrary however, since all species continuously slide, and the low density of surface species reduces collisions. There is a high degree of directionality with 98% of species now moving in a direction opposite to the tip, Figure 6-12 (b). Interestingly, the predominant hop direction has also changed from the [110] to the [110] direction. Here, few collisions occur because there is a low density of species in the manipulation pathway. Hops in this interaction regime are characterised as long, atomically precise, directed trails, whose paths are not influenced through collisions.

Figure 6-12 (a-c) illustrate that different manipulation types, hop directions and hop lengths are achievable by tuning the tip-surface interaction. We demonstrate that soft "nudges" and/or controllable sliding is possible. We show that species can be slid in
two different directions, and, that it is possible to alternate between each type by altering the $I_T$ set-point. The controllable shift in hop-type is interesting, since it is indicative of a shift in the dominant interaction type. This insinuates that multiple interactions are competing to influence defect motion. This shift in hop directions, initially towards the tip, but then away from the tip, as a function of increasing $I_T$, probably indicates a shift from an attractive to a repulsive force.

6.5.1 Tip-induced hopping

Figure 6-13 5 nm x 5 nm STM topograph of clean Cu (100). Overlayed is an illustration of the hops an adatom atom sitting in a four-fold hollow site may be expected to make. (i)-(iv) are the hop types observed during our experiments (a). There are strong indications that the centre atom in the adatom vacancy cluster is sitting in a four-fold hollow site, one monolayer beneath the surface layer. Clearly visible as the species moves is the "vacancy-part", i.e. the surrounding black part which moves in tandem with the "bright part"-i.e. the adatom (marked with red arrows).

Figure 6-13 (a) is an illustration showing how an adatom sitting in a four fold hollow site might "hop" during atomic manipulation experiments on Cu (100). Figure 6-13 (i-iv), are four high resolution image sections taken from a larger STM scan. The images show the different hop types observed during manipulation of adatom-vacancy clusters, i.e. sombreros. Examining (i) and (ii) first, i.e. single "lateral hops", it is noticed that the hopped species no longer resemble half moons, but rather a "90%
sliced lemon which is rotated". The two sites are energetically equivalent sites, but site (i) is "lower" than site (ii), because we scan at an angle to the lattice [110] direction. Hence, when a hop occurs to site (i) or site (iii), one expects with (i) being lower, to have less atom left to "see", i.e. it appears smaller. This is clearly shown in Figure 6-13 (i) v's (ii).

Figure 6-13 (iii) shows the most common hop type observed at lower perturbations. This hop type in the [110] direction is also the most likely hop type to produce hop series, i.e. trails, and is characterised by a series of half moons as shown in, Figure 6-13. The fourth hop type, is really a really a quasi-hop. It is in fact a two-step hopping process, comprising of one: hop-type (ii), and one hop-type (iii) occurring in rapid succession, to produce the hop motion shown in Figure 6-14 (iv). This is the rarest hop type observed.

6.5.2 Tip-controlled sliding

In addition to the fundamental single hops, it is possible to “slide” sombrero structures across the surface. This sliding is more correctly speaking, a repeating series of individual hops. Figure 6-14 (a) is an STM topograph of Cu (100) featuring both sombrero and hollow structures. Imaging occurs by scanning left to right as you view the image. In this image, it is possible to see trails of species. Hence, the continuous manipulations represent series of successful, but individual slice shots. In between each, the tip moves away and returns to the same species before repeating the manipulation process.

Figure 6-14 (b-d) highlights three different “sliding types”. Type (b) is the most common. It is a series of hops in the [110] direction over the two-fold bridge sites to a nearest neighbouring four-fold hollow site, 2.65 Å away. It is observed as a series of half moons. Type (c) is fundamentally equivalent though in practise rare because of the scan angle with respect to the lattice. Type (d) manipulation is not yet fully understood. It appears to occur when the defects are slid along with tip. It is only noticed by streaks and proven by collisions with other structures. When collisions occur, the streaks “drop” the slid species, sometimes picking up the species it collided with. This occurs in the fast scan direction and results in structures forming a “fence” of species around the manipulated area.
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Figure 6-14 Set of STM topographs taken in the constant-current mode where the tunnel current set-point $I_{\text{set-point}}$ exceeds a threshold value (typically 12 nA) required to induce sliding manipulation. In image (a), it is seen that 100% manipulation is achieved. This means, that all sombrero species present are relocated. The manipulations of each species vary, in both hop direction, trail length. The more common hop directions, and associated “hop-types” are indicated in images (b-d). (b) The defects are slid continuously in the [110] direction only. This indicates that atom transfer from one four-fold hollow site to the next in the [110] direction via the 2-fold bridge site. (c) This is again a unidirectional hop mode, this time in the [110] direction. Transport again occurs from four-fold hollow to four-fold hollow, but this time the hop occurs over a top site. Since the scan direction is asymmetric, with respect to the lattice [110] direction, hop type (c) differs from (b) in that the potential is unequal in length and height. This is expected to translate to a small difference in hop probability. (d) Bi-directional hopping which alternates between hop type (b) and hop type (c).

The hop behaviours outlined above is of particular interesting to us since hopping motion reflects the material being hopped, the excitation process and the underlying lattice. The hop types outlined are hops expected for simple adatoms hopping from
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one four fold hollow site to another. This then implies, that the peak at the centre of the adatom-vacancy cluster is an adatom sitting directly above a four-fold hollow site, one monolayer deep, and is responsible for the trails observed during manipulation. Furthermore it suggests, that the tip-energy coupling mechanism occurs primarily between the central atom and the tip apex.

6.6 Manipulation mechanism

Quantitative analysis of hop frequency versus $I_T$, $V_{Bias}$, and distance, indicated that a short-range repulsive force is the dominant interaction manipulating adatom-vacancy cluster structures (sombreros) at RT, Figure 6-7-9). This idea was reinforced by the "sight" of the defects being slid across the surface, in a direction away from the tip.

A graphical analysis technique developed during this thesis, indicated on the other hand, that at lower $I_T$ set-points long before 100% manipulation was achieved, different hop types also occur, Figure 6-12. Here it was shown that both, hopping and sliding occurs depending on the $I_T$ magnitude. Analysis of this hopping mode, or alternatively, the low $I_T$, low interaction mode, indicated that defect hop direction changed from a random walk-type motion to a tip directed (first towards tip-then away from tip) sliding as a function of $I_T$. This indicates that alternative, and competing interactions are present and vying to dominate the manipulation process.

In an attempt to analyse the full range of interaction types and hence manipulation mechanisms occurring during our experiments, it was decided that all hops, diffusion$^{25}$ or manipulations$^{26}$, should be counted and plotted as function of perturbation. In this manner, one ought to see a clear transition from a weakly perturbing regime to strong manipulations, with plots of hop rate versus tunnel current and/or voltage revealing the key interaction types. The difference between, diffusion and manipulation events is illustrated in Figure 6-15. During a diffusion event, the defect randomly hops, in any direction, and since the interaction timescale with the surface is the time taken to scan the image

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$^{25}$ Not visible live because of an excitation delay time, or, they are activated through the surface-phonon coupling.

$^{26}$ These are clearly seen "live", hence it appears clear that there are at least two interaction types.
(circa 3 mins), it is highly improbable that this occurs as the tip is “overhead”. Manipulation events on the other hand, only occur

![Figure 6-15](image)

**Figure 6-15** Two sequentially acquired STM topographs taken in the constant current mode of copper (100). Illustrated is the difference between defects which diffuse between images, and defects which are manipulated. There is a small % error, that the diffusion occurs as the tip is overhead. To improve the statistical analysis, it was critical to (a) count these events separately, and (b) use different interaction timescales, when calculating the hop frequencies. These are both critical features of the statistical analysis.

When the tip is overhead, so, we “see” these hop events “live”. Here the interaction timescale is the time taken to scan the defect only. **Figure 6-16** is log-log plot of tunnel current versus hop rate which is identical to **Figure 6-7** already presented except for the two fits placed on the data. With increasing tunnel current, the hop rate initially declines with a moderate, non-linear slope. Why this occurs as extra energy is
"pumped" into the system, is not immediately obvious. Following this negative sloped region we enter a positive sloped region, where hop rate increases as a function $I_T$.

![Log-log plot of hop frequency (hops/species/sec) vs. tunnel current (nA).](image)

**Figure 6-16** Log-log plot of hop frequency (hops/species/sec) vs. tunnel current (nA). The data is acquired by making videos from three different images. The before, after, and during manipulation images. In this way we can determine the initial and final positions along with the path taken. By assessing the path each species takes a total count of hops is acquired. data however contains a convolution of two interaction types: (a) Manipulations, and (B) tip-influenced diffusion events. We isolate these species based on whether the event is seen live or not, and we assign a different interaction time scale to normalise the hop frequencies.

The hop rate in this region experiences a sharp increase as a function of $I_T$. The range expands over two orders of magnitude and there is nearly three orders of magnitude of change in the hop frequency as a function of $I_T$. The interaction, or hop/rate as a function of tunnel current has a slope of $4.012 \pm 0.382$ hops/species/nA, and the onset of this exponential increase occurs at $\approx 7$ nA. The crossover point when region (ii) becomes significantly larger than region-1 however, occurs later at $\approx 12$ nA. This is a similar threshold value already identified for inducing the onset of significant manipulation.
Figure 6-7’s log-log plot of tunnel current versus hop rate is clearly divisible into two different regions, as shown in Figure 6-16. The tip-surface interaction displays a significant deviation from linearity, as expected, but a shift from a decreasing hop rate vs $I_T$ slope relationship, to an increasing in hop rate vs $I_T$ slope, is unusual. This change in the slope sign indicates a shift from a retarding to a promoting interaction mechanism, so we now attempt to elucidate these competing interaction types, and their origins.

6.6.1 Soft-manipulation: Tip-influenced diffusion

Tip-assisted diffusion has been addressed for many different systems \(^{60, 547, 391-396}\), with motion usually activated through a localised heating or field effect mechanism. In principle, it is the simplest form of repositioning, differentiated from manipulation by the degree of directional control achieved in the latter. In principle at least, there is one predominant interaction or destabilising force, which either lowers the potential energy barrier to diffusion, or provides sufficient energy to overcome it.

![Log-log plot indicating the diffusion rate as a function of tunnel current set-point. As the interaction increase, the diffusion rate decreases.](image)
The role of thermal energy during manipulation

Figure 6-8, is a log-log plot of only diffusion events as a function of increasing tunnel current. It has a similar form to the region-(i) in Figure 6-16, but it is fundamentally different. Here we only count diffusion hops, whilst in the previous section it was a convolution of diffusion and manipulations. Their similarity is a reflection of the dominating influence of this coupling mechanism at these tip-sample distances.

Quantitatively the diffusion rate has an average value of $5 \times 10^{-4}$ Hz ± $2.3 \times 10^{-4}$ Hz when imaging at 0.026 nA. The error in this signal is the standard deviation of repeated measurements. By increasing tunnel current, this value unexpectedly tends towards zero.

Sorenson et al. carried out computer simulations to identify and characterise various thermally activated process that play a role in RT diffusion experiments involving metal tips and surfaces. They found that adatoms were stabilised by the presence of the tip, and energy barriers for diffusion in the region of the tip, was increased by as much as 0.5 eV. On the other hand, Kurpick et al. found in their total energy calculations, that the activation barrier in the direction away from the tip decreased with decreasing tip height. Experimental results from Dulot et al. suggested that electrostatic forces altered the surface morphology predominantly at the centre of the tip, in turn decreasing the diffusion barrier. Berndt et al. report that even sub nA current was sufficient to cause an attractive interaction significantly increasing the atomic motion of Ag on Ag(110). On the contrary, Koch et al. suggested that Ag atoms could be trapped under a tip, with an attractive interaction drastically suppressing diffusion. Such uncertainty and specificity displayed by these results highlights the critical role the species plays in determining its diffusion rate, tip-influenced or not.

It is clear in our case, that increasing tunnel currents decreases the diffusion rate. Likewise, decreasing voltage had similar repercussions. Tip-sample distance is thus key to decreasing the diffusion rate. The sum total of joule heating, phonon excitation, inelastic scattering and field assisted diffusion processes, is less influential, than the stabilising energy.

Pethica and Oliver, originally examined tip-surface interactions present during STM and AFM measurements, noting that tip and samples jump together if interaction forces exceed a surface stiffness value. Before such instabilities or crashes occur,
considerable elastic deformation takes place. Hofer et al. [405] performed density functional theory (DFT) calculations investigating surface relaxations during high resolution STM. They noted that surface atoms were displaced up to 1 Å away from the surface at closest approach, (≈ 4 Å). Whilst discussing changes in corrugation as a function different tunnel current set-points, Clarke et al. [406] noted forces of 1 Nm⁻¹ between tip and the Cu (100) surface existed.

I thus, propose that increasing $I_T$ reduces the defect diffusion rate in the tip-sample gap region because of outward surface relaxations, which result from tip-surface interactions. These relaxation rates are different at different surface sites, thereby increasing the surface corrugation (and hence diffusion barrier). Such a process is probably enhanced in our system, since at our vacancies edges, larger, localised Erhlich-Shwoebel barriers [407, 408] are created due to reduced confinement and binding energies of the edge atoms. This in turn, results in reduced defect mobility.

### 6.6.2 Mechanism (ii): “Real” manipulation --- Tip-controlled sliding

The large sequence of manipulations shown in Figure 6-5 indicated that repeatable, reliable and controllable manipulations could be achieved at room temperature (RT). Figure 6-5 reviews some quantitative data obtained relating movement success and mode, to the various manipulation control parameters. Based on this and the graphical data available, we now analyse the tip energy coupling mechanisms.

Tunnel current vs manipulation success data indicates that more tunnel current equals more manipulation. Possible mechanisms thus include:

- Electric field migration,
- Tunnel current density or vibrational heating
- Electronic excitation, or,
- Force

#### 6.6.2.1 Electric field migration

During the $I_T$ vs manipulation success rate experiments, the defect hop rate increases over three orders of magnitude from $10^{-3}$ hops⁻¹ to ≈ 1.7 hops⁻¹. The $I_T$ range during this experiment is 0.2 to 20 nA, corresponding to at max shift in z position of ≈ 3 Å. The electric field between the tip-apex and a manipulant is typically 0.1 V/Å, though
values approaching 1V/Å can be achieved with pulses. Assuming a 100% $E_{Tip}$ coupling efficiency, this could lead to 0.3 eV energy transfer which in principle, is sufficient to significantly modify mobility values.

Despite this, voltage dependent manipulation data we obtained indicated that no significant increase in manipulation rate occurred when increasing bias voltages up to 2.8 V. Since bias voltage increase of this magnitude would lead to significantly higher localised fields than those caused by $I_T$ induced distance changes, it is highly improbable that an increase in the localised $E_{field}$ as a result of increased $I_T$, is the mechanism for inducing manipulation.

### 6.6.2.2 Tunnel current density

Tunnel current density was reported to be the responsible mechanism for manipulating these exact structures, on this exact surface in Tim Fishlock's nature paper. Increases in manipulation success with $I_T$, coupled with the lower threshold values required for sharp tips, strongly suggests this is in fact the responsible manipulation mechanism. Again, voltage dependent data, indicates that (a) no increase in hop rate occurs as a result of increase voltages, and (b) that a decrease in voltage increases the hop rate. This data is highly suggestive that distance (and therefore force), not the $I_T$ density, is the relevant destabilising mechanism.

### 6.6.2.3 Force

$I_T$ and $V$, in **Figure 6-8** and **Figure 6-11** both indicated that distance was the parameter inducing motion. This implied a force was responsible, and **Figure 6-12**'s hop direction data indicated a shift in hop type with increasing $I_T$ (hence distance, hence force). Statistics based on the "seeing" the manipulations showed, there was a shift from species moving too the tip, to away from the tip, with increasing force. This implied the interaction could be tuned, to have both attractive or repulsive forces
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(a) Manipulation success vs \((I_T), (V)\)

(b) \((F), (k_{\text{eff}}), (I_T)\), Manipulation success vs distance

Figure 6-18 (c) is an nc-AFM/STM force-distance, and tunnel current-distance curves whilst below, in (c), we present a tunnel-current distance.

dominate the manipulation process. The tunnel current vs distance overlayed on manipulation vs distance data, indicated that there was a 0.5 Å shift in the onset of exponential behaviour in each curve. This implied that the short-range repulsive force was more efficient at manipulating than its attractive counterpart.

To determine the validity of this conclusion and, the manipulation rate as a function of distance is examined and directly compared with simultaneously acquired force-distance, and \(I_T\) vs distance data. Figure 6-18 (c) is an nc-AFM/STM force-distance, and tunnel current-distance curves whilst below, in (c), we present a tunnel-current distance.
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This work directly measured force gradients and tunnel current as a function of tip-sample separation, and determined the operating conditions during STM imaging. It was found that the STM operation regime lay between the minimum of the stiffness curve and the start of repulsive force, though it is noted, that this conclusion is based on AFM/STM images being acquired at $I_T$ set-points ranging from 4 to 16 nA which is one order of magnitude higher than our starting set-point. Thus it is likely we operate in the attractive regime between when scanning between 0.2 - 4 nA.

Plots tunnel current and manipulation success rate as a function of distance observe a typical exponential shape in the tunnel current plot. This is important, since it implies the integrity of the tunnel gap remains intact during our manipulation experiments whilst ruling out tip surface contact as the manipulation mode. The onset of the a steep change in manipulation, with decay length of $\approx 0.5$ Å, is comparable to the short-range characteristic length measured by Özer et al., 0.4 Å. The authors calculate a tip-sample interaction energy of 0.85 eV at the minimum of the interaction potential. In this interaction regime, the authors record $\approx 8$ nA of current. The tunnel current set-point required to induce significant manipulation in the presented work, is $\approx 14$ nA. Based on this value, we expect to be deep in the repulsive regime.

Results presented so far, indicate that significant alterations in manipulation success are achieved by altering the tip-sample distance. With this in mind, it is prudent and necessary to examine line scans along the manipulation path. Using line scans to
elucidate manipulation mechanisms has been pioneered and extensively used by Karl Heinz Rieder’s group\cite{7}. Through their use of line profile data acquired during manipulations, they identify pushing and pulling, as repulsive or attractive interactions, respectively.

During their experiments, the tip moves in the same direction as the moving species. In our case, Figure 2-15 (b) and (c), the species are hopped perpendicular to the scan direction. In a private communication with Prof. Rieder, we discussed the line profiles seen in Figure 2-15, during which, he stated it was his opinion that the line profiles in Figure 2-15 (b) resulted from a repulsive interaction. The evidence on balance strongly indicates that short range chemical force manipulate in our experiments.

6.7 High temperature

In section 6.4, sequences of images graphically demonstrated that reliable, repeatable, and controllable manipulation of defects could be performed at room temperature (RT). Despite these successes it was noted that, for the most part, such achievements were limited to “blunt” tips. With atomically resolving sharp tips, loads on the apex atom were too great, and typically resulted in a tip reconfiguration when manipulating highly bound species. Furthermore, RT manipulation was only achieved because the complex adatom-vacancy cluster structure we moved, luckily had a diffusion barrier circa 1.3 eV. To generalise and develop these successes to include single atoms and molecules, a new approach is needed.

In chapter-4, key criteria uniquely relating to RT and HT manipulation were identified. Succinctly, the main difficulty is finding a species which has a suitable $E_B$ value, such that;

$$E_{\text{tip}} > E_B >> k_B T$$

yet can be still be manipulated. Species on the lower end of this $E_B$ spectrum, e.g. bromine on copper (100) are typically manipulated and investigated by operating the STM at Kelvin temperatures. Structures and devices built in this temperature range, are not however, easily utilised for technological gain.
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At the other end of the $E_B$ spectrum, for example bromine on silicon (111) 7x7, the bonds being broken where too strong (circa 3 eV) for the tips to manipulate using "brute force", and electronic excitation approaches, or other excitation mechanisms are required. Despite some manipulation success being realised, these processes are unsuitable for reliable manipulation, since building structures and devices, or obtaining reliable statistics, is extremely difficult to achieve.

In an attempt to overcome the RT limitations associated with strongly bound species, we attempt to couple additional external energy via thermal heating of the substrate. It is thus envisaged that the tip-coupled energy required to manipulate, $E_{\text{tip}}$, will be reduced. This should provide sufficient energy to overcome higher $E_B$ values associated with RT stable species, and ensure the STM tips do not break. If,

$$[E_{\text{thermal}} + E_{\text{tip}}] > E_B \gg (k_B T)_{RT}$$

where $E_{\text{thermal}}$ is a function of the surface temperature and the phonon-phonon coupling efficiency, $E_{\text{tip}}$ is the energy supplied by the tip, $E_B$ is the binding energy of the adsorbate to the substrate, and $(k_B T)_{RT}$ is the thermal energy at RT, then assuming energy barrier of $\approx 1-2$ eV, this suggests, extremely high surface temperatures will be required to significantly assist manipulation.

Figure 6-19 is a 20 nm x 14 nm STM topograph taken at $\approx 320$ K. The image is broken in two different regions with significant surface diffusion taking place. Region (i) is acquired at 5 nA, and already 100% of the sombrero species are moved. The manipulation rate is 7.6 hops/species/second. Poor control of directionality is noted, and the hops are now regularly observed as inverted half moons. Approximately 98% of species hop away from the tip, but the motion is best characterised as a zig-zag motion with 75-25 % in the [110] and [110] respectively. This indicates a tip assisted diffusion type manipulation. In this regime, the directional control during manipulation is somewhat lost, and their is a high number of hops both towards and away from the tip. This indicates that the attractive forces are more influential during HT manipulation. The emergence in dominance in the attractive interaction indicates that a reduced tip supplied force gradient is now sufficient to induce motion of a large quantity of defects.
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Figure 6-19 STM topograph taken in the constant current mode of copper (100) at HT. The threshold tunnel current required to induce 100% manipulation is smaller than the threshold value at RT. Manipulation in this mode is less controllable.

Region (ii), is acquired at 7 nA tunnel current set-point. The threshold for continuous sliding manipulation is now only 7 nA as opposed to 12 nA at RT. Here, all sombreros are manipulated. The manipulation success rate and average jump length both measure 12.69 hops/species. There is a higher degree of directionality, with 81% of species now moving in a direction opposite to the scanning tip. Figure 6-19 (b) This image displays dark trails which represent the sliding species.

This reduced manipulation thresholds results from either (a) the diffusion barrier being reduced, or (b), thermal energy is efficiently coupled and localised in the defect structures. It ought to be noted that the temperature changes are quite small in eV terms, in comparison to the expected tip coupled energy. So why does such small temperature change increase mobility so efficiently?

During high temperature manipulation experiments, significant changes in the manipulation behaviour occurs. Most significantly, the threshold for manipulation is
reduced from $\approx 12$ nA to $\approx 5$ nA. Directionality, is somewhat lost, and statistical analysis becomes extremely difficult.

In section-6.3.2, the importance of stationary species for quantifying manipulation was outlined. Briefly, to assess how a particle has moved, you need a before, after and during image, where (a) you see the manipulation pathway "live", and (b), you have reference atoms so you can tell exactly how far it has moved. Without this, or atomic resolution of the underlying lattice, it is extremely difficult to count the number of hops a species undergoes. During HT manipulation, the diffusion rate increases by up to three orders of magnitude, yet the tip still interacts with species and manipulates. To quantify this interaction, a new technique is developed for calculating the hop-frequency.

Figure 6-20 Two STM topographs of manipulated defect on copper (100) at high temperature. (a) Because so many defects hop in between images due to a higher diffusion rate, it is impossible to use our previous before, during and afterwards method to calculate the hop frequency. (b) To overcome this limitation a new technique is developed. In this technique, the time taken until the defect hops is recorded. Since it takes a finite time to scan a defect, a stability lifetime $r_i$ can be assigned to each defect. We first calculate the length of the half moon. This is $d_i$. Since it takes a finite time to scan this $d$, we can calculate the lifetime, until it is moved by the tip. The inverse of this lifetime value, then gives the hop frequency.
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Figure shows two STM topographs taken at high temperature. In image (a), many particles are seen to diffuse in addition to those which are manipulated. Using techniques developed in section 6.5, we can distinguish between hops and manipulations. To calculate the manipulation rate or hop frequency, the stability lifetime of the species is now measured. The stability lifetime is the period of time one can scan the defect before it hops. To calculate this value, the defects are observed in the dual manipulation-imaging mode developed in this work. Then, as seen in figure, the length of a half moon is measured. Since it takes a finite time to scan the defect before it hopped (scan speed x number of lines/nm x nm), we can calculate the defects lifetime. The inverse of the lifetime, then gives the hop frequency of the defect. Thus, a new mechanism for calculating the hop frequency of manipulated species is developed.

We now utilise these two techniques together to calculate the energy required to manipulate a defect.

6.8 Using variable temperature STM to quantify atom manipulation

As mentioned in chapter-1, a key issue regarding atom manipulation is the quantification of the amount of energy or force coupled into a system. This is partially because an STM cannot directly measure either force or energy, and, because of experimental difficulties already outlined with acquiring such data with nc-AFM.

In this section we outline a technique developed which can directly measure the energy “pumped” into the system using an STM tip. This technique is unique, since it measure energy and not the force to move an atom. Thus it is applicable to electronic transitions which would be difficult to measure with an AFM.

In addition to measuring the energy pumped into the system, it is simultaneously capable of determining the change in the potential energy landscape as a function of tunneling conditions. This dynamic response of the surface corrugation to the tip as a function of tunneling conditions is typically ignored, but as we have already seen, this interaction can dominate the manipulation process. Thus it is timely its influence is determined quantitatively.

Figure 6-21 is a linear plot of hop frequency vs tunnel current at three different temperatures. Hop frequencies are calculated using the dual manipulation-imaging.
mode outlined in section, to calculate stability lifetimes which are subsequently then converted to hop frequencies. This technique is cross calibrated against the standard method of calculation, i.e. count number of hops per atom in a given time. The method was found to calculate identical values in most cases. The increased thermal energy associated with the increase in surface temperature serves to reduce the manipulation threshold value, ensuring that more defects move with less tip-surface energy coupled. This (a) causes different interaction types to dominate the manipulation process, (b), protects STM tips. The general exponential nature is retained and is indicative the force is still the dominate interaction. Unlike like Avouris and co-workers, thermal energy is found to increase the manipulation success rate. The data is fit to exponential growth curves. The lateral shift in the manipulation success indicates that the force interaction required can be tuned by careful choice of surface temperature. The primary interaction, as determined by atom hop direction (attractive=hops towards tip, repulsive= predominantly hops away from tip) change from a short-range repulsive force at room temperature to an attractive force at 345 K.
The role of thermal energy during manipulation

**Figure 6-22** Linear plot of hop frequency vs tunnel current at three different temperatures. Hop frequencies are calculated using the dual manipulation-imaging mode to calculate stability lifetimes which are subsequently converted to hop frequencies. This method was cross calibrated against the standard method of calculation. The increased thermal energy associated with the increase in surface temperature serves to reduce the manipulation threshold values, ensuring that more defects move with less tip-surface energy coupled. This (a) causes different interaction types to dominate the manipulation process, (b), protects STM tips. The general exponential nature is retained and is indicative the force is still the dominate interaction. Unlike Avouris and co-workers, thermal energy is found to increase the manipulation success rate. The data are fit with exponential growth curves. The lateral shift in the manipulation success indicates that the force interaction required can be tuned by careful choice of surface temperature.

The external energy is coupled into the system via surface heating. As shown in Figure 6-23 thermal energy transfer occurs by phonon-phonon coupling from the surface atoms to the adsorbate sitting inside a potential energy well. This serves to increase the adsorbates average energy, in turn giving it a higher statistical probability of overcoming the potential barrier.
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Arrhenius Relation

\[ v(T) = v_0(T) \exp \left( -\frac{E_B}{k_B T} \right) \]

Figure 6-24 Graphic illustration of phonon-phonon coupling of thermal energy from the surface to the adsorbate sitting inside a potential energy well. The probability of a particle overcoming the energy barrier is given by the Arrhenius equation as shown. Typically the problem with determining the barrier is the precise determination of \( v_0 \), the attempt frequency. \( v_0 \) is itself both species and temperature dependent. To overcome this limitation, plots of \( \log v \) vs \( \frac{1}{k_B T} \) are created, with the slope of the graph then giving \( E_B \).

Figure 6-25 Log-log plots of hop frequency vs tunnel current at three different temperature.
The role of thermal energy during manipulation

Arrhenius plots as a function tunnel current

As tip approaches Alter potential energy landscape

\[ E_{B\text{ (effective)}} = (E_{\text{Barrier}} - E_{\text{Tip}}) \]

Hop frequency at diff. temps.

Arrhenius plots

Measure effect of tip on local energy landscape = \( E_{\text{Tip}} \)

Figure 6-26 Graphic illustration of how the STM tips proximity to the surface can influence the hop frequency. Calculating the hop frequency as a function of temperature and tunnel current set-point will elucidate a combination of (a) the amount of energy coupled into the system and (b) how the potential energy barrier is altered.

Diffusion is an activated process and a such its behaviour is well described by an Arrhenius type rate equation. Typically, the problem with determining the barrier is related to the precise determination of \( v_0 \), the attempt frequency. \( v_0 \) is itself both species and temperature dependent. To overcome this limitation, plots of log \( v \) vs \( (1/k_b \ T) \) are created, with the slope of the graph then giving \( E_B \). Plots of this nature were shown in section to be capable of determining the energy barrier to diffusion assuming an unperturbed barrier.

If the barrier is perturbed, then recording the same graphs as a function of tunnel current, or any interaction control parameter, gives a direct measure of how this parameter changes the potential energy landscape and the energy within the system. As such, with careful analysis, the energy to move an atom can be calculated.
The role of thermal energy during manipulation

**Figure 6-27** Arrhenius plots for the manipulation of the sombrero defects on copper (100) as a function tunnel current. As the interaction is "turned on" the slope of the graph changes. The slope of the graphs is a measure of $E_{B\text{ effective}}$ which is $E_B$ plus the influence of the tip. The influence of the tip has two components, (a) it can alter the potential energy landscape, and thus lower or higher $E_B$, and (b), the amount of energy "pumped" into the adsorbate substrate system from the tip. Once surface corrugation displacements reached saturation, the change in slope is a direct measure of the energy coupled into the system. A unique point of this mechanism is that it can measure both the electronic energy coupled into the system and the physical (force) energy coupled into the system. If the technique is used in combination with a nc-AFM/STM, we would be able to separate out the force components and the electrical components of the tip-coupled manipulation energy.

**Figure 6-28** Arrhenius plots for the manipulation of the sombrero defects on copper (100) as a function tunnel current. As the interaction is "turned on" the slope of the graph changes. The slope of the graphs is a measure of $E_{B\text{ effective}}$ which is $E_B$ plus the
Figure 6-29 Quantitative analysis of the tips influence on the potential energy landscape, and, a direct measure of how much energy it couples into the "adsorbate"-substrate system via short-range attractive and repulsive forces. (a) The effective diffusion barrier in eV as a function of tunnel current. The barrier initially declines rapidly in section marked which is followed by a small increase. This increase is likely to be due to the outward tip surface relaxations increasing the surface corrugation in response to an attractive force. This increased corrugation then translates itself into a larger diffusion barrier even as extra energy is pumped into the system (higher $I_T$). This is followed by a somewhat linear decline in $E_B$ with increasing $I_T$. (b) Change in diffusion barrier, or interaction energy as a function of $I_T$.

Influence of the tip. The influence of the tip has two components, (a) it can alter the potential energy landscape, and thus lower or higher $E_B$, and (b), the amount of energy "pumped" into the adsorbate substrate system from the tip. Once surface corrugation displacements reached saturation, the change in slope is a direct measure of the energy coupled into the system. A unique point of this mechanism is that it can measure both the electronic energy coupled into the system and the physical (force) energy coupled into the system. If the technique is used in combination with a nc-AFM/STM, we would be able to separate out the force components and the electrical components of the tip-coupled manipulation energy.

Figure 6-30 Quantitative analysis of the tips influence on the potential energy landscape, and, a direct measure of how much energy it couples into the "adsorbate"-substrate system via short-range attractive and repulsive forces. (a) The effective diffusion barrier in eV as a function of tunnel current. The barrier initially declines
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rapidly in section marked which is followed by a small increase. This increase is likely to be due to the outward tip surface relaxations increasing the surface corrugation in response to an attractive force. This increased corrugation then translates itself into a larger diffusion barrier even as extra energy is pumped into the system (higher $I_T$). This is followed by a somewhat linear decline in $E_B$ with increasing $I_T$. (b) Change in diffusion barrier, or interaction energy as a function of $I_T$.

The slopes in region (a) and (c) are found to be repulsive whilst in region (b) the interaction is attractive. The respective energy coupling rates is $-0.124 \text{ eV/nA}$, $-0.0241 \text{ eV/nA}$, and $0.0158 \text{ eV/nA}$. The amount of energy coupled into the system from the tip to reach threshold or complete manipulation is $0.45 \text{ eV}$, approximately $33\%$ of the barrier. Using simple geometric argument this equates to $0.497 \text{ nN}$ of force, which according to the nc-AFM data acquired at comparable tunnel currents implies an ener
7 CONCLUSIONS

Room temperature (RT), high temperature (HT) and variable temperature (VT) manipulation has been performed using a scanning tunneling microscope (STM) on copper (100). This was facilitated by the development of a new adatom–vacancy cluster structure, which was stable, tuneable and manipulable at RT.

In chapter-one, a comprehensive literature review detailing the current understandings, achievements, and possible goals for STM manipulation was outlined. Chief amongst these goals was an analysis of experiments attempting to measure the force required to move an atom, the advancement of atom-by-atom engineering at RT, and a need to understand the role of thermal energy in nanostructures and manipulation. I inculcate the importance of functionality by discussing quantum holography and introducing the gold charging experiments.

Chapters two and three introduced the theories of tunneling, atomic forces, and their precise measurement. This introduction is expected to give any student enough knowledge to begin performing, and analysing, experiments independently. In reality though, they simply serve as a gateway to a vast array of books and literature detailing the massive array of knowledge required to fully master the development of techniques, which are required for perform truly novel experiments.

In chapter four, the energetics and constraints of high temperature manipulation are for the first time outlined in detail. This serves as a set of guidelines which along
with the tricks developed for cheating these constraints, namely the coupling of external energy into the system, provides key theoretical know-how for HT manipulation.

Chapter five details a new adatom-vacancy cluster structure, which proves to have extremely unusual diffusivity, electronic, and stability properties. Chief amongst these anomalous properties was its stability which was useful for manipulation, its electronic excitation properties, which modified its electronic and physical properties.

Finally, we manipulated at RT. The chief interaction responsible for the controlled and deliberate sliding was the short-range force interaction. Both repulsive and attractive force were used, and the dominant interaction utilised was selectable by appropriately choosing the tunnelling parameters, or, by coupling in thermal energy into the system.

Using these techniques with new statistical analysis and graphical analysis techniques developed during this work, variable temperature manipulation was performed. This permitted the construction of Arrhenius type plots, from which, an effective $E_B$ was calculated. This term included the tip-coupled energy term, which was separable, and quantifiable. This allowed the direct measurement of the energy "pumped" into an adsorbate during manipulation, and through careful analysis of diffusion rates, a direct measure of tip induced alteration to the potential energy landscape. This result is unique, since in addition to measuring the force coupled into the system, it will allows with further technique refinement (in combination with AFM), the measurement and separation of the physical (e.g. forces) and electronic (e.g. tunnel current density) components of the interaction during atomic manipulation.
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